

Synthetic Strategies to Target Heterometallic Metal-Organic Frameworks and Polyoxometalate-based Coordination Polymers Using Metalloligand Approaches

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The projects discussed in this PhD thesis were conducted from 1st of January 2021 to 31st of May 2025 at the Institute of Nanotechnology (INT) and Institute of Inorganic Chemistry (AOC), Faculty of Chemistry and Biosciences of the Karlsruhe Institute of Technology (KIT) under the supervision of Prof. Dr. Annie K. Powell. This work was funded by the German Academic Exchange Service (DAAD).

III. List of Abbreviations

AcO or OAc	Acetate
A	Absorbance
AC	Alternating Current
AE	Anderson-Evans
CB	Conduction Band
CHN	Carbon Nitrogen Hydrogen
DC	Directing Current
DEF	Diethyl Formamide
DMF	Dimethyl Formamide
DMSO	Dimethyl Sulphoxide
ET	Energy Transfer
FT	Fourier Transform
Hdnb	3,5-Dinitrobenzoic Acid
HER	Hydrogen Evolution Reaction
HL	Hybrid Linker
HOMO	Highest Unoccupied Molecular Orbital
HMOF	Heterometallic Metal Organic Framework
H ₂ aip	5-Aminoisophthalic Acid
H ₂ hip	5-Hydroxyisophthalic Acid
H ₂ ipa or H ₂ ip	Isophthalic Acid
H ₂ nip	5-Nitroisophthalic Acid
H ₃ btc	1,3,5-Benzenetricarboxylic Acid
H ₃ btb	1,3,5-Tris(4-Carboxyphenyl) Benzene
H ₄ bptc	3,3',5,5'-Biphenyltetracarboxylic Acid
H ₄ tbaPy	4,4',4'',4'''-(Pyrene-1,3,6,8-Tetrayl) Tetrabenzoic Acid
H ₄ tccp	Tetrakis(4-Carboxyphenyl) Porphyrin
H ₄ tcpa	Tetrakis(4-Carboxyphenyl) Adamantane
IR	Infra-Red
Ln	Lanthanide Ions Including Y
LUMO	Lowest Unoccupied Molecular Orbital

MeCN	Acetonitrile
MeOH	Methanol
MOF	Metal-Organic Framework
n Bu ₄ N or TBA	Tetrabutylammonium
NIR	Near Infrared
OEt	Ethoxy
OH	Hydroxy
OMe	Methoxy
POM	Polyoxometalate
POMOF	Polyoxometalate-Based Metal-Organic Framework
POMCP	Polyoxometalate-Based Coordination Polymers
PXRD	Powder X-Ray Diffraction
Pt	Platinum
QTM	Quantum Tunnelling of Magnetisation
SAC	Single Atom Catalyst
SCXRD	Single Crystal X-Ray Diffraction
SMM	Single Molecule Magnet
SQUID	Superconducting Quantum Interference Device
TRIS	Tris(hydroxymethyl)aminomethane
UV-Vis	Ultraviolet-Visible
VB	Valence Band
VR	Vibrational Relaxation
Z	Numbers of molecules in a unit cell
ZFQTM	Zero Field QTM

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1. Kurzzusammenfassung/Abstract

Kurzzusammenfassung

In dieser Arbeit wird der Einsatz von Metalloliganden-Strategien zur Herstellung von heterometallischen metallorganischen Gerüsten (HMOFs) und Koordinationspolymeren auf Polyoxometalatbasis (POMCPs) untersucht. Diese Arbeit beleuchtet die Kristallisationsdynamik, strukturelle Umwandlungen und die Synthese von strukturell vielfältigen Hybridmaterialien. Außerdem werden detaillierte Beobachtungen zu metastabilen Zwischenprodukten, lösungsmittelvermittelten Umwandlungen, Koordinationsgeometrien und strukturellen Störungen vorgestellt, die einen tieferen Einblick in die Bildung und Stabilität der resultierenden Verbindungen bieten.

In den Kapiteln 2 und 3 werden Motivation und Zielsetzung erörtert und eine Einführung in die relevanten Materialien und den theoretischen Hintergrund der in dieser Arbeit behandelten physikalischen Methoden gegeben.

Das Kapitel 4 befasst sich mit der Entwicklung eines Metallogels auf Kupferbasis (Cu-H₂nip-Metallogel) unter Verwendung von 5-nitroisophthalsäure (H₂nip). Dieses Metallogel wurde durch rheologische, optische und elektronenmikroskopische Untersuchungen charakterisiert. Seine Fähigkeit, das Kristallwachstum zu steuern, wurde durch die Synthese neuer La- und Ln-basierter HMOFs demonstriert. Zwei weitere Familien von Verbindungen, darunter La₂Cu₃- und Ln₂Cu₂-Typen, wurden durch hydrothermale Verfahren gewonnen. Infolge der Ostwald-Reifung war die Kristallisation von metastabilen Zwischenstufen möglich, die strukturell charakterisiert wurden.

In Kapitel 5 wird die Verwendung des Cu-H₂nip-Metallogels in einem Wasser-DMF-Medium beschrieben, um weitere Ln-basierte Gerüste zu synthetisieren, darunter La₄Cu₆- und Ln₂Cu-Verbindungen. Einige dieser Materialien erfuhren während der Synthese oder Lagerung lösungsmittelvermittelte Umwandlungen, die entweder zu homometallischen MOFs oder zu neuen komplizierten Strukturen mit faszinierender Metallfehlordnung führten, was die Komplexität ihrer Bildungswege widerspiegelt.

In Kapitel 6 werden funktionalisierte Anderson-Evans-Polyoxometalate (AE-POMs) als Metalloliganden vorgestellt. Sechs Hybridlinker wurden über Schiff-Base-Reaktionen unter Verwendung von tris(hydroxymethyl)aminomethan (TRIS)-funktionalisierten AE-POMs und Aldehyden mit unterschiedlicher Funktionalisierung synthetisiert. Diese

wurden verwendet, um POMCPs auf La-Basis entweder durch Ether diffusion oder durch Schichtbildung herzustellen. Es wurden zwei verschiedene Strukturtypen mit unterschiedlichen La^{3+} -Koordinationsmodi identifiziert. Die Verwendung von hybriden POMs als Linker eröffnet neue Wege in der Materialchemie, die sowohl MOF- als auch POM-Eigenschaften beinhalten.

Das Kapitel 7 beschreibt die Erforschung von kobalthaltigen AE-POMs mit TRIS-Dekoration. Es wurden zwei isomere Formen synthetisiert ($\{\delta/\delta\text{-CoMo}_6(\text{TRIS})_2\}$ und $\{\delta/\chi\text{-CoMo}_6(\text{TRIS})_2\}$) sowie ein neuer Co^{2+} -basierter Polyoxomolybdat-Cluster $\text{CoMo}_3(\text{TRIS})_3$. Die letztgenannte Struktur weist ein Co^{2+} in einer Geometrie zwischen idealisiertem Oktaeder und trigonalem Prisma auf und wurde mittels UV-Vis-Spektroskopie und SQUID-Magnetometrie charakterisiert. Vorläufige Untersuchungen des Clusters deuten auf sein Potenzial als Co-Katalysator für die Wasserstoffentwicklung hin.

Das Kapitel 8 fasst diese Arbeit zusammen und zeigt das Potenzial von Metalloliganden und POM-Hybriden für den Aufbau strukturell vielfältiger und funktionell vielversprechender Koordinationsnetzwerke. Das Cu- H_2nip -Metallogel erwies sich als hervorragender Ausgangspunkt für die Untersuchung der Kristallisationsdynamik bei der Synthese von lanthanoidhaltigen HMOFs. Die vielseitigen multifunktionalen Hybrid-Linker mit dem AE-Polyoxometalat-Kern eröffnen neue Möglichkeiten für Materialien wie POMCPs und metallorganische Gerüste auf Polyoxometalatbasis (POMOFs).

Das Kapitel 9 beschreibt die experimentellen Methoden. Alle Verbindungen wurden umfassend durch Einkristall-Röntgenbeugung, Pulver-Röntgenbeugung, Infrarotspektroskopie und CHN-Elementaranalyse charakterisiert.

Abstract

This thesis explores the use of metalloligand strategies to construct Heterometallic Metal-Organic Frameworks (HMOFs) and Polyoxometalate-based Coordination Polymers (POMCPs). This work highlights crystallization dynamics, structural transformations, and the synthesis of structurally diverse hybrid materials. It also presents detailed observations on metastable intermediates, solvent-mediated transformations, coordination geometries and structural disorders, offering deeper insight into the formation and stability of the resulting compounds.

Chapters 2 and 3 discuss the motivation and objective and give an introduction to relevant materials and the theoretical background of physical methods discussed in this thesis.

Chapter 4 focuses on the development of a copper-based metallogel (Cu-H₂nip metallogel) using 5-nitroisophthalic acid (H₂nip). This metallogel was characterized by rheology and optical and electron microscopy. Its ability to direct crystal growth was demonstrated through the synthesis of new La- and Ln-based HMOFs. Two further families of compounds, including La₂Cu₃ and Ln₂Cu₂ types, were obtained via hydrothermal methods. As a result of Ostwald ripening, the crystallization of metastable intermediates was possible and these were structurally characterized.

Chapter 5 describes the use of the Cu-H₂nip metallogel in a water–DMF medium in order to synthesize additional Ln-based frameworks, including La₄Cu₆ and Ln₂Cu compounds. Some of these materials underwent solvent-mediated transformations during synthesis or storage, leading to either homometallic MOFs or new complicated structures with intriguing metal disorder, reflecting the complexity of their formation pathways.

Chapter 6 introduces functionalized Anderson-Evans polyoxometalates (AE-POMs) as metalloligands. Six hybrid linkers were synthesized via Schiff-base reactions using tris(hydroxymethyl)aminomethane (TRIS)-functionalized AE-POMs and aldehydes with varying functionalisation. These were used to prepare La-based POMCPs via either ether diffusion or layering methods. Two distinct structural types were identified, with different La³⁺ coordination modes. This use of hybrid POMs as linkers opens new pathways in materials chemistry incorporating both MOF and POM properties.

Chapter 7 describes an exploration of cobalt-containing AE-POMs with TRIS decoration. Two isomeric forms were synthesized ($\{\delta/\delta\text{-CoMo}_6(\text{TRIS})_2\}$ and $\{\delta/\chi\text{-CoMo}_6(\text{TRIS})_2\}$), along with a new Co^{2+} -based polyoxomolybdate cluster $\text{CoMo}_3(\text{TRIS})_3$. The latter structure has a Co^{2+} in a geometry lying between idealised octahedral and trigonal prismatic and was characterized using UV-Vis spectroscopy and SQUID-magnetometry. Preliminary studies on the cluster indicate its potential as a co-catalyst for hydrogen evolution.

Chapter 8 summarises this work, demonstrating the potential of metalloligands and POM hybrids for constructing structurally diverse and functionally promising coordination networks. The $\text{Cu-H}_2\text{nip}$ metallogel was found to be an excellent starting point for investigation of crystallisation dynamics in the synthesis of lanthanide-containing HMOFs. The versatile multifunctional hybrid linkers with the AE polyoxometalate core open up new possibilities for materials like POMCPs and polyoxometalate-based metal-organic frameworks (POMOFs).

Chapter 9 describes the experimental methods. All compounds were characterized comprehensively by single-crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy and CHN elemental analysis.

2. Motivation and Objective

By the late 20th century, several research fields in inorganic and material chemistry have found an emerging interest in the fields of coordination polymers (CPs) and specifically, metal-organic frameworks (MOFs). The potential applications of these materials include heterogeneous catalysis, sensing, selective molecular recognition, gas separation, and storage. The straightforward synthesis of these crystalline materials opened up paths to optimize the certain parameters like pore size, accessible metal sites etc., which are relevant for each application. Porosity was one of the keys of MOFs previously, but nowadays it is not always a defining property to call a framework material as MOFs. According to the Cambridge Crystallographic Data Centre, several thousand of porous and non-porous molecules have been reported until now and the both are broadly classified under MOFs. The crystalline nature of these compounds has proven to be an advantage in terms of structure-property correlations. With advances in crystallographic techniques and other characterisation methods, detailed studies of MOF materials have made good progress in material chemistry.

As the name suggest, MOFs are constructed by linking of metal ions as with organic ligands. Although initial syntheses were focused on homometallic structures, the 3d–4f heterometallic coordination polymers and heterometallic metal-organic frameworks (HMOFs) are of particular interests due to their interesting topologies, as well as their potential applications in magnetism, cryogenic magnetic coolers, luminescent materials, catalysis etc. One of the key factors that makes heterometallic systems interesting is the synergistic effect of lanthanide (Ln) ions and transition metal (TM) ions. However, the assembly of HMOFs remains a challenging task for several reasons. For instance, the high and variable coordination numbers of lanthanide ions and their small energy difference among various coordination geometries, makes it unpredictable its final coordination environment in the final structure. Also, interactions among two different types of metal centres and organic ligand are complicated. Sometimes, there is competition between 3d and 4f metals in coordinating to a ligand, finally leading to homometallic coordination polymers rather than heterometallic ones.

The synthesis of Ln-TM heterometallic metal-organic frameworks (HMOFs) typically involves two synthetic strategies. The first one is a step-by-step process whereby firstly a single-metal metalloligand Ln/TM complexes are made and then Ln–organic segments are introduced to form bimetallic and multimetallic target HMOFs. Secondly,

the one-pot approach is considered where the self-assembly of a mixture of metal ions and suitable organic ligands with O- and N-donor atoms, or a mixture of ligands is used, following the hard and soft acids and bases (HSAB) theory. The formation of heterometallic structures can be influenced by several factors, including the metal ion source, the organic ligand, the metal-to-ligand ratio, pH value, solvent, reaction temperature, methodology and reaction time.

The objective of this work is to evaluate a few metalloligand approaches to synthesize HMOFs and systematically characterize these materials. The central idea was to synthesize two types of metalloligands and evaluate them for new HMOF structures. This project was aimed for a step-by-step investigation of reactions parameters to obtain HMOFs in pure phase. Crystallisation processes including Ostwald ripening and structural transformations were also of interest as the investigation of the intermediate compounds involved in the formation of HMOFs would provide some idea about reaction dynamics. This would open up new directions in the field of crystal engineering for new materials.

3. Introduction

3.1. Metal-Organic Frameworks (MOFs)

The synthesis of molecules so called metal-organic frameworks (MOFs) has attracted wide interest since the 1990s due to their diverse structures and tunability for applications in various fields. The initial phase of the research field in this direction could focus on identifying certain molecules in coordination and solid-state/zeolite chemistry.^[1-2] The coordination polymers were formed by the linking of metal ions as with organic ligands and some compounds like as Prussian blue compounds and Hofmann clathrates were known since long time. Coordination polymers with framework structures made from rodlike connecting units were studied by Richard Robson in the late 1980s.^[3-4] The term MOF became popular from the works by Omar Yaghi and coworkers^[5-6] during the '90s and since then a lot of one-dimensional, two dimensional and three-dimensional MOFs has been synthesized. These materials are featured by metal-containing units called the secondary building units (SBUs) which are connected with organic linkers, forming net like structures (reticular synthesis).^[7] The same SBU can be joined by a variety of linkers that have same coordination modes, but with different size, length, and functional groups attached to them. This approach is called isorecticular synthesis and resultant MOFs are called isorecticular metal-organic framework (IRMOF) (Figure 3.1). MOF-5, $[\text{Zn}_4\text{O}(\text{bdc})_3](\text{DMF})_x$ (also known as IRMOF-1),^[5] where bdc =1,4-benzene dicarboxylate, is one of the most studied MOFs.

While understanding the synthetic considerations for MOFs, the reaction temperature plays an important role. Solvothermal and non- solvothermal methods are the most common ones that has worked out for the synthesis of MOFs. According to the definition by Rabenau the reactions taking place in closed vessels under autogenous pressure above the boiling point of the solvent are considered as solvothermal reactions.^[8] The non-solvothermal reactions take place below or at the boiling point under ambient pressure and also include the room-temperature reactions. Reactions that take place in a closed setup at a temperature below but close to the boiling point of a solvent may be ambiguously referred to as solvothermal reactions or mild solvothermal reactions, as a small internal pressure is also generated in this case. Other methodologies like microwave assisted synthesis, ball milling, etc. have also become popular.^[2]

The term Metal-Organic Frameworks (MOFs) is given for porous and crystalline material which are constructed from metal ions and organic linkers. By the copolymerization, a lot of such structures have been successfully synthesized under 'crystal engineering' field.

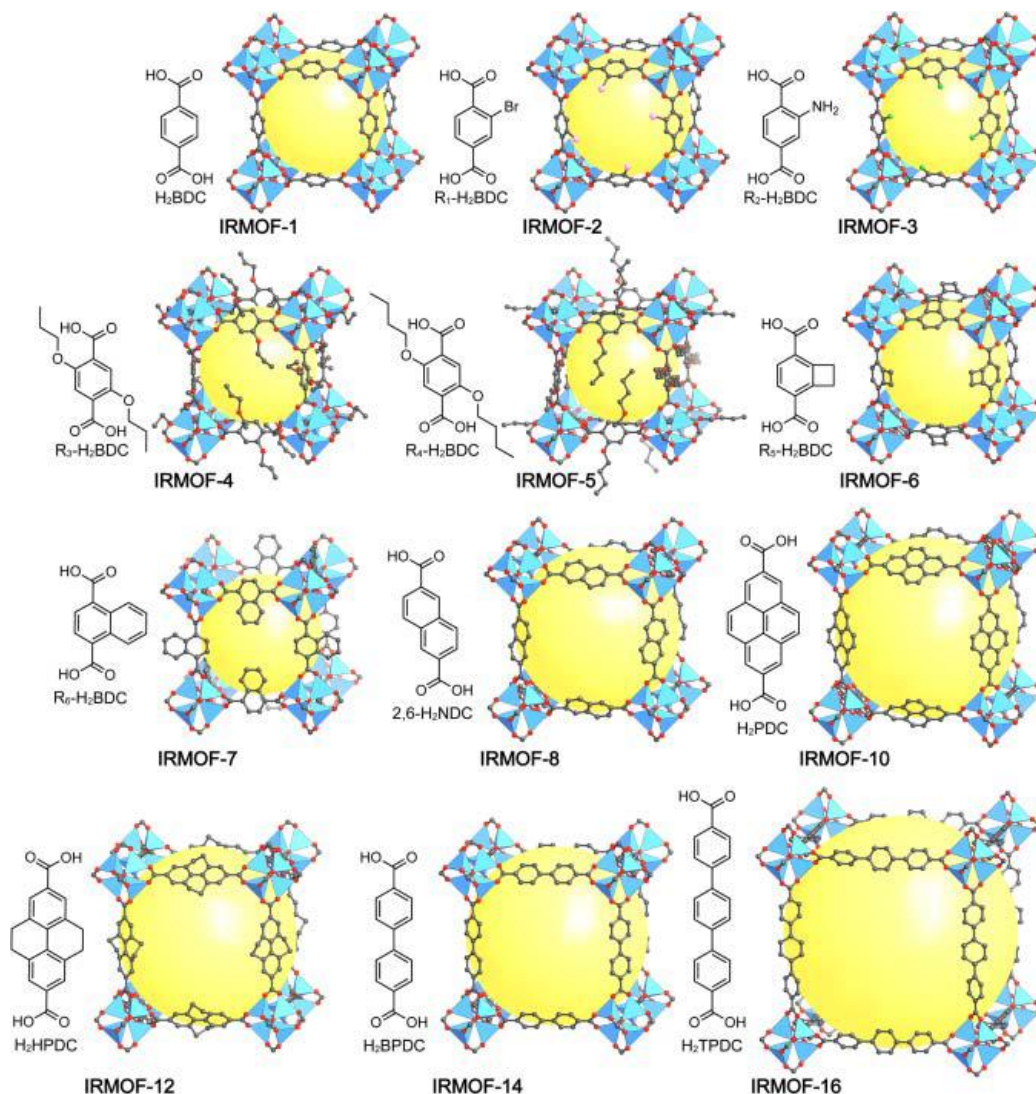


Figure 3.1. Isoreticular metal-organic framework (IRMOF) series based on MOF-5. Reproduced with permission from reference [1].

The porosity is one of the key features of these materials that makes MOFs an important candidate in applications such as gas storage and separation, catalysis etc.^[9] However, the structural and thermal stability and recyclability are some of the limitations of porous frameworks. Nonporous MOFs having robust backbone structures have been synthesized as alternatives.

Furthermore, one-dimensional (1D) and two-dimensional (2D) and three-dimensional (3D) coordination polymers are also broadly classified under MOFs these days.^[10-11]

Although porosity is a valuable feature of MOFs, it is not always a defining property to call a framework material as MOFs.

MOF materials have been applied in the fields of gas storage, separation, magnetism, optical materials, (enantioselective) catalysis, waste water treatment etc.^[9, 12-22] Understanding the structural components of MOFs is essential due to their versatile architectures and potential applications. MOFs consist of rigid inorganic clusters acting as nodes and rod-like organic linkers that influence material properties. The use of SBUs in directing MOF assembly ensures structural integrity and rigidity, making reticular synthesis a crucial approach in their design.

3.1.1. Secondary Building Units (SBUs) and Organic Linkers

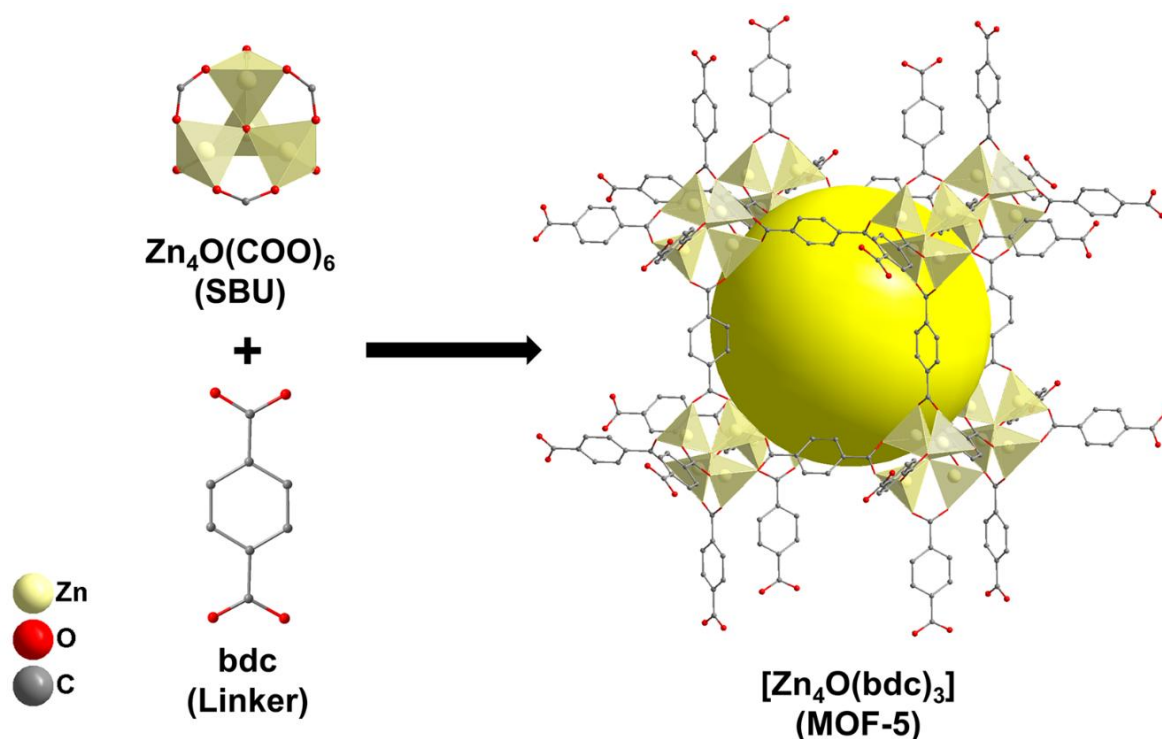


Figure 3.2. MOF-5 constructed from the inorganic SBU and the organic linker. Yellow sphere in the MOF structure represents the largest sphere that can occupy the pores without coming within the van der Waals size of the framework.

In MOFs, polynuclear clusters with defined geometrical shapes and extension points are referred to as secondary building units (SBUs).^[7, 23-24] These inorganic SBUs, typically metal-oxygen clusters, form through coordination with the carboxylate groups of linker molecules in MOFs.^[5, 25-26] For example in MOF-5 ($[\text{Zn}_4\text{O}(\text{bdc})_3](\text{DMF})_x$), four ZnO_4 tetrahedra with a common vertex (O) and six carboxylate C atoms of the

terephthalic acid (H_2bdc) forms an octahedral SBU $\text{Zn}_4\text{O}(\text{CO}_2)_6$ (Figure 3.2)^[5]. These SBUs are linked by the benzene group of terephthalic acid, which serves as the linker.

A few inorganic SBUs are shown in Figure 3.3.

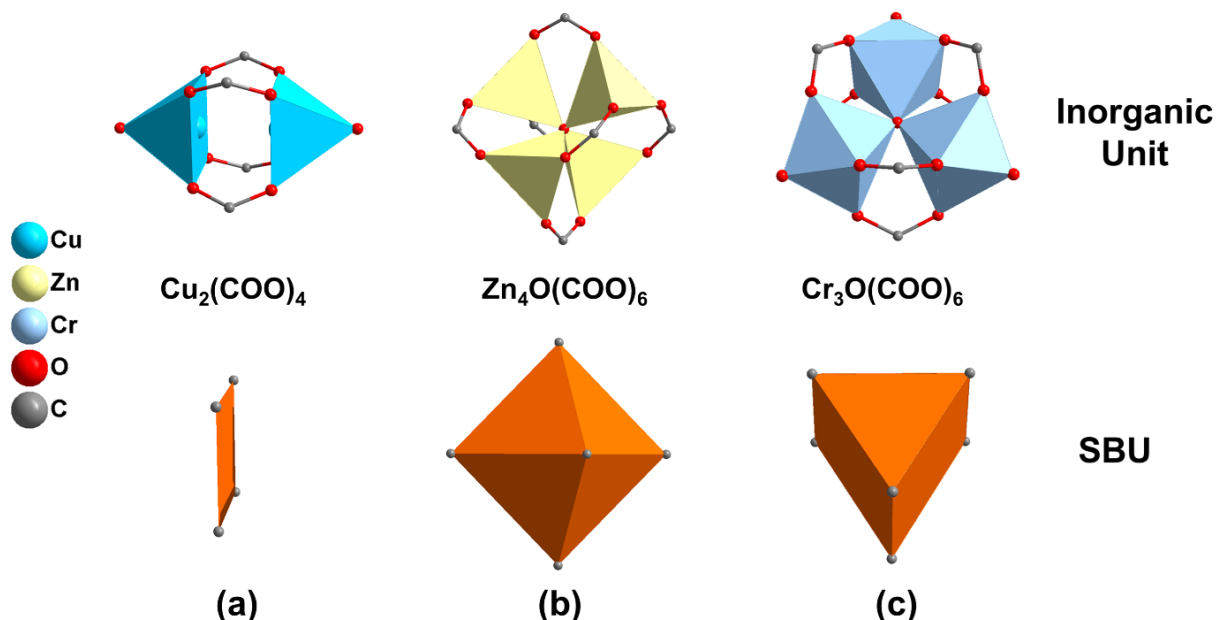


Figure 3.3. Different inorganic SBUs.

The organic ligands, that contain functional groups such as carboxylate, amine, pyridyl, nitrile, sulfonate or phosphonate can act as linkers in MOFs. In these molecules, there are coordinating atoms e.g., O, N atoms which connects the SBUs in different directions. Coordination polymers were synthesized earlier using neutral donor linkers bipyridines and nitriles. These were then replaced by charged chelating linkers with functional groups like carboxylates. There are a few advantages for the carboxylate-based linkers over neutral donor linkers:

- Since the charged carboxylates neutralize the positive charges of the metal nodes, additional counter cations are not required to make charge neutral frameworks
- Carboxylate groups are excellent choice as chelating ligands, providing structural rigidity for frameworks.
- Strong bond formation between organic linkers and metal ions results in MOFs with high thermal, mechanical, and chemical stability.

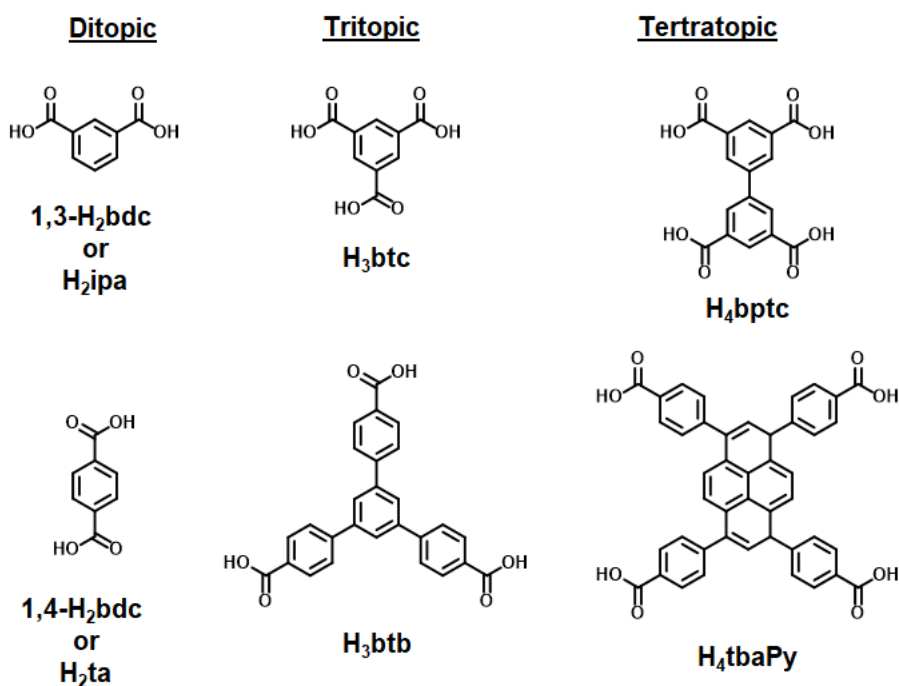


Figure 3.4. Organic linkers with different topicity.

The linker molecules typically have points of extension like two, three, four, six, eight which can coordinate with metal ions leading to MOFs. Such ligands are described as ditopic, tritopic, tetratopic etc. and there are quite a lot of linkers of a given geometrical shape and points of extensions (topicity) leading to the formation of frameworks of different topologies.^[24] A few linkers with different topicity are shown in Figure 3.4.

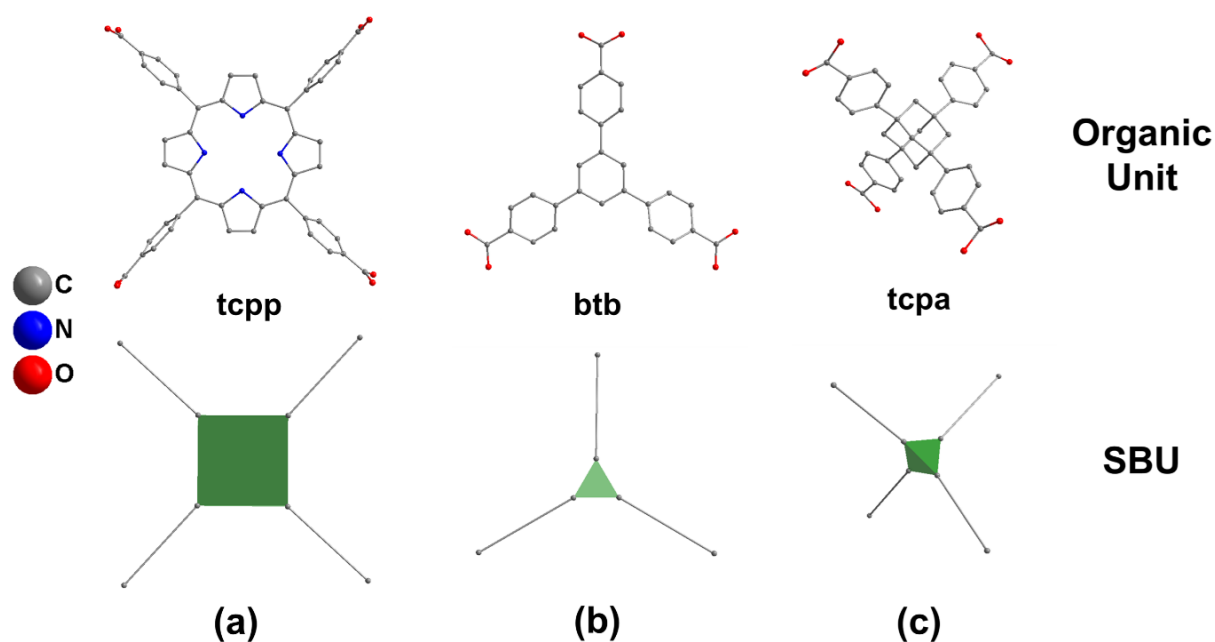


Figure 3.5. Different organic SBUs.

The organic linkers which are connected to inorganic SBUs can be also represented as polygons or polyhedrons or in other words as organic SBUs (Figure 3.5). Thus, the MOFs can be represented with the inorganic SBUs joined together by organic SBU links as shown in Figure 3.6 for the MOF-5.

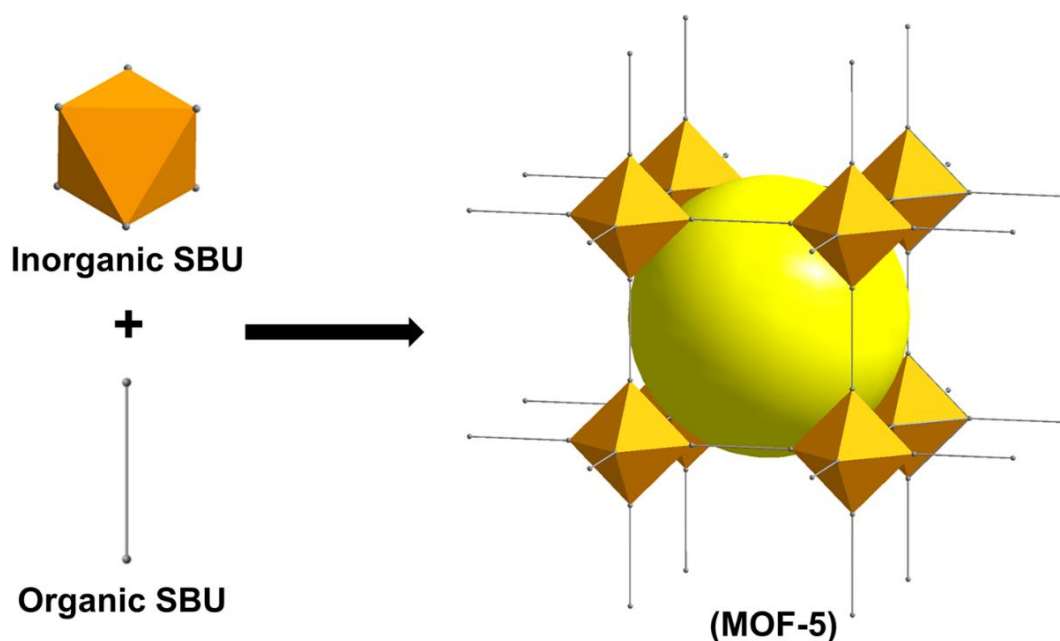


Figure 3.6. The topology of the structure (primitive cubic net) shown using the SBU representation of MOF-5. The void is represented as yellow sphere.

3.1.2. Homometallic and Heterometallic Metal-Organic Frameworks (HMOFs)

Conventional MOFs were mostly based on only one type of metal (homometallic). This applies to the ones based on 3d metal ions (E.g. MOF-5, based on Zn^{2+}), HKUST-1, based on Cu^{2+}) as well as the ones based on lanthanide ions (E.g. MOF-76,^[27] Figure 3.7). The metal–ligand bond strength determines the stability of homometallic MOFs and can be correlated by the Lewis acid- base concept.^[28] For example, metals with high charges (typically M^{3+} or M^{4+}) can be considered as strong Lewis acids that will interact with the groups like carboxylates (COO^-), which are strong Lewis bases.

The heterometallic metal-organic frameworks (HMOFs) and coordination polymers (HCPs) are another class of MOF compounds that feature mixed metal SBUs. These materials are of particular interests due to their interesting topologies, as well as their potential applications in magnetism, cryogenic magnetic coolers, luminescent materials, catalysis. Compared to the entire literature reports of MOFs, the ones for HMOFs are still marginal, which is linked to their synthetic challenges. HMOFs or mixed-metal MOFs

are usually synthesised by doping of a homometallic MOF with another metal ion and majority of these are based on transition metal ions.^[29]

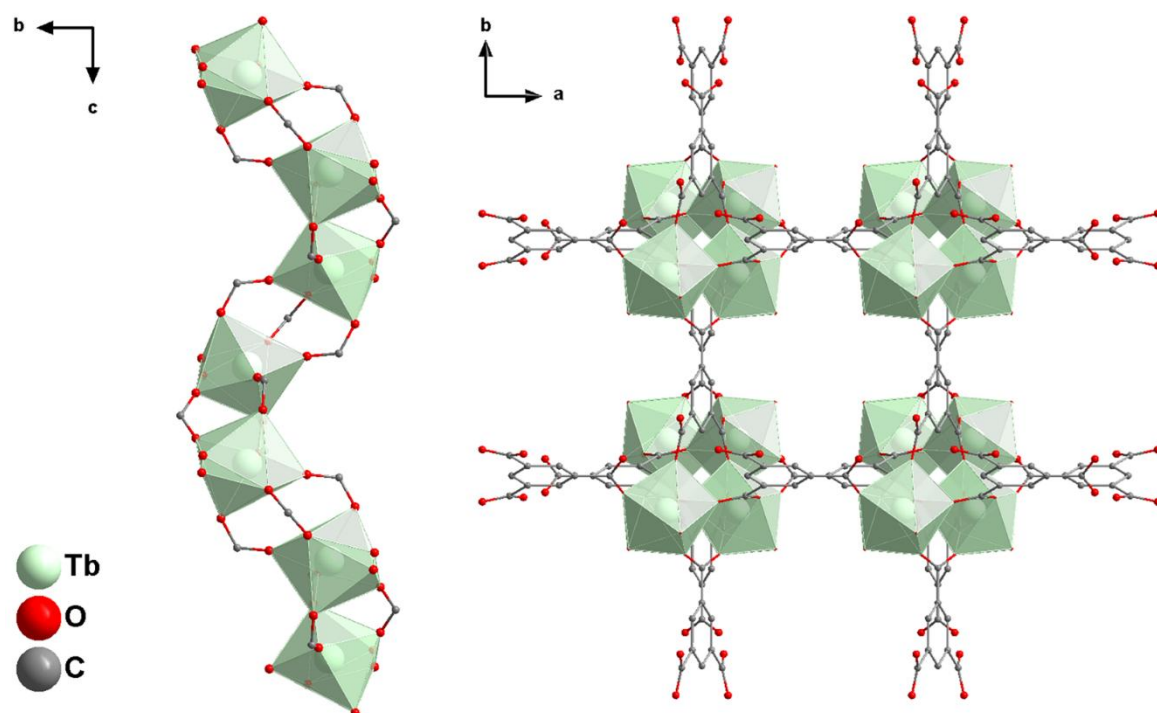


Figure 3.7. The SBU and the three-dimensional structure of MOF-76, which is based on Tb^{3+} .

Among the HMOFs, the ones based on 3d (transition metal) & 4f (lanthanide) metal ions are of particular interests (Figure 3.8).^[30] Property wise, these have excellent performance compared to monometallic MOFs and also modulated chemical reactivity of MOFs due to its multi-metallic sites. This is important especially in the field of molecular magnetism and catalysis.^[31-32] Also, the thermodynamic stability for HMOFs is higher.^[33] However, the assembly of 3d-4f heterometallic systems remains a challenging task for several reasons. This includes understandings in the thermodynamics and kinetics of their formation.

The high and variable coordination numbers of lanthanide ions and their small energy difference among various coordination geometries, makes it unpredictable its final coordination environment in the final structure. Also, interactions among two different types of metal centres and organic ligand are complicated. Sometimes, there is competition between 3d and 4f metals in coordinating to a ligand, finally leading to homometallic coordination polymers rather than heterometallic ones.^[32]

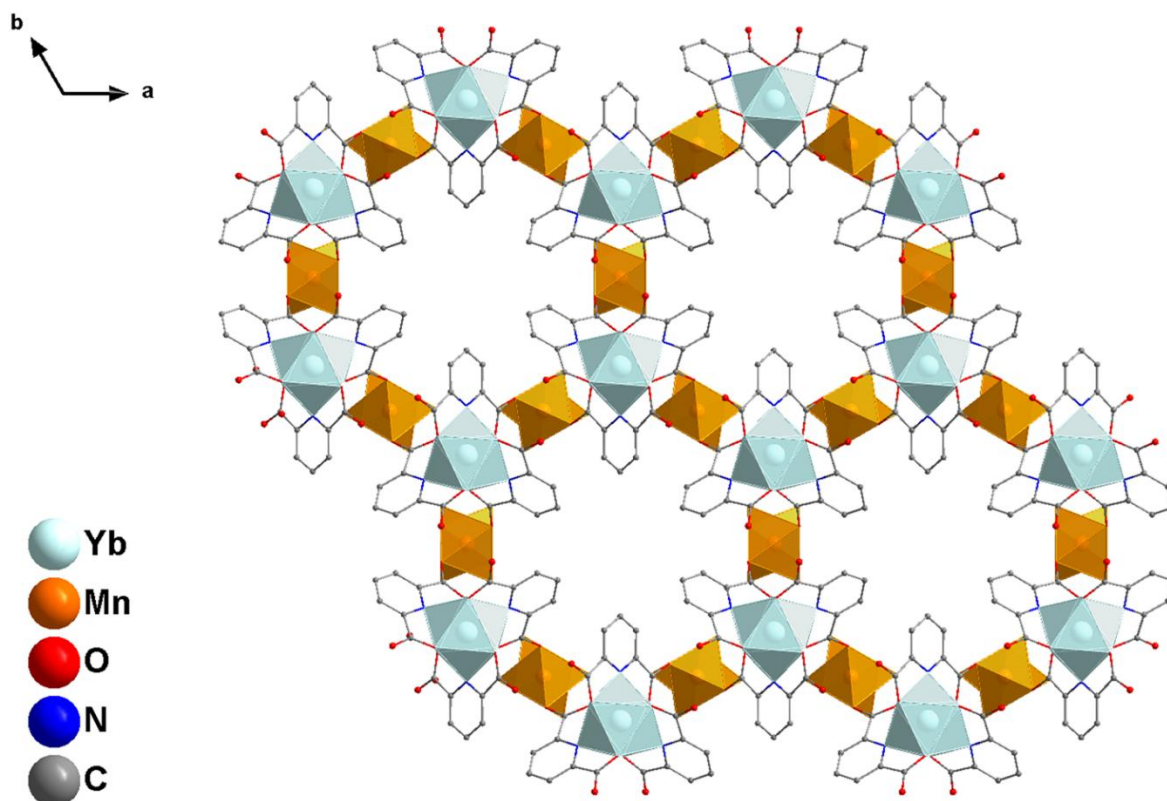


Figure 3.8. A 3d-4f heterometallic coordination polymer based on Mn^{2+} and Yb^{3+} .

The synthesis of Ln-TM heterometallic metal-organic frameworks (HMOFs) typically involves two synthetic strategies. The first one is a step-by-step process where firstly metalloligand (a 3d metal based complex) is made and then the 4f metal ions are introduced to form multimetallic MOFs. Secondly, the one-pot approach is considered where the self-assembly of a mixture of metal ions and suitable organic ligands with O- and N-donor atoms, or a mixture of ligands is used, following the hard and soft acids and bases (HSAB) theory.^[34]

3.2. Polyoxometalates (POMs)

Polyoxometalates (POMs) are a large class of anionic polynuclear metal-oxo clusters composed of early transition metals, characterized by oxo-bridges connecting the individual units.^[35] These molecules exhibit versatile chemical and physical properties and consist of assemblies of addenda atoms M (e.g., W, Mo) in their highest oxidation state, coordinated with oxygen ligands to form $\{\text{MO}_n\}$ polyhedra. The most common MO_6 octahedra are interconnected through corner- and edge-sharing.

All-inorganic POMs are commonly synthesized by the condensation of simple anionic building blocks (e.g. VO_4^{3-} , MoO_4^{2-} , WO_4^{2-} etc.) in solution (typically water) under various pH and temperature conditions (Figure 3.9)^[36]. Many POMs have been extensively

studied for their interesting characteristics^[37] and potential applications in catalysis,^[38] medicine,^[39] electrochemistry,^[40] photochromism,^[41] magnetism^[42] etc. They are particularly interesting due to their unique combination of redox properties, large sizes, high negative charges, nucleophilicity etc. They also demonstrate outstanding redox and stability thermal stability in solution.

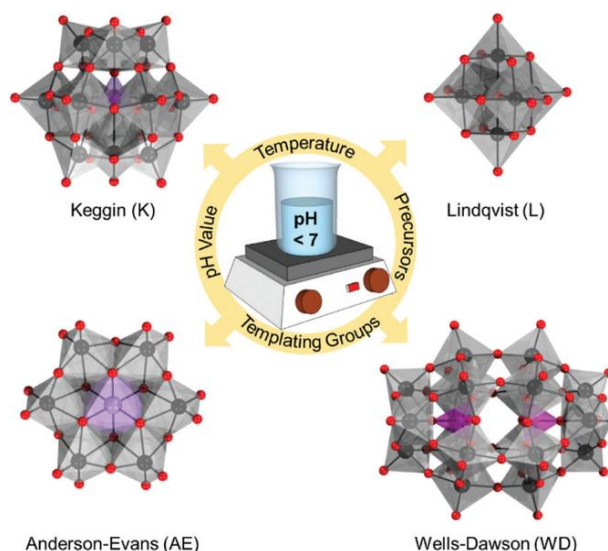


Figure 3.9. Combined ball-and-stick and polyhedral representation of the four classical POM archetypes formed typically in aqueous media by condensation of simple anionic building blocks (e.g., VO_4^{3-} , MoO_4^{2-} , WO_4^{2-} etc.) and heteroatoms. Colour code: M = black balls, O = red balls, $\{\text{MO}_6\}$ = grey octahedra, $\{\text{XO}_6\}/\{\text{XO}_4\}$ = violet octahedra/ tetrahedra. Adapted from reference [36].

The electronic properties of POM anions make them highly useful in various applications. Their ability to function as molecular 'electron sponges,' particularly in stable super-reduced states, enhances their potential for high-capacity molecular cluster batteries.^[43-46] Thus, POMs are promising candidates for robust electrode materials in batteries. Furthermore, POMs have been also used as electrocatalysts for oxygen evolution reactions (OER).^[47-48]

Another important property of POMs is their photoactivity. The metal ions within the polyanion have vacant d-orbitals, facilitating ligand-to-metal charge transfer (LMCT) processes, which are typically high-energy and occur in the UV region of the spectrum. In catalysis, where multi-electron processes are common, POMs serve as effective photocatalysts due to their ability to undergo stepwise reduction and function as electron

reservoirs. This makes them particularly well-suited for proton-coupled multi-electron transfer reactions, such as the hydrogen evolution reaction (HER).^[49-50]

3.2.1. Classification

Polyoxometalates are generally categorized into isopolyanions (isopolymetalates) $[H_xM_yO_z]^{n-}$ and heteropolyanions (heteropolymetalates) $[X_xM_mO_y]^{q-}$ where X represents a heteroatom such as Si, Ge, P or As. Isopolyanions are composed solely of addenda metal atoms (M) linked through oxygen bridges, forming extended metal-oxide networks. In contrast, heteropolyanions incorporate heteroatoms into their structure, which act as central templating units, influencing the overall geometry and electronic properties of the cluster. The incorporation of heteroatoms typically enhances the structural stability and redox properties of heteropolyanions, making them more robust and versatile for applications in catalysis, materials science and medicine.

Isopolyoxometalates (IPOMs)

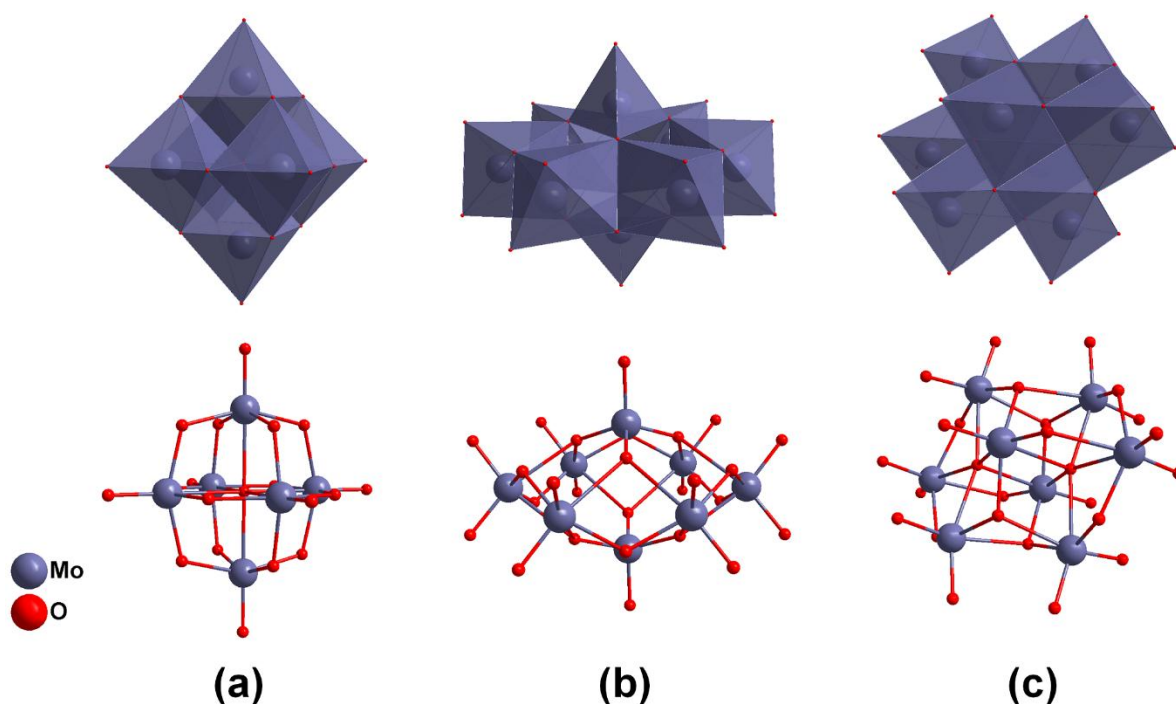


Figure 3.10. Examples for IPOMs. (a) $[Mo_6O_{19}]^{2-}$; (b) $[\alpha-Mo_8O_{26}]^{4-}$; (c) $[\beta-Mo_8O_{26}]^{4-}$. (Polyhedral representation on top & ball-and-stick representation at bottom).

Important examples of IPOMs include the Lindqvist anion ($[Mo_6O_{19}]^{2-}$, $[Nb_6O_{19}]^{8-}$, $[Ta_6O_{19}]^{8-}$ along with octamolybdate ($[Mo_8O_{26}]^{4-}$), heptamolybdate ($[Mo_7O_{24}]^{6-}$) and the decavanadate anion $[V_{10}O_{28}]^{6-}$.

The Lindqvist anion $[\text{Mo}_6\text{O}_{19}]^{2-}$ is constructed from six edge-shared $\{\text{MoO}_6\}^{6-}$ octahedral units. The α - isomer of the octamolybdate anion $[\text{Mo}_8\text{O}_{26}]^{4-}$ comprises a ring of six edge-sharing distorted $\{\text{MoO}_6\}^{6-}$ octahedra capped by two $\{\text{MoO}_4\}^{2-}$ tetrahedral units. In contrast, the β - isomer of $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion is composed entirely of eight edge-sharing distorted $\{\text{MoO}_6\}^{6-}$ octahedral units (Figure 3.10).

Heteropolyoxometalates (HPOMs)

Examples of polyoxometalate anions include the Keggin anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, the Wells-Dawson anion $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, and the Anderson-Evans anion $[\text{AlMo}_6\text{O}_{18}(\text{OH})_6]^{3-}$ each characterized by distinct structural motifs and coordination geometries (Figure 3.11).

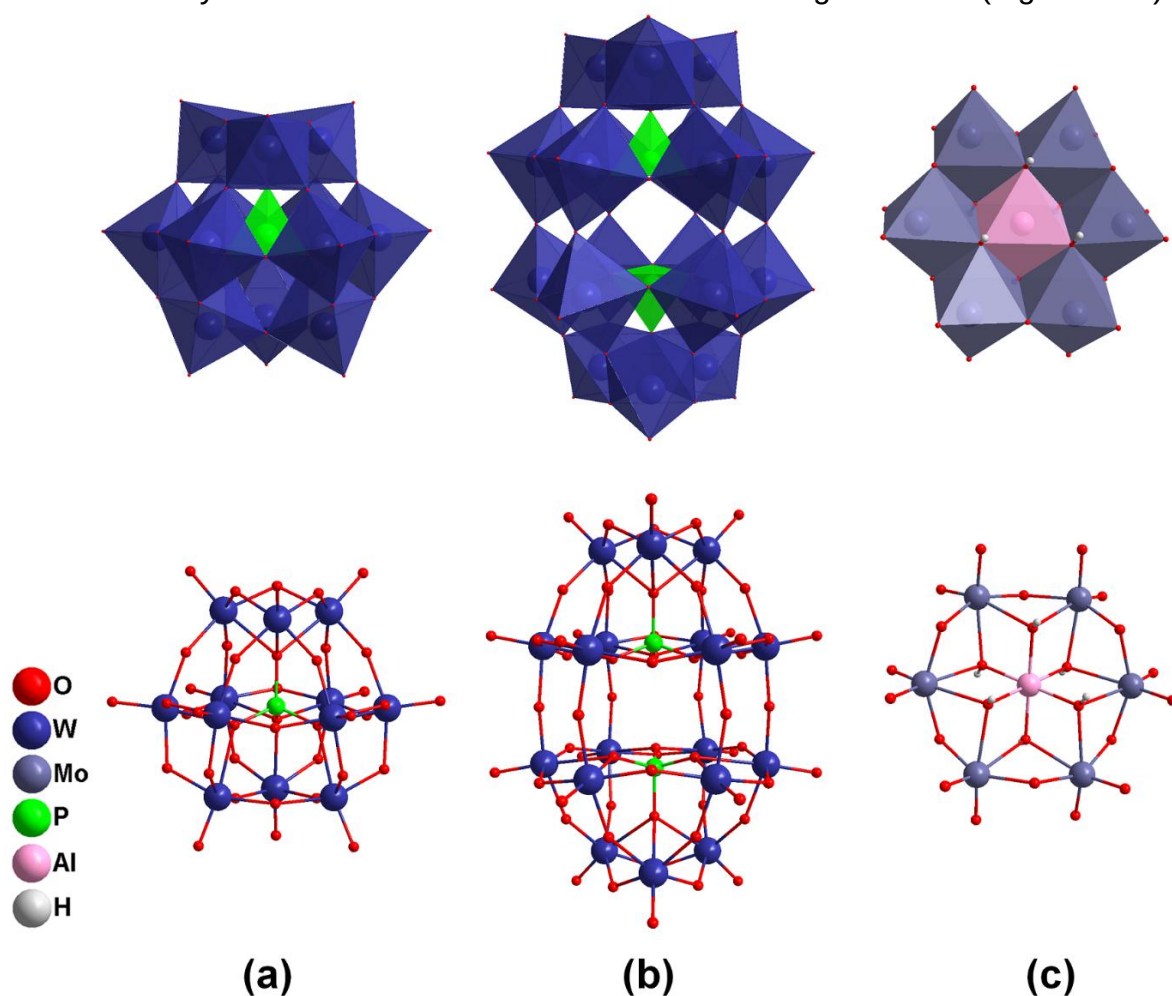


Figure 3.11. Examples for HPOMs. (a) $[\text{PMo}_{12}\text{O}_{40}]^{3-}$; (b) $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$; (c) $[\text{H}_6\text{AlMo}_6\text{O}_{24}]^{3-}$. (Polyhedral representation on top & ball-and-stick representation at bottom).

3.2.2. Organic Functionalization in Anderson-Evans POMs

The combination of inorganic polyoxometalates with organic ligands possessing specific functionalities results in the formation of hybrid compounds, which significantly enhances the diversity of POM structures.^[51] The structure and properties of these

hybrids depend on the nature of both the inorganic and organic components. Such materials are particularly promising for applications like efficient, recyclable multifunctional catalysts, where interactions between organic molecules and oxide surfaces can be explored.^[52] The chemistry and principles behind hybrid organic–inorganic structures, particularly those based on Anderson-Evans POMs, have been extensively studied, offering valuable insights into their potential uses.^[53–54]

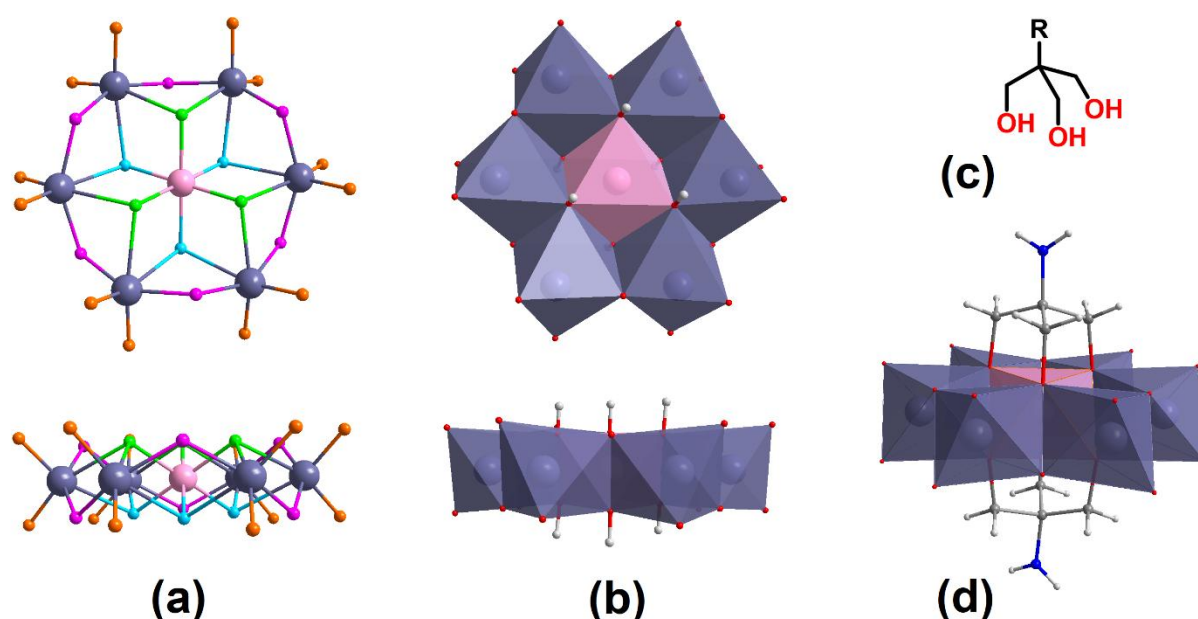
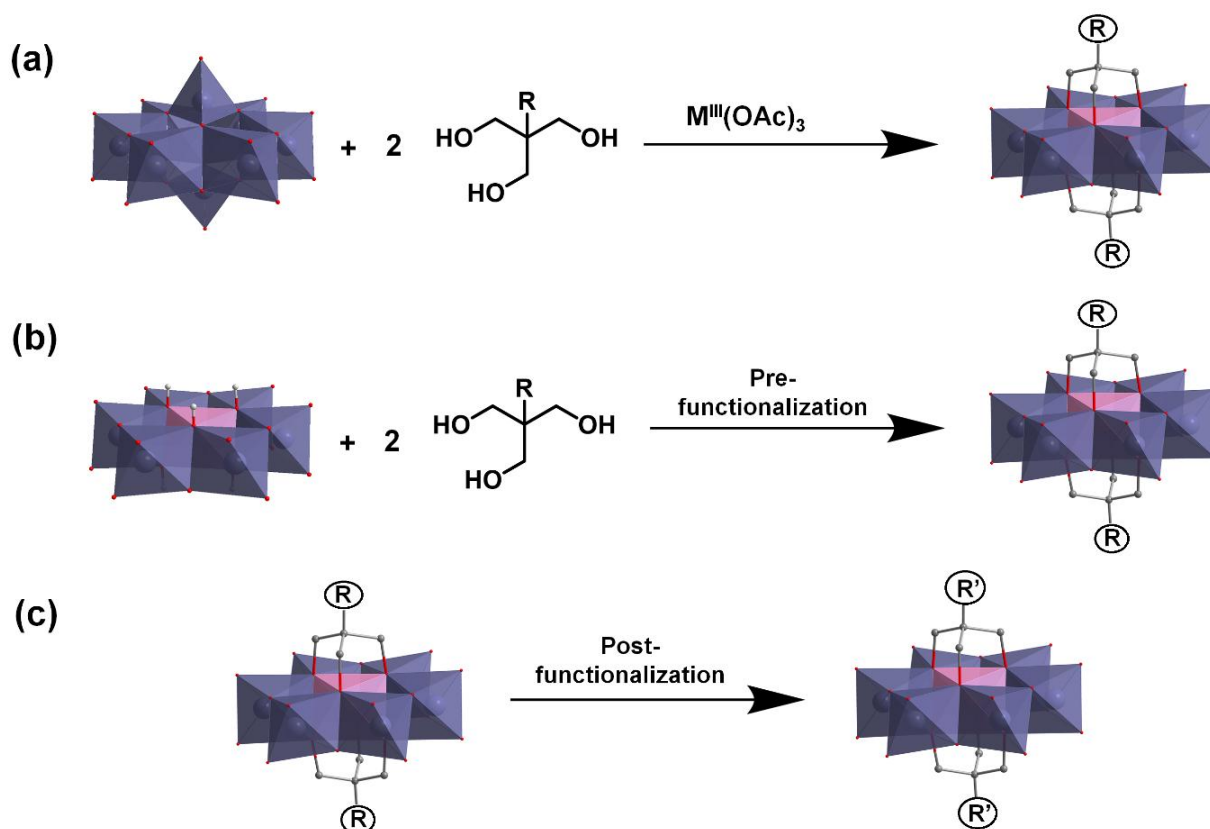


Figure 3.12. (a) Top and side view of ball-and-stick representation of the Anderson–Evans anion showcasing different oxygen atoms (green and blue spheres: μ_3 -O in each plane, pink spheres: μ_2 -O, orange sphere: O_t); (b) Top and side view of the polyhedral representation of B-Type POM with the protonated μ_3 -O atoms; (c) tris-R ligand; (d) tris(hydroxymethyl)aminomethane functionalized Anderson POM. (Blue-grey sphere and octahedra = the addenda atoms M; rose spheres and octahedron = the hetero atoms X; dark-grey spheres = carbon atoms; red spheres = oxygen atoms; pale-grey spheres = hydrogen atoms).

Anderson-Evans (AE) type POM has a general formula $[H_y(XO_6)M_6O_{18}]^{n-}$, where $y = 0–6$, $n = 2–8$, X = heteroatom like Mn^{3+} , Fe^{3+} , Co^{3+} etc. and M = addenda atoms like Mo^{6+} , W^{6+} etc. The central heteroatom has an octahedral geometry ($\{XO_6\}$ core) surrounded by six edge-sharing $\{MO_6\}$ octahedra, in a planar disc-like arrangement. In the structure, there are three different types of oxygen atoms: triple-bridged (μ_3 -O), double-bridged (μ_2 -O) and terminal oxygen atoms (O_t) (Figure 3.12a). Based on the protonation of the μ_3 -O atoms, the AE structure can be classified into two: non-protonated A-type with the general formula $[X^{n+}M_6O_{24}]^{(12-n)-}$, where the central heteroatoms are in high oxidation states (e.g., Te^{6+} , I^{7+}) and the protonated B-type (Figure 3.12b) with the general formula

$[X^{n+}(OH)_6M_6O_{18}]^{(6-n)-}$, where the heteroatoms are in low oxidation states (e.g., Cr^{3+} , Al^{3+}).

The alkoxylation at the μ_3 -O has been a popular synthetic strategy for organic functionalization of the Anderson-Evans POMs, where the tris(hydroxymethyl) methane derivatives (tris-R), $(CH_2OH)_3C$ -R, [where -R= $-NH_2$, $-OH$, $-CH_2OH$, etc.], or simply, tris-alkoxide/triol ligand are used (Figure 3.12c). This covalent functionalization can be viewed as replacing all three hydroxo groups on each side of the POM by the three alkoxy groups (Figure 3.12d). This is facilitated by the high lability of the oxo ligands in the POM, which allows substitution with tridentate ligands or triolates $\{(OCH_2)_3C-R\}^{3-}$.
[52]



The synthetic strategies^[55] for preparing tris-functionalized Anderson–Evans POMs (Figure 3.13) can be broadly divided into three categories:

- (a) Rearrangement of octamolybdate $[\text{Mo}_8\text{O}_{26}]^{4-}$ salt, tris-R ligands, and a transition metal salt in suitable solvents to form the AE-POM hybrid.^[56-57]
- (b) *Pre*-functionalization, where the tris-R ligands are first synthesized and then attached to the pre-synthesized AE-POM via a condensation reaction.
- (c) *Post*-functionalization, where tris-R ligands already grafted onto the AE-POM can be further modified by organic reactions.

The tris-functionalization of Anderson–Evans POMs can occur either a single sided or double sided. The tripodal tris- ligand can bind to various sites on the POM, leading to isomerism (*vide infra*). The resulting structural properties of these hybrids depend on several factors, including the source of addenda atoms, the hetero atom, the tripodal ligand and the synthetic protocol.^[58-62]

The presence of an R-group on the alkoxyl ligands expands the structural diversity and tunability of the resulting POM hybrids.^[60] For example, when the triol ligand is Tris-NH₂ (TRIS, Trishydroxymethylaminomethane), post-functionalization at the NH₂-group can be achieved through amide, imine, coupling reactions etc.^[36, 52]

3.2.3. Isomerism in Anderson-Evans POM hybrids

The binding position of the tripodal tris-alkoxide ligand in Anderson–Evans (AE) POM hybrids determine two possible structural forms (Figure 3.14). In the δ -form, the three μ_3 -O ligands from the $\{\text{XO}_6\}$ octahedron are substituted, with the tripodal ligand capping one of its triangular faces. In contrast, the χ -form arises when two μ_3 -O ligands from the $\{\text{XO}_6\}$ octahedron and a μ_2 -O ligand from the $\{(\text{MO}_6)_6\}$ ring are replaced, resulting in the tripodal ligand capping a tetrahedral void.^[52, 58]

By controlling the degree of protonation of the μ_3 -O atoms in the AE POMs, single- or double-sided functionalized hybrids can be synthesized. There are five possible arrangements of the ligands as shown in Figure 3.15.

- a) Single-sided δ -isomer: $\delta\text{-}\{\text{XM}_6\text{O}_{21}((\text{OCH}_2)_3\text{C-R})\}$
- b) Double-sided axial symmetric δ -isomer: $\delta/\delta\text{-}\{\text{XM}_6\text{O}_{18}((\text{OCH}_2)_3\text{C-R})_2\}$
- c) Single-sided χ - $\{\text{XM}_6\text{O}_{21}((\text{OCH}_2)_3\text{C-R})\}$

- d) Double-sided helical symmetric χ/χ - $\{XM_6O_{18}((OCH_2)_3C-R)_2\}$
 e) δ/χ - $\{XM_6O_{18}((OCH_2)_3C-R)_2\}$ in malposition

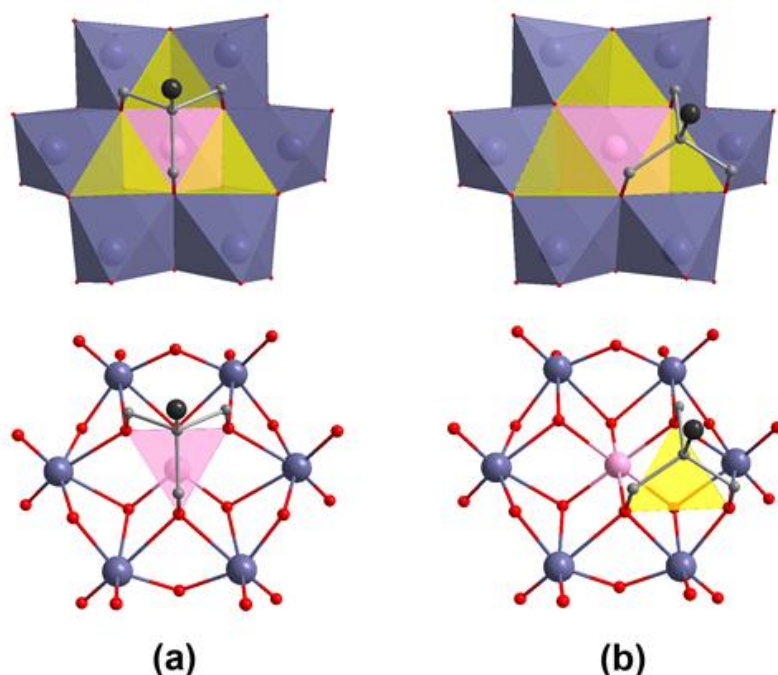


Figure 3.14. Polyhedral (top) and ball-and-stick (bottom) representation of Anderson-Evans POM hybrid showing the tripodal ligand (a) capping triangular face of $\{XO_6\}$ octahedron, where X is the heteroatom (shown in rose colour); (b) capping one of the three tetrahedral voids (shown in yellow colour). Blue-grey sphere and octahedra = the addenda atoms M; rose spheres and octahedron = the hetero atoms X; dark-grey spheres = carbon atoms; red spheres = oxygen atoms; black spheres = R-group on the tripodal ligand.

Among these five AE platforms, the compounds based on δ/δ - $\{XM_6O_{18}((OCH_2)_3C-R)_2\}$ are the most studied ones, especially the derivatives of $[MnMo_6O_{18}((OCH_2)_3C-NH_2)_2]^{3-}$ polyanion which is made from Mn^{3+} , Mo^{6+} and Tris- NH_2 (TRIS) ligand.^[57] The double-sided δ/χ -isomer, in which one triol ligand replaces three μ_3 -O atoms on one side and the other triol ligand substitutes one μ_2 -O and two μ_3 -O atoms on the opposite side, is a rare configuration.^[58]

With cobalt metal ion as heteroatom, different isomers were reported with a variety of triol ligands.^[60] The chemistry of self-assembly depends mostly on the reaction conditions, heteroatom, triol ligand, pH and the solvent.

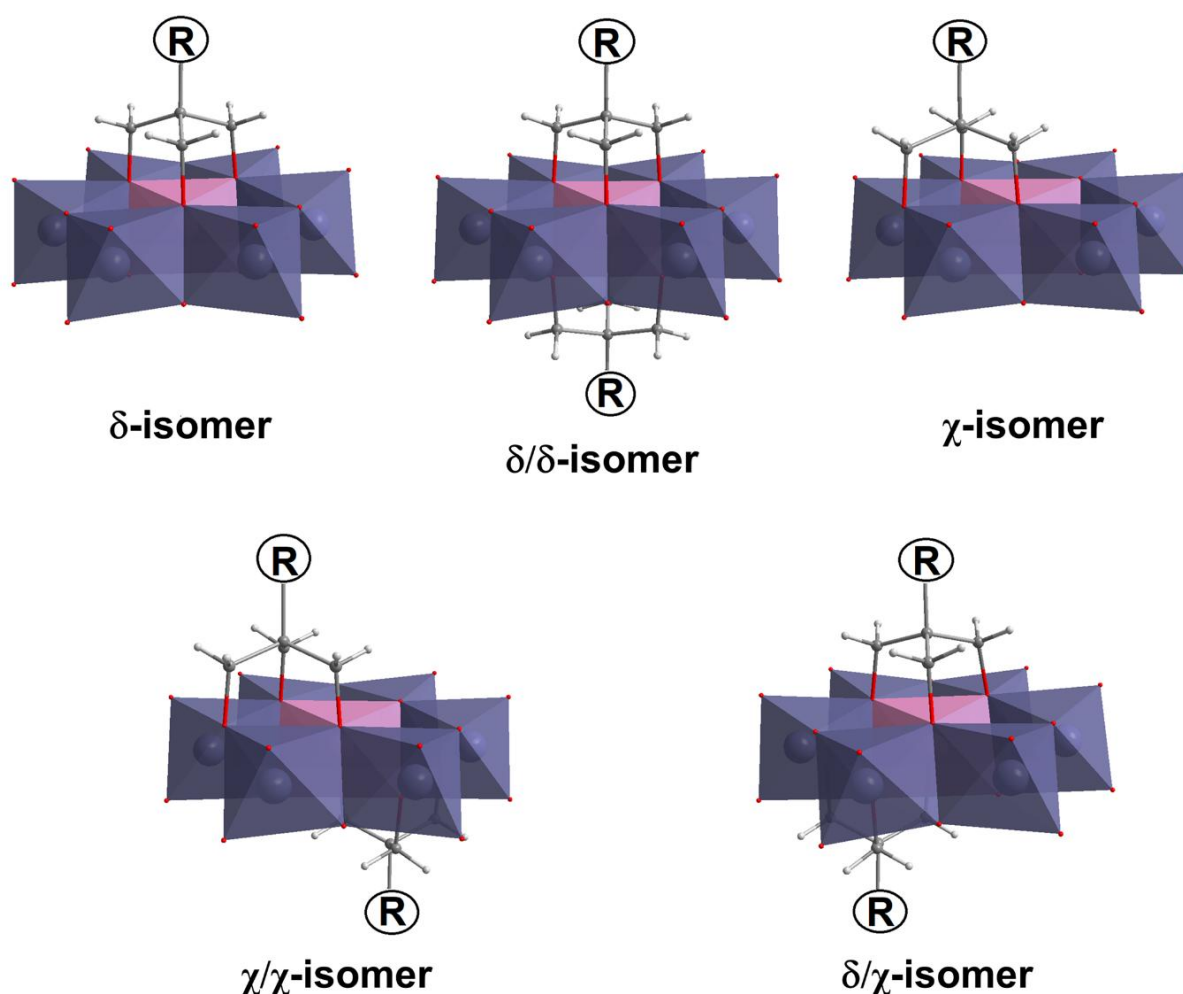


Figure 3.15. Polyhedral representation of isomeric species of Anderson- Evans POM hybrids, with the coordinated triol ligands. Color code: Heteroatom octahedron $\{XO_6\}$ = rose octahedra; addenda octahedron $\{MO_6\}$ = Blue-grey; C = grey; O = red; H = pale grey; R = functional group or atom of the triol ligand.

3.3. Polyoxometalate-Based Metal-Organic Frameworks (POMOFs) and Polyoxometalate-Based Coordination Polymers (POMCPs)

A new class of compounds known as polyoxometalate-based metal-organic frameworks (POMOFs) has gained popularity in recent years.^[55, 63] These materials are designed by combining POMs and MOFs to enhance or integrate the properties of both components.^[64-66] POMOFs can be classified into three types (Figure 3.16):

- (a) POM@MOF, where POMs are incorporated into the cavities of a MOF
- (b) POM as SBUs within the MOF structure
- (c) POM as part of the linker of the MOF structure.

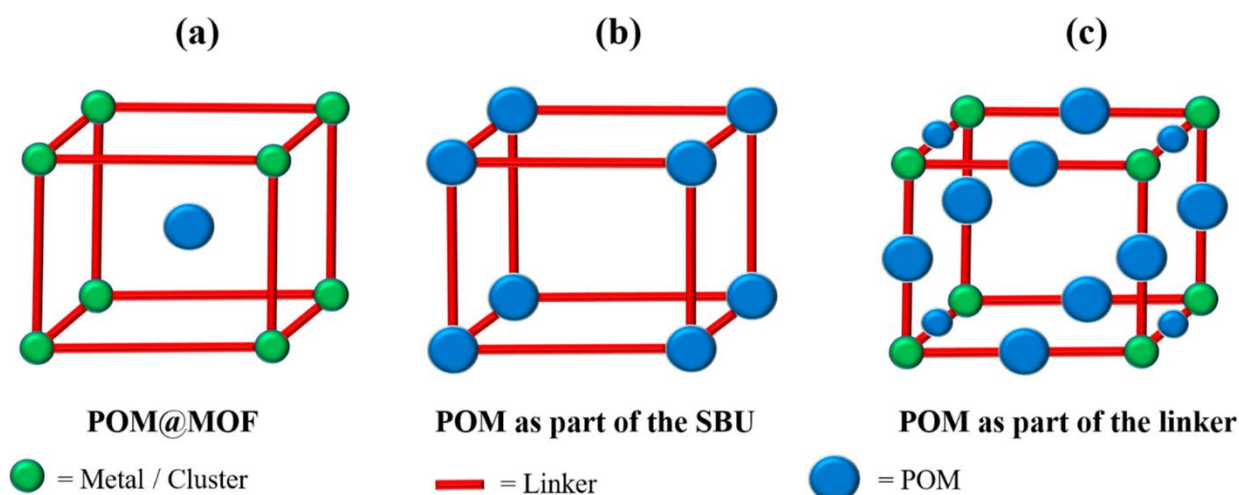


Figure 3.16. The three types of POMOFs: (a) POMs occupying the cavities of a MOF structure (POM@MOF); (b) POMs as SBUs in the MOF network; (c) POMs as part of the linker of the framework. Adapted from reference [67].

The POMs in the first two types are mostly Keggin-based structures. There are also a few reports on the use of Anderson-Evans based hybrid molecules as the linkers to make heterometallic cluster organic frameworks. Marcel *et. al.* reported use of the carboxylate-functionalized Anderson-Evans POM hybrid molecules to synthesize lanthanide containing POMOFs. The free carboxylate groups from the organic component and terminal oxygen (O_t) atoms from the inorganic $MnMo_6O_{24}$ core of this hybrid were coordinated with lanthanide ions.^[67] On a broader context, several Polyoxometalate-based Coordination Polymers (POMCPs) have been reported using Anderson-Evans based hybrid linkers.^[68]

3.4. Metalloligand

A metalloligand is a coordination complex that functions as a modular unit for assembling supramolecular architectures, such as metal-organic frameworks (MOFs). These compounds contain functional group(s) capable of binding to secondary metal ions, often facilitating the formation of extended polymeric networks.^[69] The functional groups often participate in weak interactions, such as hydrogen bonding, or contain moieties capable of forming coordinate bonds.

The metalloligand approach offers several advantages over the conventional strategy of directly mixing the organic ligand and metal salts, particularly for the design of bimetallic and multimetallic MOFs.^[70] Metalloligands are typically rigid and allow precise control over the positioning of functional groups which promote selective coordination

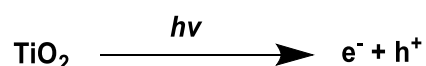
with target metal centres. In contrast, the purely organic scaffolds are more flexible which can lead to less controlled assembly and may lead to homometallic products.^[32]

3.5. Photocatalytic Reactions and POM Single Atom Photocatalysts

3.5.1. Photocatalytic Reactions

Photocatalytic processes are broadly defined as the processes where light energy (photon) is used to accelerate a chemical reaction. A photocatalyst is a material which can efficiently absorb light and convert it to charge carriers (electrons/holes) which then take part in the chemical reaction. Since the 1970s, water splitting using solar energy has been an important field of research for converting solar energy to chemical energy as renewable hydrogen fuel.^[71-72] There have been several developments in this field with new molecular and composite materials as photocatalyst and photoelectrocatalysts.^[73] Detailed discussions of these are out of the scope of this thesis, but a basic introduction in context to the TiO₂-based photocatalytic hydrogen evolution reactions (discussed in Chapter 7) is described here.

For water splitting reaction,^[74] metal oxides (e.g., titania (TiO₂)) represent a common class of semiconductor photocatalyst. Upon irradiation by light (where the energy of the incident photons larger than the band gap of the semiconductor) an electron-hole pair is formed in the semiconductor.^[75] ^[76] An electron can get move to the conduction band (CB), forming a hole in the valence band (VB). These can either recombine without taking part in any further reaction or proceed to either an oxidation or reduction reaction.



In water splitting reaction, there are two redox processes:

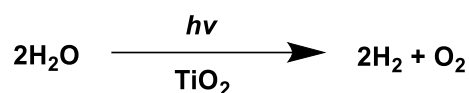
- Two molecules of water consume four photogenerated holes to create one molecule of O₂ and four protons. This is called water oxidation or oxygen evolution reaction (OER).



- The generated protons can be reduced to H₂ by consumption of photogenerated electrons and this is called the hydrogen evolution reaction (HER).

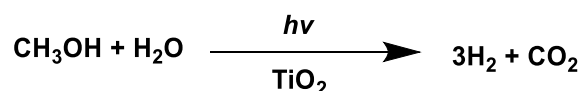


The overall reaction is given as:



The water splitting reaction is an endergonic reaction ($\Delta G > 0$) and the back reaction is thermodynamically favoured. There is also another bottleneck here as the OER is a four-electron transfer process and require a significant activation energy, which translates to a high overpotential $E_0(\text{O}_2/\text{H}_2\text{O}) = +1.23 \text{ V vs. NHE}$. Precious metal catalysts like IrO_2 are used as OER catalysts.^[77] Furthermore, co-catalysts like Pt serve as electron traps and active sites for proton reduction and are usually deposited onto the surface of the photocatalyst, in particular for the HER.^[76] These co-catalysts extract the charge carriers (electrons and holes) from the semiconductor and thereby favour higher degree of separation and lower recombination rates.

Different strategies are considered to improve the efficiency with respect to H_2 production. Use of sacrificial agents such as methanol, which is more readily oxidized has been a popular strategy.^[78] The holes generated on the surface of the photocatalyst are consumed by methanol, which is later oxidised into CO_2 and H_2 . This process is called photo-reforming or photo-oxidation of methanol.



TiO_2 is one of the most studied materials as photocatalyst^[79] and is also used in this work (Chapter 7). The choice of photocatalyst is based a suitable band gap. The position of the CB and VB of the semiconductor photocatalyst is compared to the redox potentials of oxidation and reduction half-reactions of the water-splitting reaction.^[80] The reduction half-reaction would be feasible when the CB has a more negative potential than the proton reduction reaction (H^+/H_2). The higher the potential difference between the bands and redox potential of the half-reaction, the higher the driving force for the respective reaction. In the context of HER, TiO_2 is used because of other reasons as well. It is an abundant material with excellent physiochemical properties and has good chemical and thermal stability. It is also less toxic compared to noble metal catalysts those based on iridium and ruthenium.

3.5.2. Background about POM Single Atom Photocatalysts

Over several decades, there have been continuous efforts to optimize the performance of catalysts in the field of heterogeneous catalysis. Decreasing the size of the metal particle, and thereby increasing the surface-area-to-volume ratio of particles has been an important approach for this. The development of single atom catalysts (SACs)^[81] has been of interest in recent years as more high-resolution characterization techniques (such as electron microscopy) became useful in understanding the chemistry. In SACs, the single metal atoms act as catalytic sites and are usually stabilised by hosts/supports featuring strong binding motifs. Polyoxometalates (POMs) are one of the most important classes of inorganic molecular materials in this aspect, as their rigid metal-oxo frameworks with terminal M=O and bridging M-O-M groups can bind with metal centres coordinatively.^[81-82]

The reduction of H^+ to yield H_2 (HER) and the oxidation of water to form O_2 (OER) are the two redox processes constitute the water splitting reaction, which is one of the prominent research areas for renewable energy sources. There are electrochemical, photochemical and photoelectrochemical water splitting catalysts.^[83-84] As for the SACs, Co-based compounds were identified for hydrogen evolution reaction (HER).^[85]

In the photoredox chemistry which allow the conversion of solar light into useful chemicals, polyoxometalate clusters can be useful in photosensitisation as they typically absorb light in the UV-region. However, self-aggregation of POM clusters and the poor stability of molecular photosensitizers under the turnover conditions limit their long-term performance. Hence, in photoactive catalysis, POM heterogenization on the surface of photoactive supports is an active method in practice for the preparation of photocatalysts. Here, the structurally and compositionally well-defined POM co-catalysts are immobilised on the semiconducting support, which provides an efficient and stable light absorption. The structural stability of individual POM clusters and the electronic communication between the absorber and the catalyst are improved. Furthermore, POMs being a redox active molecule can extract the charge carriers (electrons and holes) from the semiconductor photocatalyst and thereby favour the improve the catalytic activity.^[82]

3.6. Theoretical Background on Physical Properties

3.6.1. Optical Properties

When molecules are irradiated with an electromagnetic radiation, the electrons can be excited by the energy of photons. This can be studied with the help of UV-Vis absorption spectroscopy, where wavelength range between 200 and 800 nm are examined. In this range most complexes display characteristic electronic transitions. When a sample is irradiated with a certain intensity I_0 , a portion of the radiation is absorbed by it and the transmitted intensity is detected by the spectrometer. For solution-state studies, the Beer-Lambert law is useful to analyse the electronic excitations.

$$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot l \quad \text{Equation 1}$$

where A = absorbance, I_0 = incident intensity, I = transmitted intensity, ϵ = extinction coefficient, c = concentration and l = pathlength of the radiation = thickness of the medium.

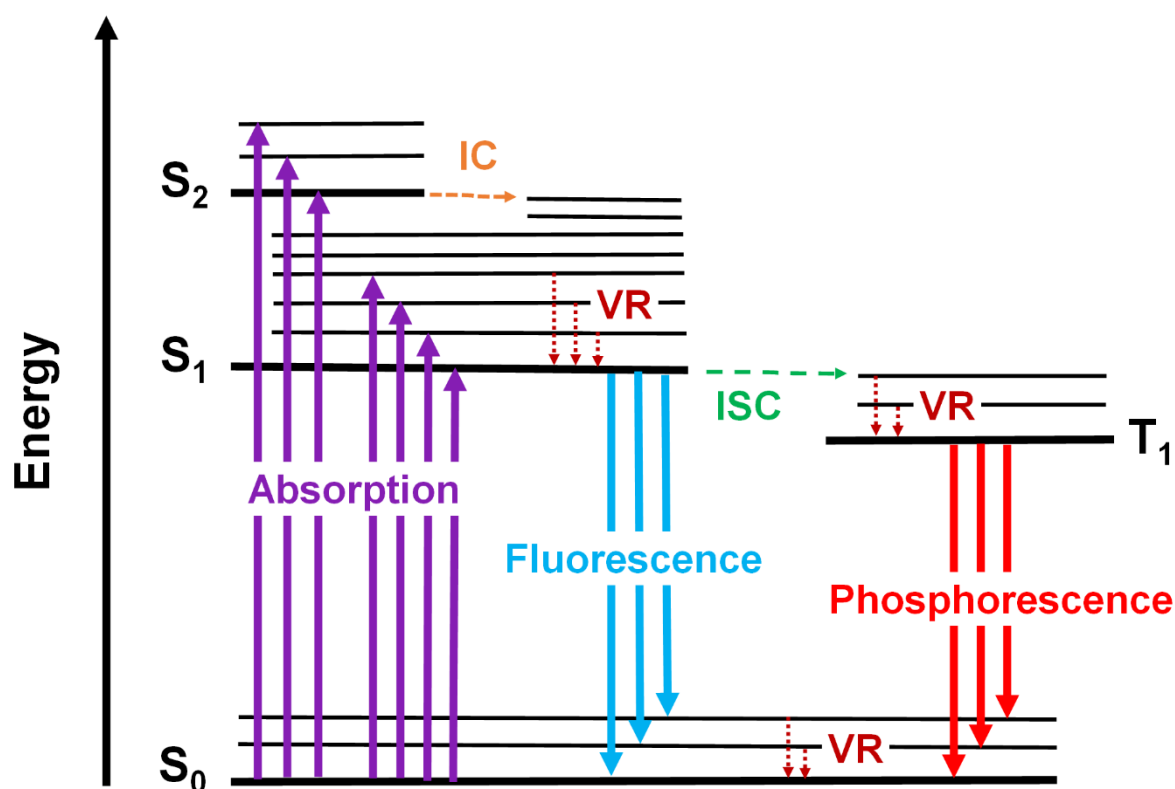


Figure 3.17. Jablonski diagram. (VR= Vibrational relaxation; IC = Internal Conversion; ISC = Inter System Crossing)

The photoexcited molecules can return to ground state in various relaxation pathways. The electronic transitions and relaxation processes can be illustrated using Jablonski diagram (Figure 3.17).^[86]

The first transition involves the excitation of an electron from a lower energy level to a higher energy level by the absorption of photon. This process is from the singlet ground state S_0 to the excited singlet state S_1 , S_2 , etc. Each of the electronic states have several vibrational energy levels and will be populated with the electrons with different energies. The ones at higher levels can undergo vibrational relaxation (VR), which is a non-radiative process and reach lower levels. If the energy levels are closer, the excited electron can undergo a transition from a vibration level in one electronic state to another vibration level in a lower electronic state (e.g., the second excited singlet state S_2 to an excited vibrational level of the S_1 state). This process is called internal conversion (IC) and also proceeds without the emission of photon.

When the electrons in the populated S_1 level relax back into the ground state ($S_1 \rightarrow S_0$) a photon that has a lower energy than the absorbed photon is re-emitted. This radiative process is known as fluorescence. Here, the electron transitions are from electronic states of same multiplicity and hence are allowed. Since the electronic states are associated with several vibrational levels, these transitions are of different energies resulting in a fluorescence spectrum with multiple peaks. The timescale for fluorescence can vary from a few nanoseconds to microseconds.

From the excited singlet state (S_1), the system can also undergo a transition into a lower lying triplet state (T_1), which involves a change of spin. This is called intersystem crossing (ISC) and such transitions are usually forbidden. After VR, the electron will be then in the vibrational ground state of the T_1 electronic state, from where it relaxes to S_0 ground state. This radiative process is called phosphorescence. Like fluorescence, the emitted photon has less energy than the absorbed photon. The timescale for this process can be higher (from a few milliseconds to seconds) due to the spin flip.

The overall process described above refers to the excitation of molecules with electromagnetic radiation (photons) which is followed by an emission of a photon upon relaxation. This is termed as photoluminescence (PL). The timescale of luminescence phenomena can be described with a single exponential decay:

$$I(t) = I(0) \cdot \exp\left(\frac{-t}{T_1}\right) \quad \text{Equation 2}$$

where,

$I(t)$ = Measured intensity at time t

$I(0)$ = Measured intensity at time $t = 0$

T_1 = Optical lifetime of the excited state

In the case of 3d metal ions, the energies of the electronic levels are determined by the ligand field surrounding it. The molecular orbitals are prone to the ligand field splitting and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in ions determine their optical properties.

According to the Laporte rules, the electronic transitions between states of the same parity (symmetry) are forbidden for centrosymmetric molecules. The d-d transitions in 3d complexes will be hence Laporte forbidden as all the d orbitals have gerade (g) symmetry. However, the rule is relaxed for tetrahedral (Td) complexes which lack an inversion centre, allowing the electronic transitions here. As a result, tetrahedral complexes are generally more intensely coloured than octahedral ones.

The strength of the ligand field (strong or weak) also determines the spin state of the complex, for metal ions with d^4 , d^5 , d^6 and d^7 electron configurations. As previously mentioned, the electronic transitions that involve a spin change are forbidden. So, depending on the spin state (high spin or low spin) of the complex, the d-d transitions may be further restricted which result in pale-coloured complexes.

In contrast, for the 4f metal (Ln^{3+}) complexes, the electronic properties are independent of their ligand field. Thus, the optical properties are specific to metal ion and the energies for transitions typically occur in the visible range (approximately 400–800 nm) and near-infrared region (approximately 800–2000 nm) of the electromagnetic spectrum.^[87]

Since the parity of the f-orbitals is ungerade (g), the f-f transitions, are also forbidden. However, in practice, these transitions become partially allowed due to two main factors: the low-symmetry coordination environment and the spin-orbit coupling (SOC) perturbs the system, which mixes different states. Hence the selection rules are relaxed here, allowing the f-f transitions.

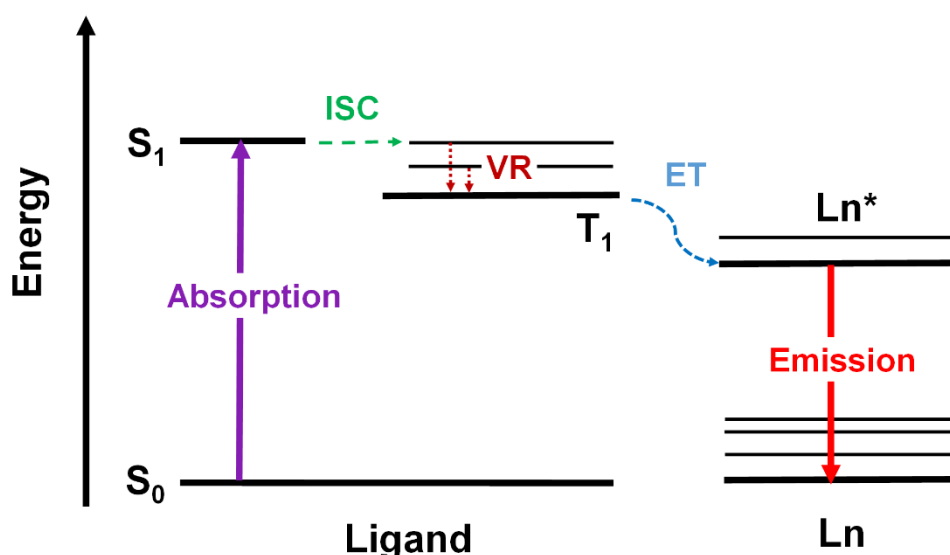


Figure 3.18. Antenna effect in sensitized photoluminescence.

Another way of observing 4f-4f transitions of Ln^{3+} ions is by sensitized photoluminescence. Here, the (organic) ligands in a lanthanide complex absorb photons to reach an excited state. The absorbed energy later transferred to the central lanthanide ion. This energy transfer (ET) is called the antenna effect (Figure 3.18) and populate the emissive excited states of the metal ions, giving rise to characteristic emission bands. In addition to organic fluorophores,^[88] polyoxometalates (POMs) can also sensitize 4f-metal ions via ligand-to-metal charge-transfer (LCMT).^[89]

3.6.2. Basic Principles in Rheology

Viscosity and elasticity are two important properties that govern the mechanics of a material. When a force is applied to a fluid, it shows a resistance to flow. This dissipation of the energy is called viscosity, and has been first studied by Newton. Elasticity is the ability of a material to store energy and release it by resuming its normal shape after being stretched or compressed (deformed) and is governed by Hook's law.

When a material is subjected to a shear force (F), i.e. component of force vector parallel to the material cross section (A), it experiences a shear stress (σ). This component of stress is also coplanar to the material cross section and is given by:

$$\sigma = \frac{F}{A} \quad \text{Equation 3}$$

From Hook's law, deformation (γ) is proportional to the stress. Hence,

$$\sigma = G \cdot \gamma \quad \text{Equation 4}$$

where G is the proportionality constant, called shear modulus.

When a force is applied, it may change the dimensions (like length, shape, or volume) of a material from its original values. The ratio of this change is called strain and is a measure of deformation in a material.

In strain-controlled oscillatory measurements, the strain amplitude γ_0 follows a sinusoidal excitation and the deformation γ is given by:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad \text{Equation 5}$$

where, ω is the excitation frequency and t is the time. At the same time, the stress will follow with a phase lag δ . The resulting stress is given by:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad \text{Equation 6}$$

where, σ_0 is the shear stress amplitude.

For the shear stress, there are contributions from in-phase ($\sigma'(t)$) and an 90° out-of-phase ($\sigma''(t)$) with respect to the excitation:

$$\sigma(t) = \sigma'(t) + \sigma''(t)$$

$$\sigma(t) = \sigma_0' \sin(\omega t) + \sigma_0'' \cos(\omega t) \quad \text{Equation 7}$$

Dividing equation 06 with strain amplitude γ_0 ,

$$\frac{\sigma(t)}{\gamma_0} = \frac{\sigma_0'}{\gamma_0} \sin(\omega t) + \frac{\sigma_0''}{\gamma_0} \cos(\omega t)$$

$$G^* = G' \sin(\omega t) + G'' \cos(\omega t) \quad \text{Equation 8}$$

where,

$$G^* = \frac{\sigma(t)}{\gamma_0}$$

$$G' = \frac{\sigma_0'}{\gamma_0}$$

$$G'' = \frac{\sigma_0''}{\gamma_0}$$

Equation 9

Here, σ_0 = shear stress amplitude, γ_0 = strain amplitude, σ_0/γ_0 = amplitude ratio, t = time, ω is the excitation (driving) frequency. G' is the real part constituting the elastic part (also known as elastic modulus) and G'' is the imaginary part constituting the viscous part (viscous modulus) of the complex modulus G^* .

Since gels have a viscoelastic nature, the angular frequency-dependent storage modulus (G') and the loss modulus (G'') can be analysed using a rheometer. G^* accounts for the entire viscoelastic behaviour of a sample.^[90]

4. Copper-Lanthanide Heterometallic Metal-Organic Frameworks Synthesized in Aqueous Media

4.1. Introduction

The use of metalloligands for the synthesis of heterometallic metal-organic frameworks (HMOFs) based on transition metal and lanthanide ions has long been explored, particularly for the potential applications of these bimetallic systems. The HMOFs have applications in the fields of catalysis, biosensors and therapeutics, magnetism, gas adsorption, luminescence etc.^[91] Metalloligands are preformed metal complexes and two main factors are considered in their use: firstly, the selection of organic ligands that have at least two different coordination donor sites for constructing stable metal complex systems. Secondly, such complexes can be regarded as new metal-containing ligands capable of coordinating to another metal ion. Compared to the classical one-pot approach, the metalloligand can provide a better control over the final product.^[32]

In this chapter, the synthesis of HMOFs using a metallogel approach in aqueous media was carried out. The metallogel (hereafter simply referred to as the Cu-H₂nip metallogel / Cu-H₂nip gel) was synthesized from copper acetate and 5-nitroisophthalic acid (H₂nip) in water. The metallogel was subsequently used as a metalloligand precursor to introduce lanthanide ions in the formation of heterometallic MOFs. H₂nip is a dicarboxylic acid, capable of coordinating with multiple metal ions simultaneously. Additionally, the nitro- group at the 5-position of the benzene ring of the ligand is a good H-bond acceptor, making it a suitable ligand for use in aqueous media.

4.2. Cu₅-Cluster MOF and Cu-H₂nip Metallogel System

As reported by Y. Zhao *et al*, a Cu²⁺-containing MOF compound was synthesized by the reaction of copper acetate and 5-nitroisophthalic acid in water.^[16] Hydrothermal synthesis yielded crystals of a three-dimensional (3D) framework containing (Figure 4.1a) a high density of active Cu sites [Cu₅(OH)₂(nip)₄(H₂O)₆]·4.25H₂O (**Cu-nip**). This MOF is made up of pentameric Cu₅ secondary building unit (SBU) coordinated via nip²⁻ ligands with three crystallographically independent copper sites which are in a rectangular plane. Cu1 is located at the centre of the rectangular plane, and each of the opposite corners are occupied by Cu2 and Cu2' and Cu3 and Cu3', respectively (Figure 4.1d).

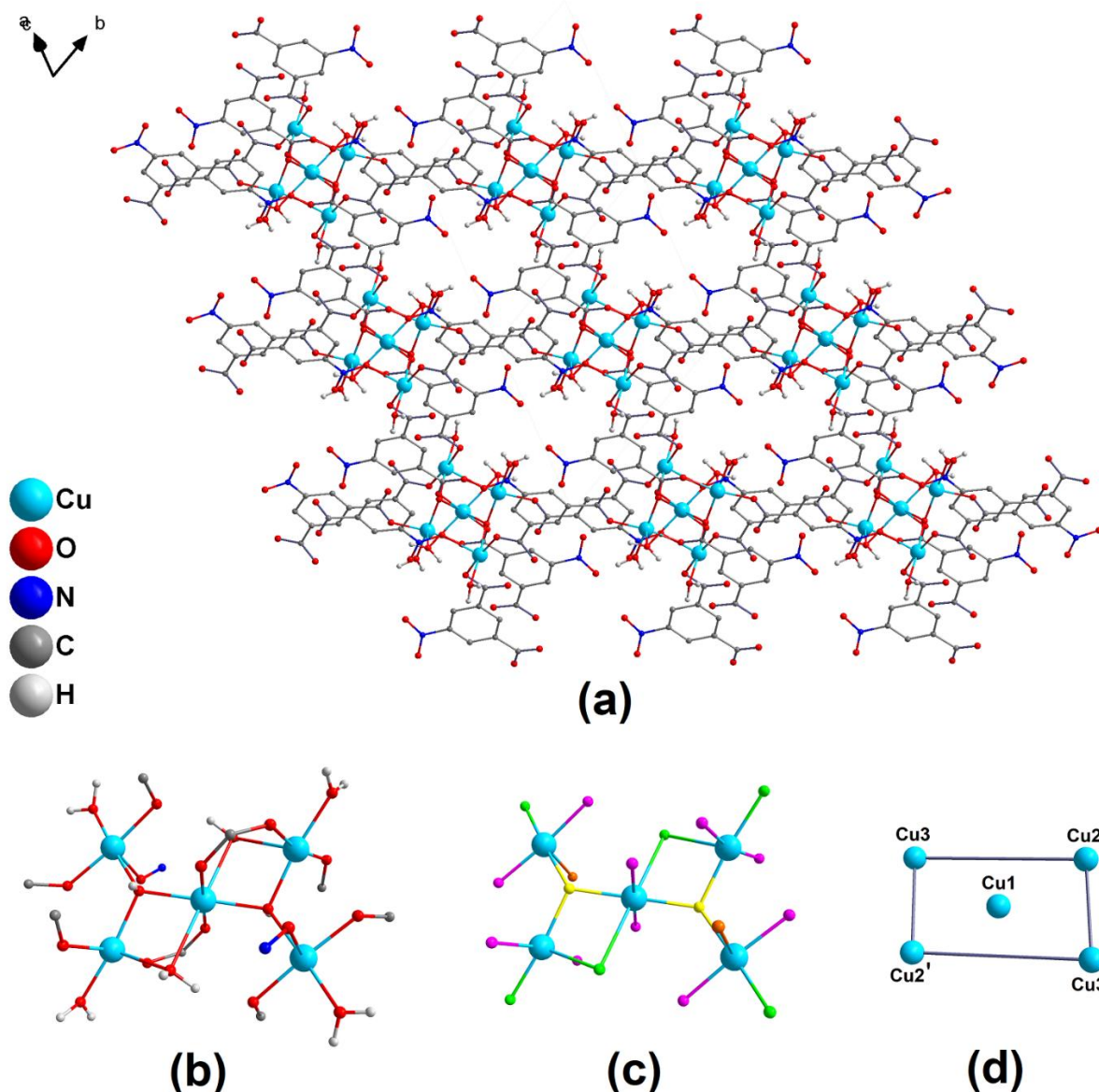


Figure 4.1. (a) Three-dimensional (3D) framework structure of **Cu-nip** showcasing Cu₅-cluster units; (b) The coordination environment around the Cu atoms in the Cu₅-cluster MOF; (c) Different oxygen atoms around each Cu atoms (pink: carboxyl O, green: μ_2 -O atom from water, yellow: μ_3 -O atom from OH, orange: nitro O atoms); (d) rectangular plane formed by the Cu atoms in the Cu₅ cluster.^[16]

Cu1 is six-coordinated by two carboxyl O atoms from two separate nip ligands, two μ_2 -O atoms from two water molecules and two μ_3 -O atoms from OH⁻ groups; Cu2 is penta-coordinated by two carboxyl O atoms from two separate ligands, one μ_3 -O atom from OH⁻ group, one μ_2 -O atom and one O atom from a water molecule; Cu3 is also penta-coordinated by two carboxyl O atoms from two separate ligands, one nitro O atom from the third ligand, one μ_3 -O atom from an OH⁻ group and one O atom from a water molecule.

The reaction of copper acetate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$) and 5-nitroisophthalic acid (H_2nip) in water at room temperature yields a blue gel. According to the reported procedure, the heating is done at 120 °C but lower temperature (e.g., 95 °C or 75 °C) can be used to obtain the crystals of Cu_5 -cluster MOF (**Cu-nip**) (Figure 4.2).

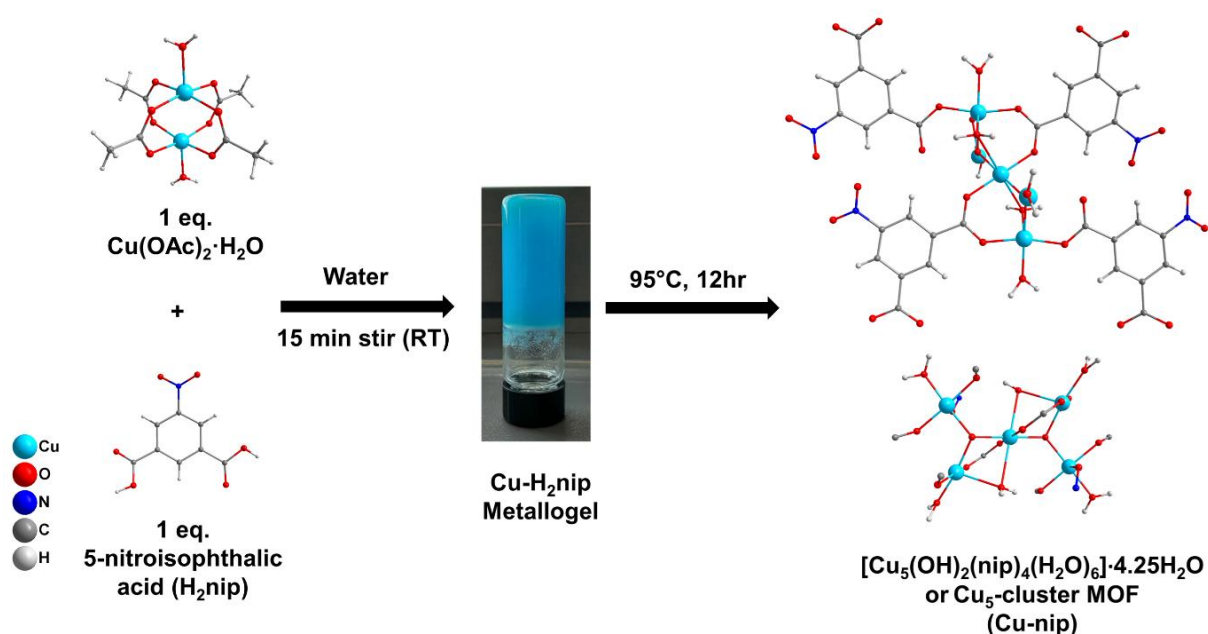


Figure 4.2. Synthesis of the Cu- H_2nip metallo gel and the Cu_5 -cluster MOF (**Cu-nip**).

Although Cu^{2+} and H_2nip have been used for MOF synthesis, in-depth studies have not been performed on the Cu- H_2nip metallo gel system. The fundamental aspects and chemistry behind gel formation, as well as the potential applications, remain unexplored. The constituents of the gel include Cu^{2+} ions, acetate ions (AcO^-), 5-nitroisophthalic acid (H_2nip) and water. This chapter first provides a systematic analysis of role of each of these constituents. In subsequent sections, the synthesis and characterization of HMOFs derived from the Cu- H_2nip metallo gel are discussed. The chapter concludes by highlighting why a step-by-step method using a metalloligand is preferred over a one-pot reaction for the synthesis of HMOFs. Hereafter the term ‘Cu- H_2nip metallo gel’ indicates the gelatinous mixture prepared by the reaction of 1 eq. of H_2nip ligand (0.5 mmol) with 1 eq. of copper acetate (0.5 mmol) in 10 mL water.

4.3. Analysis of Cu- H_2nip Metallo gel

4.3.1. Rheological Studies of Cu- H_2nip Metallo gel

The rheological analysis of Cu- H_2nip metallo gel showcases its viscous and elastic properties.

As a general procedure for the synthesis of Cu-H₂nip metallogel for rheological analysis, 0.5 mmol of Cu(OAc)₂·H₂O (100 mg, 0.5 mmol) was dissolved in 10 mL water in a 20 mL Wheaton glass vial with a base diameter of 2.5 cm. To the pale blue clear solution, 0.5 mmol of H₂nip (106 mg) was added and it was stirred at room temperature for 15 minutes until a uniform blue gelatinous mixture was formed. The uniformity of the mixture was ensured by occasionally agitating the magnetic stir-bar inside the vial with an external magnet. This is important in order to avoid the formation of clumps of H₂nip (of particle size >0.1mm). Also, when the stirring is done in a narrow vial (base diameter of 2 cm), the consistency of the gel is non-uniform across the height of the mixture in the vial due to differential stirring inside the thick mixture. After the 15-minutes of stirring, the mixture was put aside for about 5 minutes before transferring to the rheometer. During this resting time, the gelatinous mixture thickens and forms the gel.

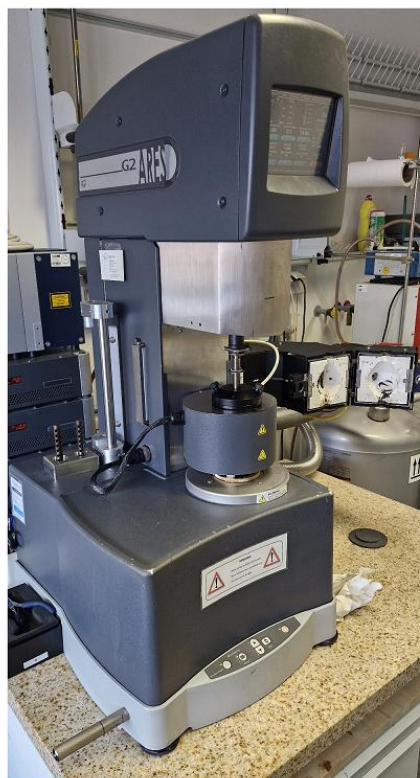


Figure 4.3. G2 ARES Rheometer.

The rheological experiments were performed at 25 °C using an ARES G2 rotational rheometer from TA instruments (Figure 4.3). This is the shear rheology measurement where the sample gel was placed between two plates (25 mm geometry) at a distance of about 1 mm. In order to produce a uniform layer of gel between the plates (conditioning the sample), a pre-shear was applied for 20 s at a shear rate of 10 s⁻¹.

As a start, a strain sweep was performed where G' and G'' were measured as a function of the strain amplitude γ_0 . Below a value for $\gamma_0 = 0.01$ the sample is in linear regime. For the next step, a strain amplitude ($\gamma_0 = 0.001$) in the linear regime is selected for the frequency sweep test (Figure 4.4a).

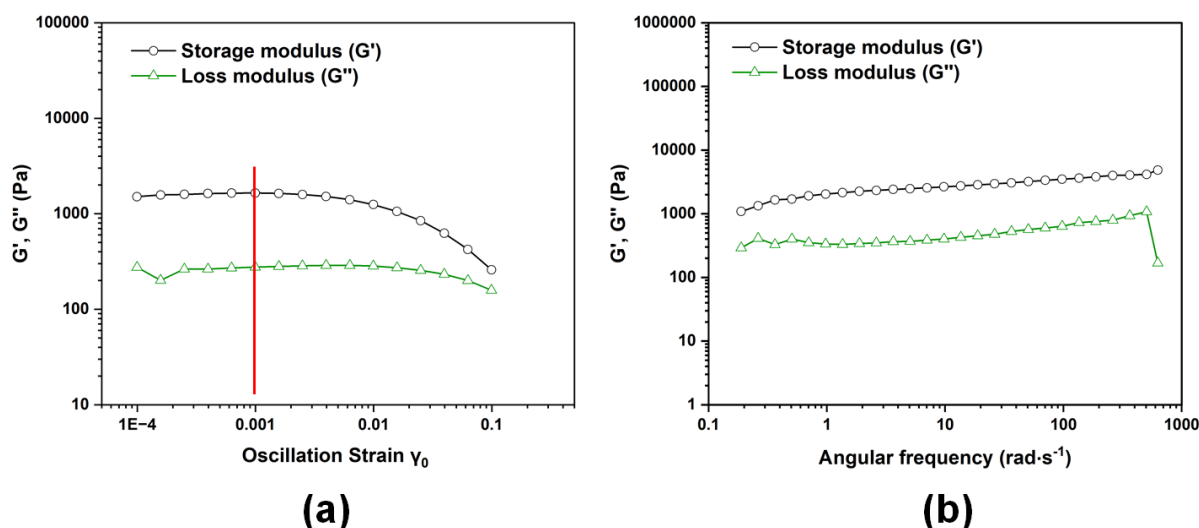


Figure 4.4. Plots of storage modulus (G') and loss modulus (G'') of Cu- H_2nip metallogel showing (a) strain sweep; (b) frequency sweep with a deviation above an angular frequency of $500 \text{ rad}\cdot\text{s}^{-1}$.

During the subsequent frequency sweep experiment (Figure 4.4b), the G' of the Cu- H_2nip gel was found to be higher than the G'' and these values remained essentially constant over an angular frequency range of 10 to $500 \text{ rad}\cdot\text{s}^{-1}$. This substantiates the gel nature of Cu- H_2nip metallogel, as also seen for some previously studied supramolecular Cu^{2+} - metallogels.^[92] The Cu- H_2nip metallogel was not very robust as it collapsed beyond an angular frequency of $500 \text{ rad}\cdot\text{s}^{-1}$. This could be attributed to the disruption of the hydrogen bonds between the H_2nip ligands and the water present in the gel, which led to its instability. After the measurement, it was observed that the gel became dry, forming a blue sticky mass which suggests the loss of water (Figure 4.5). This is also visible from Figure 4.3b where the lines diverge beyond the angular frequency of $500 \text{ rad}\cdot\text{s}^{-1}$. Later experiments were hence limited to this value.

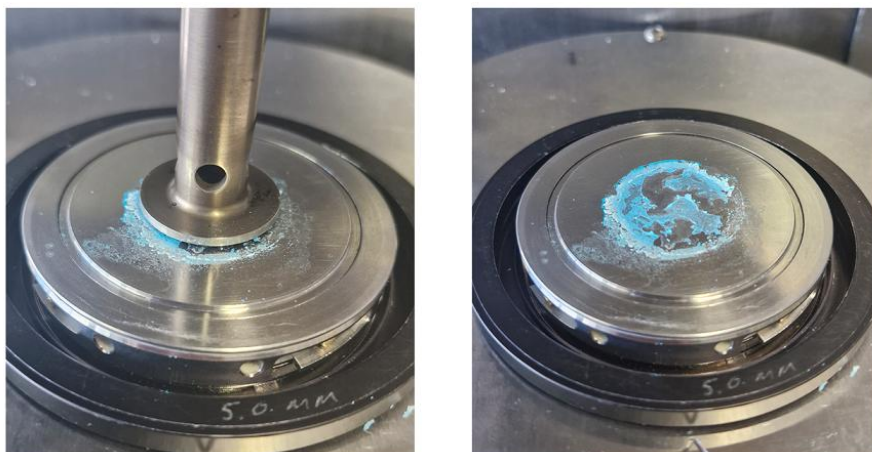


Figure 4.5. The blue sticky mass formed as a result of dehydration of Cu-H₂nip gel.

The angular frequency-based rheological measurements were repeated for various samples of Cu-H₂nip metallogel under different conditions (Figure 4.6). The variations in the absolute values storage modulus (G') and loss modulus (G'') in each experiment may be accounted for by fluctuations in temperature during the gel synthesis and stirring rate. In addition, the stirring often becomes inhomogeneous during the preparation of viscous material like gels. This is because of the difference in viscosity of the material at different regions of stirring. Samples of Cu-H₂nip metallogels were prepared at two ambient temperatures with two different stirring rates and their G' , G'' values were compared. In all the experiments, the stirring time of 15 minutes and the resting time of 5 minutes were followed.

First, a pair of the metallogels were prepared at an ambient temperature 15 °C, with the stirring rates of 700 rpm (revolutions per minute) and 1000 rpm. The metallogel that was prepared with a stirring rate of 1000 rpm was thicker than the one prepared at 700 rpm, which is also reflected in the respective G' and G'' values (Figure 4.6a and b). A similar trend is observed for the gels that were prepared at a higher ambient temperature (22 °C), although the absolute values were different now (Figure 4.6c and d). Thus, it was observed that the stirring rate and ambient temperature during the metallogel synthesis had significant impact on the values of G' and the G'' . For later optimised experiments, the stirring rate of 1000 rpm was preferred.

In a time-dependent experiment, the G' and G'' values of the metallogel were measured at regular intervals as a function of angular frequency. First, the rheological measurements of the freshly prepared gel were performed. Then the measurements

were repeated after aging the same gel for 30, 60 and 120 minutes. It was observed that the structural integrity of the gel was slowly degrading with time. The decrease in values of G' and G'' substantiate this (Figure 4.7). The absolute values of G' and G'' of the Cu-H₂nip metallo gel measured at an angular frequency of 100 rad·s⁻¹ is given in Table 4.1.

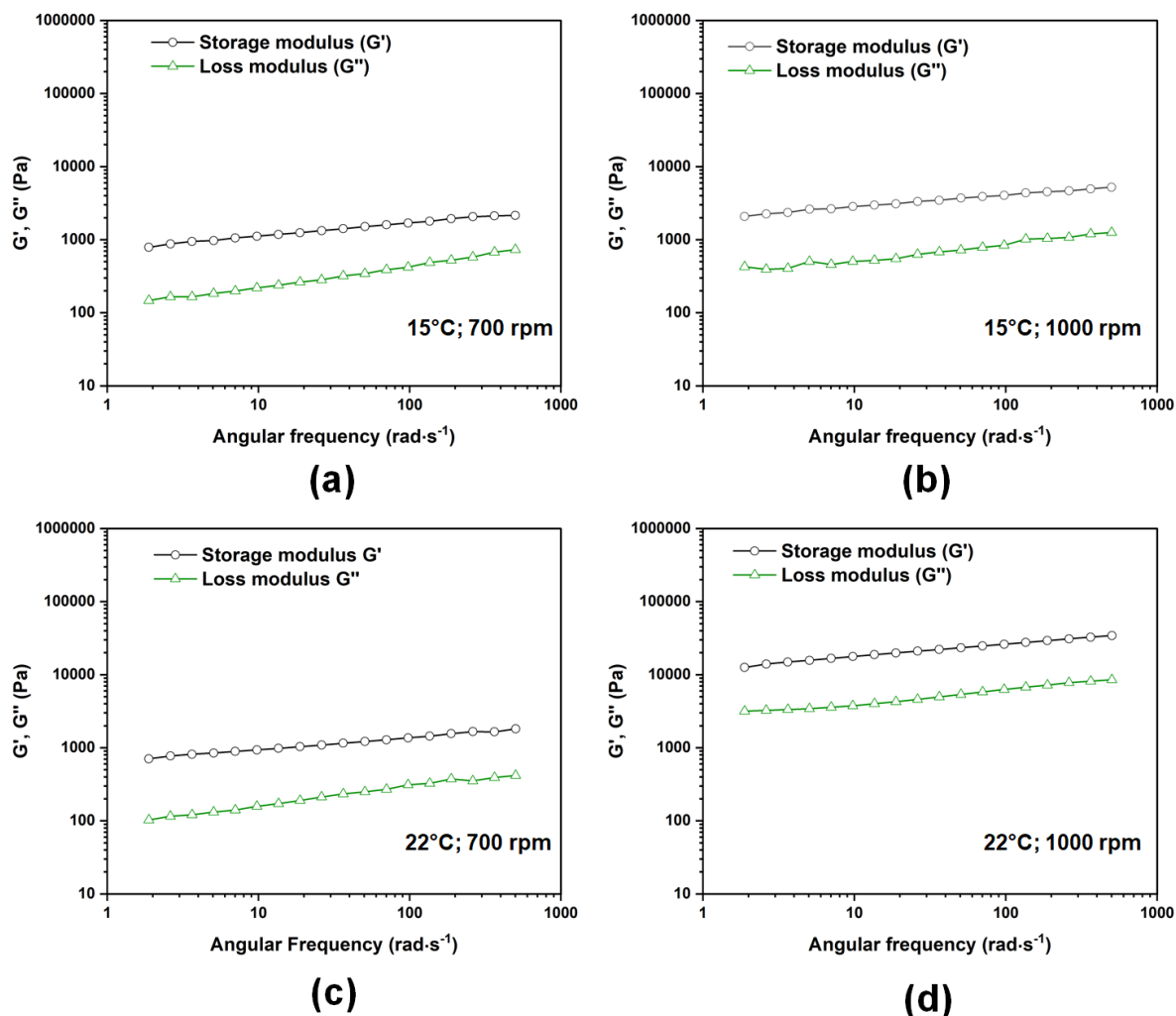


Figure 4.6. Angular frequency-dependent rheological analysis of Cu-H₂nip metallo gel prepared at an ambient temperature and stirring rate of (a) 15 °C and 700 rpm; (b) 15 °C and 1000 rpm; (c) 22 °C and 700 rpm; (d) 22 °C and 1000 rpm respectively.

From the rheology measurements the gel behaviour of the Cu-H₂nip metallo gel was confirmed. The rigidity and thickness of the gel is dependent on parameters during the synthesis such as stirring speed and temperature. Since the main focus was on the qualitative analysis and not the quantitative analysis of the gel, further rheology-based experiments were not performed.

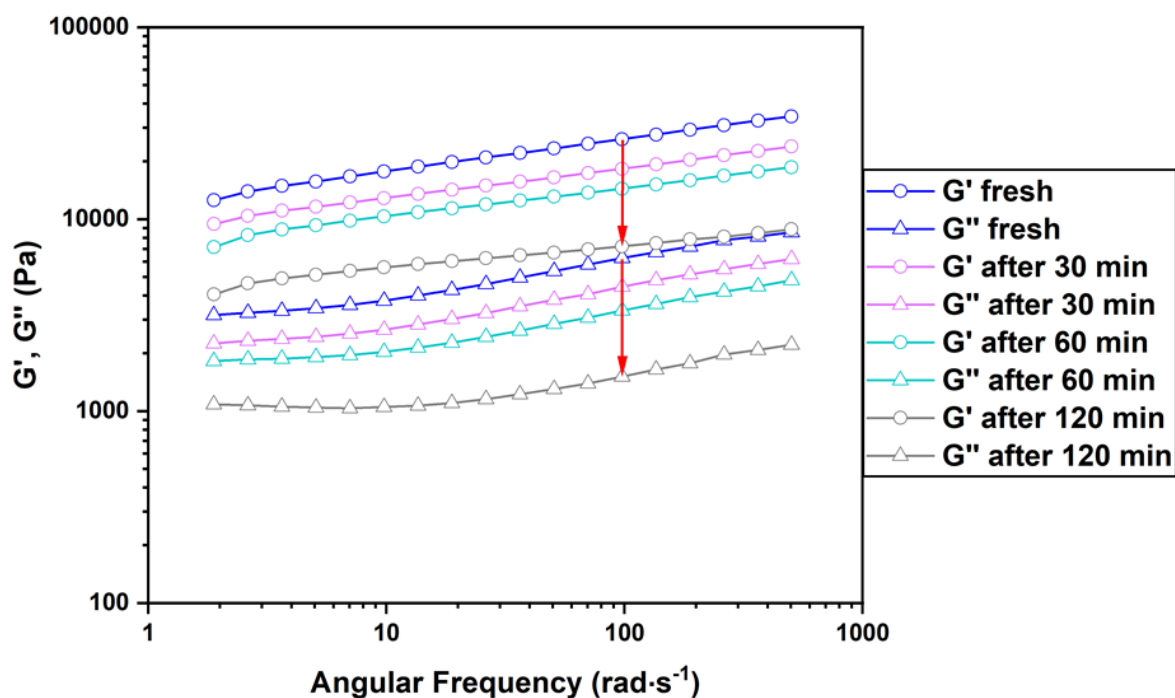


Figure 4.7. Time- dependent rheological measurements of the Cu-H₂nip metallogel.

Table 4.1. The absolute values of G' and G'' of the Cu-H₂nip metallogel measured at an angular frequency of 100 rad·s⁻¹.

Time (min)	G' (Pa)	G'' (Pa)
0	26113	6264
30	18296	4449
60	14399	3339
120	7216	1510

4.3.2. Microscopy and FT-IR Spectroscopy

Polarized light microscopy images of the aged gel (Figure 4.8a and b) also show the presence of some crystalline phases in the reaction mixture. The SEM image of the aged gel shows fibrous networks. (Figure 4.8c). This probably indicates that the reactants in the gel have started to form the polymeric chains which are the functional units in the compound **Cu-nip**. As the gel ages, it collapses into sol (Figure 4.8d).

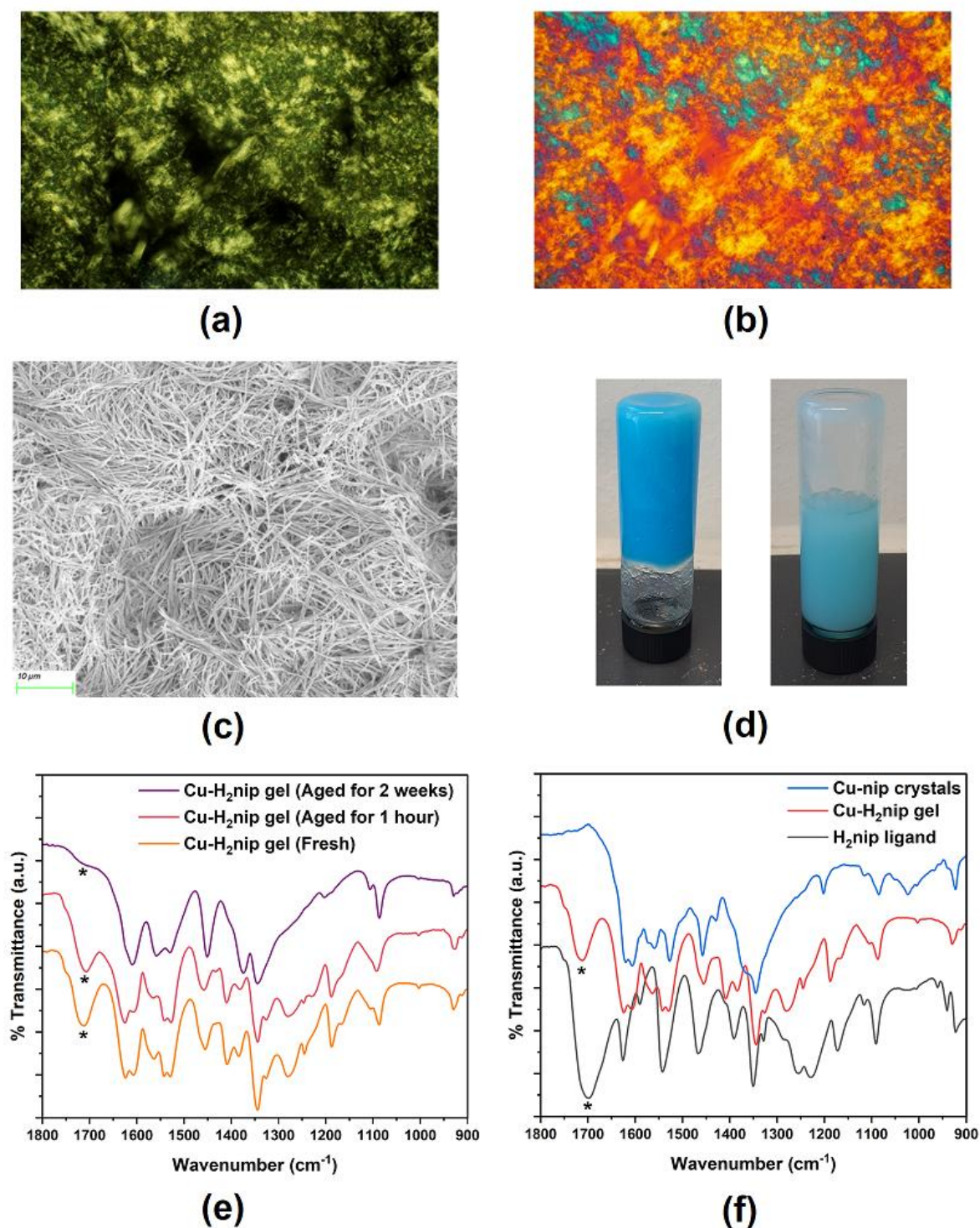


Figure 4.8. (a) and (b) Polarised light microscopy image of the aged gel indicating the formation of crystalline phase in gel (dark green coloured region in the figure); (c) SEM image of aged gel; (d) Fresh Cu-H₂nip metallogel and sol obtained from aging the gel; (e) FT-IR spectra (1800-900 cm⁻¹ range) showcasing the change in degree of deprotonation of carboxylate of ligand in the gel with ageing; (f) FT-IR spectra (1800-900 cm⁻¹ range) of H₂nip ligand, semi-dried Cu-H₂nip metallogel and crystals of **Cu-nip** (* indicate the protonated carboxylate group).

The Cu-H₂nip metallogel is a complex mixture of Cu²⁺ ions, acetate ions (AcO⁻) and the linker 5-nitroisophthalic acid molecules with different deprotonation levels, namely nip²⁻ (doubly deprotonated) and Hnip⁻ (singly deprotonated). As the Cu²⁺ ions and the acetate ions in solution react with H₂nip ligand forming the gel, the amount of protonated ligand decreases with time. This is clear from the FT-IR spectra of the semi-dried gel (Figure 4.8e). The sharp signal at 1712 cm⁻¹ indicates the protonated carboxylic acid in the mixture. However, this signal is absent in the case of **Cu-nip** crystals indicating that the carboxylate groups here are completely deprotonated (Figure 4.8f).

4.3.3. Detailed Analysis of Constituents of Cu-H₂nip Metallogel

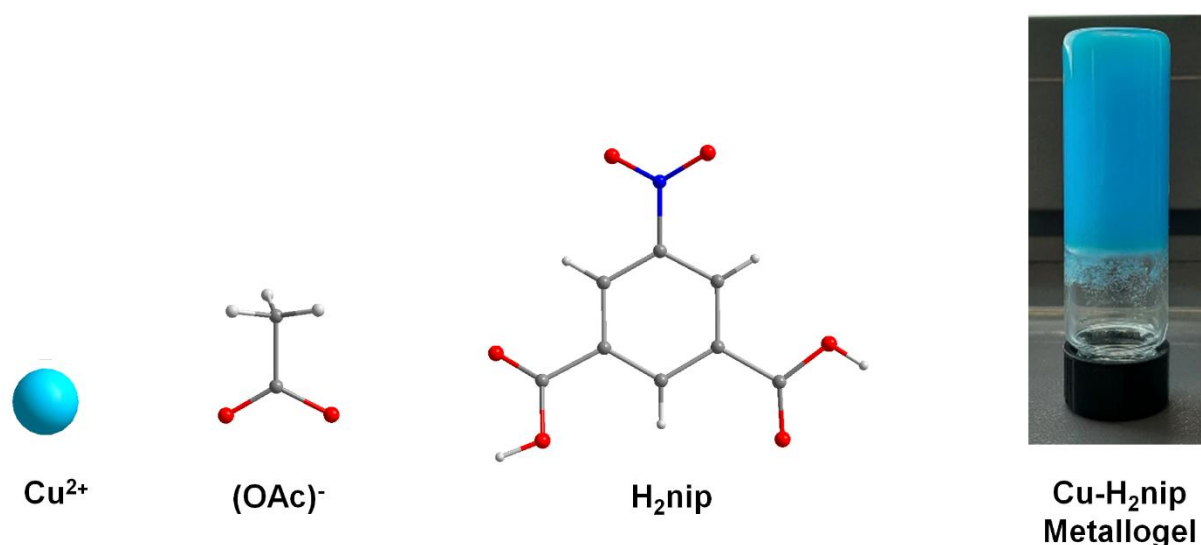


Figure 4.9. Constituents in the Cu-H₂nip metallogel.

The constituents in the Cu-H₂nip metallogel, i.e. Cu²⁺ and (AcO⁻) ions from copper acetate salt and the 5-nitroisophthalic acid (H₂nip) ligand (Figure 4.9) are examined in detail below. Copper acetate, as the Cu²⁺ precursor, was compared with other salts containing different anions such as nitrate, chloride and sulphate. Also, various divalent transition metal acetate salts were tested under similar conditions. Finally, different aromatic carboxylic acids that are structurally similar to 5-nitroisophthalic acid were studied to gain a deeper understanding of the underlying chemistry.

4.3.3.1. Effect of Anion Variation in Cu²⁺ Salts

Firstly, the role of the acetate ion (CH₃COO⁻ or AcO⁻) from copper acetate in the gel formation was quantified. To evaluate this, copper nitrate was used as an alternative source of Cu²⁺ ions in two test systems (Figure 4.10).

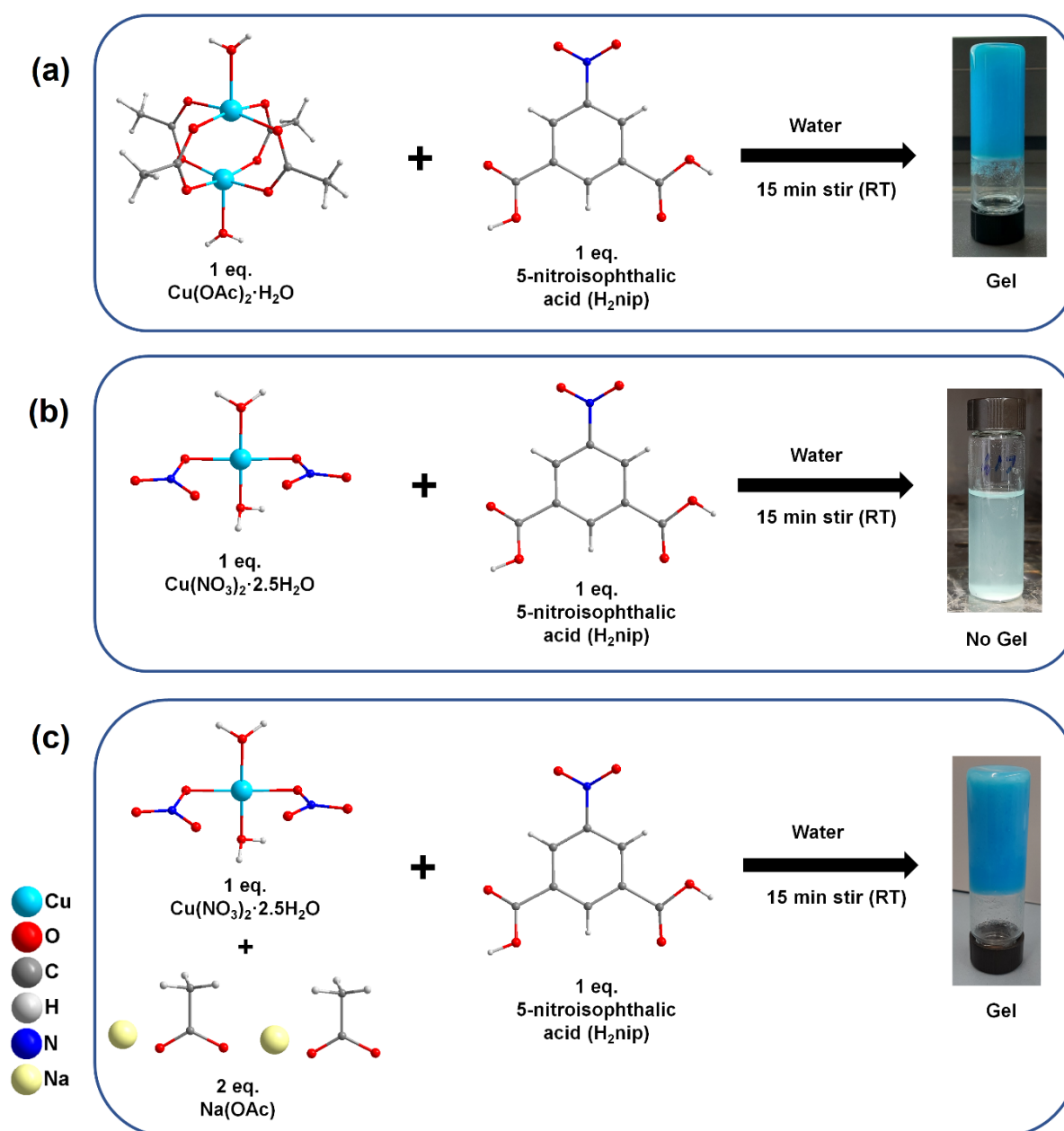


Figure 4.10. Role of acetate ions in metallogel formation of Cu^{2+} ions with 5-nitroisophthalic acid.

In the first case, 1 equivalent of copper nitrate (Figure 4.10b) was used in place of copper acetate (Figure 4.10a) and was made to react with 1 equivalent of H_2nip . Gel formation was not observed here and a pale-blue suspension was obtained, which upon heating in the oven resulted in a clear blue solution. After two days, the reaction vial was removed from the oven and left to stand at room temperature and crystallisation of H_2nip ligand was observed. Similar results were observed when copper chloride and copper sulphate were used as the Cu^{2+} source.

In the second test reaction 1 equivalent of copper nitrate and an additional 2 equivalents of sodium acetate were dissolved in water (since there are two AcO^- ions per Cu^{2+} ion in $\text{Cu}(\text{OAc})_2$). Subsequently, the addition of 1 equivalent of H_2nip to this reaction mixture yielded a blue gel (Figure 4.10b) which later transformed into the Cu_5 -cluster MOF (**Cu-nip**) upon heating in oven at 95°C .

HNO_3 ($\text{pK}_a = -1.37$) is a strong acid, therefore its conjugate base (NO_3^-) ($\text{pK}_b = 15.37$) is weak. Similarly, HCl ($\text{pK}_a = -7$) and H_2SO_4 ($\text{pK}_a = -2.8$) has the conjugate bases Cl^- ($\text{pK}_b = 18$) and $(\text{HSO}_4)^- / (\text{SO}_4)^{2-}$ ($\text{pK}_b = 17 / 12.1$), which are also weak. On the other hand, CH_3COOH ($\text{pK}_a = 4.76$) is a weak acid, and its conjugate base CH_3COO^- or AcO^- ($\text{pK}_b = 9.80$) is strong enough to deprotonate H_2nip . During the gel formation, the H_2nip molecules ($\text{pK}_a = 2.81$) are slowly deprotonated by the acetate anions, followed by the coordination to the Cu^{2+} ions. The pH of the gel solution is approximately 3.

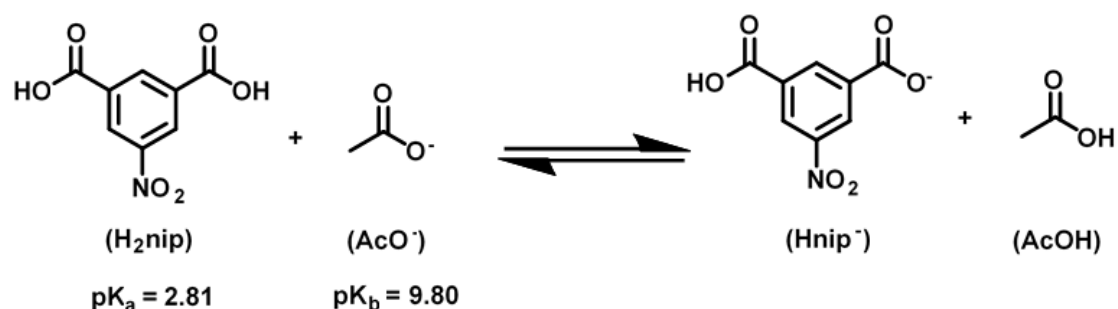


Figure 4.11. Deprotonation of H_2nip by the acetate anion.

Similarly, copper pivalate ($\text{Cu}(\text{OPiv})_2$) was used as a source of Cu^{2+} ions. The structure and the basicity of the pivalate ion (PivO^-) is similar to that of acetate (pK_b of pivalate = 8.97), but the solubility of this salt in water is very low. Hence during the experiments, a uniform mixture of copper pivalate and H_2nip was not obtained in water. However, the hydrothermal reaction of the mixture predominantly yielded the compound **Cu-nip**.

4.3.3.2. Effect of Variation of Divalent Transition Metal Ions in Acetate Salts

This section describes the use of acetate salts of several divalent first-series transition metal ions, including $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, to investigate their role in metallogel formation and their potential use as metalloligands. These salts form clear solutions in water, with distinct colours: Co^{2+} (pink), Ni^{2+} (green), Zn^{2+} (colourless) and Cu^{2+} (blue).

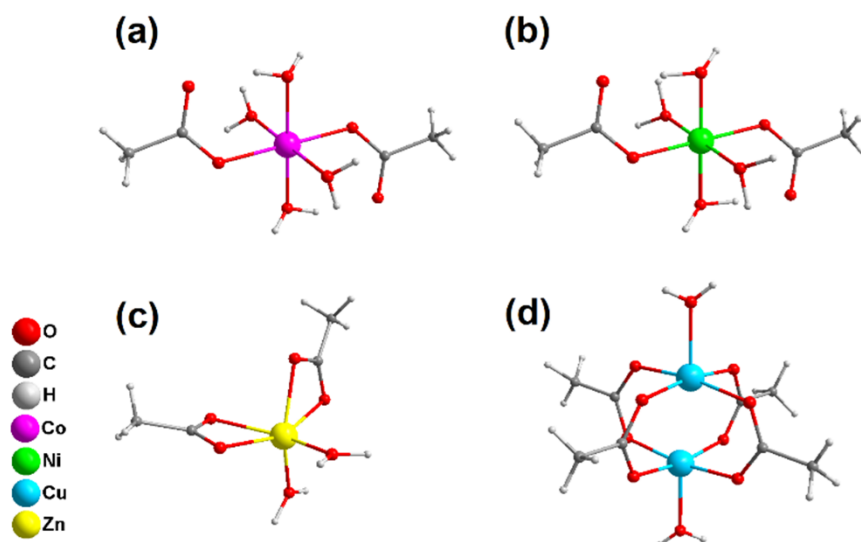


Figure 4.12. (a) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; (b) $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; (c) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$; (d) $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$.

As described earlier, the H_2nip ligand reacts with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in water to form a gel, and heating the resultant mixture yields crystals of $[\text{Cu}_5(\text{OH})_2(\text{nip})_4(\text{H}_2\text{O})_6] \cdot 4.25\text{H}_2\text{O}$ (**Cu-nip**). However, it was observed that the solutions of acetate salts of Co^{2+} , Ni^{2+} and Zn^{2+} yield clear solutions upon the ligand addition and these mixtures upon hydrothermal treatment gave crystals of $[\text{Co}(\text{nip})(\text{H}_2\text{O})_5]$ (**Co-nip**), $[\text{Ni}(\text{nip})(\text{H}_2\text{O})_5]$ (**Ni-nip**), and $[\text{Zn}(\text{nip})(\text{H}_2\text{O})]$ (**Zn-nip**) respectively.

The molecular structures of the various transition metal acetates used here are shown in Figure 4.12 for (a) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, (b) $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, (c) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, (d) $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$. Copper acetate exist as dimeric molecule and the rest of them as monometallic complex. The dimeric paddle wheel structure is observed only for $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, which makes it unique from the rest. Now, from the $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ - H_2nip mixture in water, the crystals of **Cu-nip** are obtained during heating in the oven. In the three-dimensional network, there are intramolecular hydrogen bonds between the protons on water molecule coordinated to Cu^{2+} ions and the carboxylate oxygen of the ligand (Figure 4.13d).

In the case of acetate salts of cobalt and nickel, the complexes obtained with H_2nip in water are nearly isostructural. Here, a discrete unit $[\text{M}(\text{nip})(\text{H}_2\text{O})_5]$ (**M-nip**) is formed, where M^{2+} ($\text{M} = \text{Co}$ or Ni) ions are surrounded octahedrally by five water molecules and one oxygen from doubly deprotonated nip^{2-} ligand.

The individual core units in **Co-nip** and **Ni-nip** are connected by hydrogen bonds between the protons on the water molecules coordinated to the transition metal ions of a molecule and the carboxylate oxygen of the ligand of neighbouring molecules (inter-molecular hydrogen bonding) (Figure 4.13a, b).

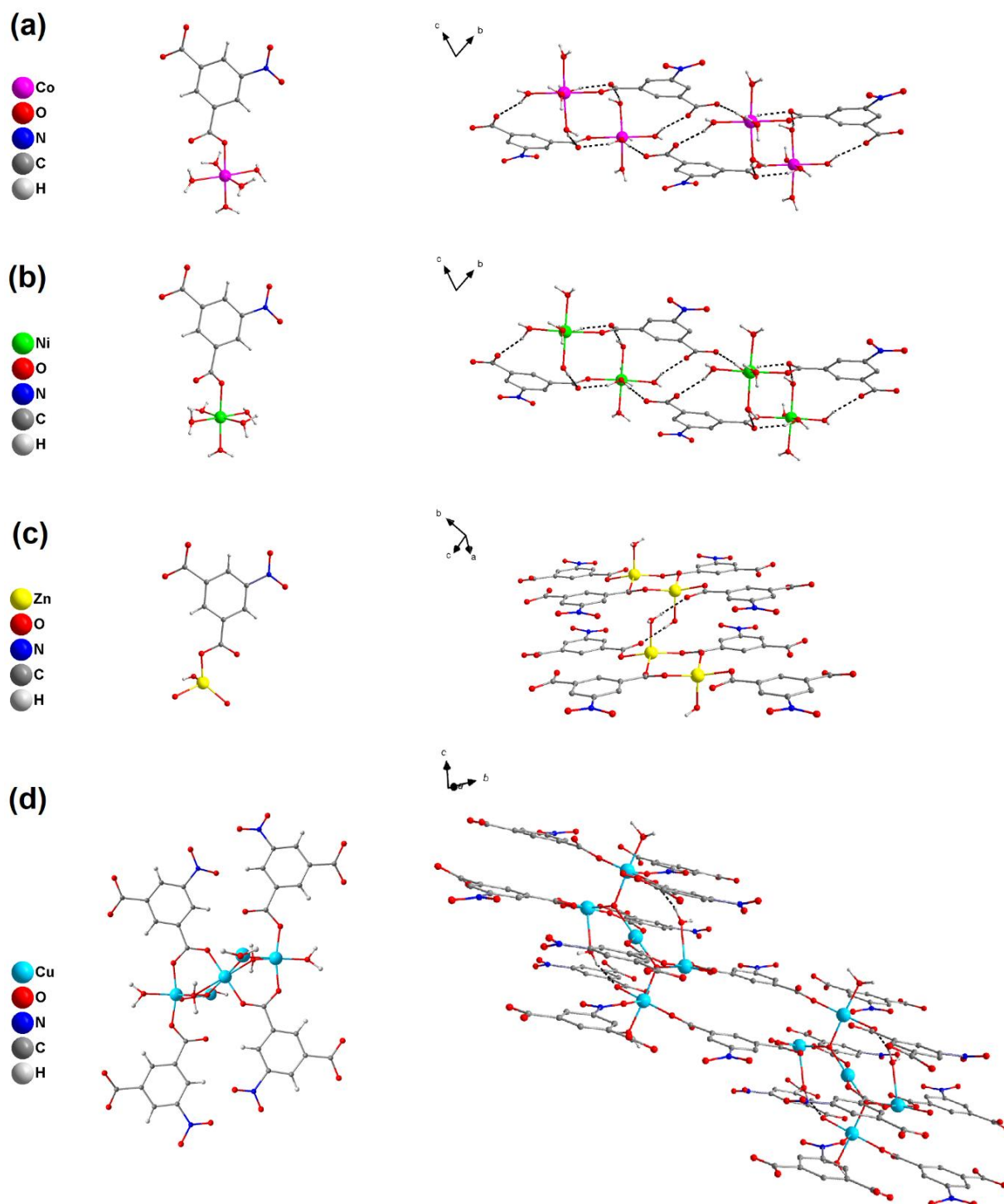


Figure 4.13. Crystal structure and packing of (a) [Co(nip)(H₂O)₅] (**Co-nip**); (b) [Ni(nip)(H₂O)₅] (**Ni-nip**); (c) [Zn(nip)(H₂O)] (**Zn-nip**); (d) [Cu₅(OH)₂(nip)₄(H₂O)₆]·4.25H₂O (**Cu-nip**). Hydrogen bonds are denoted with dotted lines.

As for the case of zinc acetate with H₂nip, the complex obtained [Zn(nip)(H₂O)] (**Zn-nip**) features a Zn²⁺ ion in a distorted tetrahedral environment formed by three carboxylate oxygen atoms and a water molecule. There are also hydrogen bonds between the protons on the water molecule coordinated to Zn²⁺ ions of a molecule and the carboxylate oxygens of neighbouring molecule (Figure 4.13c). This is a previously reported compound.^[93]

Clearly, the metal-ligand complex is unique in the case of Cu²⁺ ions. It is noteworthy that among the acetate salts of some first-row transition metal ions such as Mn²⁺, Mn³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺, only Cu²⁺ forms a metallogel with H₂nip.

4.3.3.3. Effect of Aromatic Carboxylic Acid Variations

For the synthesis of multifunctional metal–organic frameworks (MOFs), the linker molecules are crucial. The linker plays an important role in determining the unique structures and properties of the molecules.^[94]

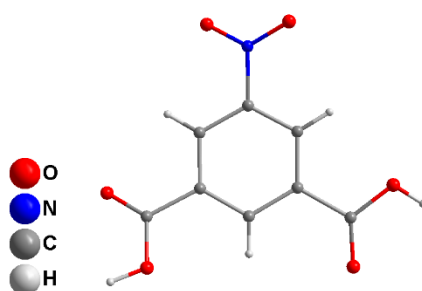


Figure 4.14. H₂nip ligand

Concerning the structure of the 5-nitroisophthalic acid (H₂nip) molecule, it has two carboxylate groups at 1, 3- positions that usually result in metal coordination during MOF synthesis (Figure 4.14). The nitro group (-NO₂) at the 5-position is usually non-coordinating and acts as an electron-withdrawing group on the aromatic backbone, making the carboxylates more acidic compared to the ones in isophthalic acid. The nitro group and conjugated aromatic rings present good chemical and thermal stabilities for the coordination compounds of H₂nip.^[95] Under suitable conditions, either one or both of the two carboxylate groups may be deprotonated, which makes it a very good candidate to act as a multidendate ligand.^[96] The two carboxylate groups are at an angle of 120° to each other which makes them suitable for bridging metal ions (for example oxophilic lanthanide ions) through various coordination modes. This is why the metalloligand

made from H₂nip is interesting for the synthesis of HMOFs as discussed in later sections. Furthermore, the nitro group in the molecule can act as a hydrogen bond acceptor, thereby improving its solubility in water. H₂nip is soluble in hot water (above 85 °C).

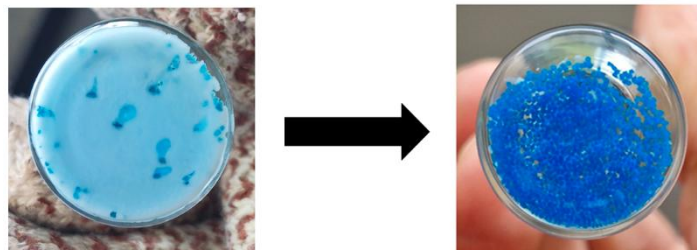


Figure 4.15. Crystal growth of **Cu-nip** from precipitate through Ostwald ripening.

As described previously, the Cu-H₂nip (1:1) metallogel is obtained when 1 equivalent each of Cu(OAc)₂·H₂O and 5-nitroisophthalic acid (H₂nip) are stirred in 10 mL water. When this is heated at 95 °C, crystals of the MOF [Cu₅(OH)₂(nip)₄(H₂O)₆]·4.25(H₂O) (**Cu-nip**) are obtained. The crystal growth starts from the blue precipitate which forms as the gel is heated (Figure 4.15). This is an example of Ostwald ripening^[97-99] where the particles in the precipitate slowly dissolve and then redeposit as crystals. The solubility of H₂nip ligand in hot water is one of the reasons which facilitates the dissolution of solid reaction mixture (precipitate) into the solvent.

Due to the structural similarity with 5-nitroisophthalic acid (H₂nip), three other aromatic carboxylic acids, namely 5-aminoisophthalic acid (H₂aip), 5-hydroxyisophthalic acid (H₂hip), and simple isophthalic acid (H₂ip) (Figure 4.16), were subjected to the same reaction conditions for metalloligand formation with copper acetate (Cu²⁺ : carboxylic acid = 1 : 1). However, none of these carboxylic acids yielded a gel or crystals upon heating.

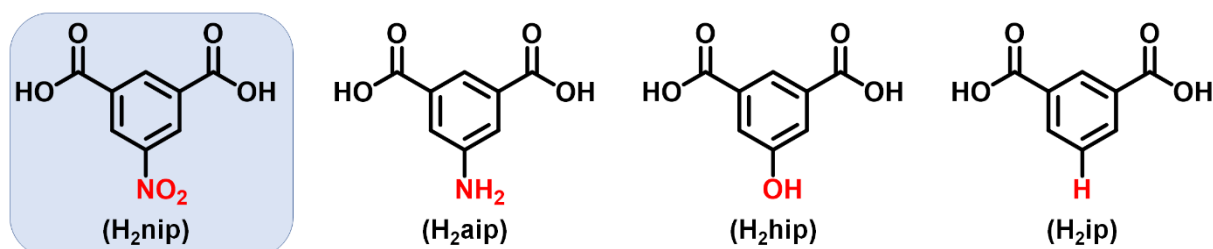


Figure 4.16. 5-nitroisophthalic acid and other substituted isophthalic acid

Clearly, the presence of the nitro group at the 5-position of H₂nip plays a vital role in metallogel formation. This nitro group acts as a hydrogen bond acceptor and activates

the carboxylate groups, promoting deprotonation. Such activation is thus a crucial in the gel formation and also during the crystallization.

The H₂nip molecule contains a nitro group (-NO₂) and two carboxylic acid (-COOH) groups, and now two other extreme cases are considered. In the first case, the nitro group is replaced with a carboxylic acid group, i.e 1,3,5-benzenetricarboxylic acid (H₃btc) was used. In the other case, one of the carboxylic acid groups is replaced with a nitro group, i.e. 3,5 dinitrobenzoic acid (Hdnb) was used (Figure 4.17).

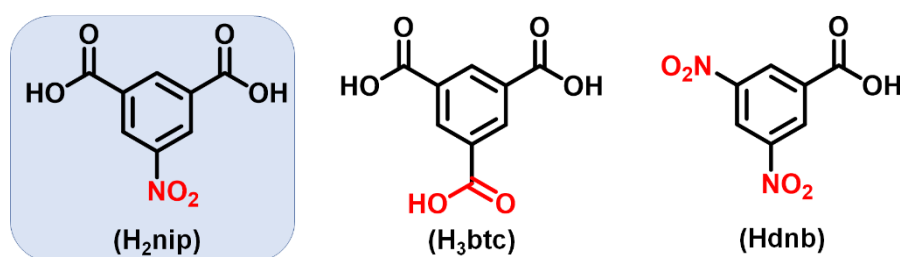


Figure 4.17. 5-nitroisophthalic acid, 1,3,5-benzene tricarboxylic acid and 3,5-dinitrobenzoic acid.

Gel formation was not observed when these ligands were reacted with copper acetate in water. With these, Cu²⁺ containing coordination polymers, namely [Cu(Hbtc)(H₂O)₃] (**Cu-Hbtc**) and [Cu(dnb)(OH)] (**Cu-dnb**) and were formed when the reaction mixtures were heated at 95 °C in the oven (Figure 4.18).

The compound **Cu-Hbtc** has been previously reported, but using a different synthetic procedure.^[100] **Cu-dnb** is has a [Cu(OH)(COO)]_n chain, similar to that in a known MOF, MIL-121 which is based on Al³⁺.^[101]

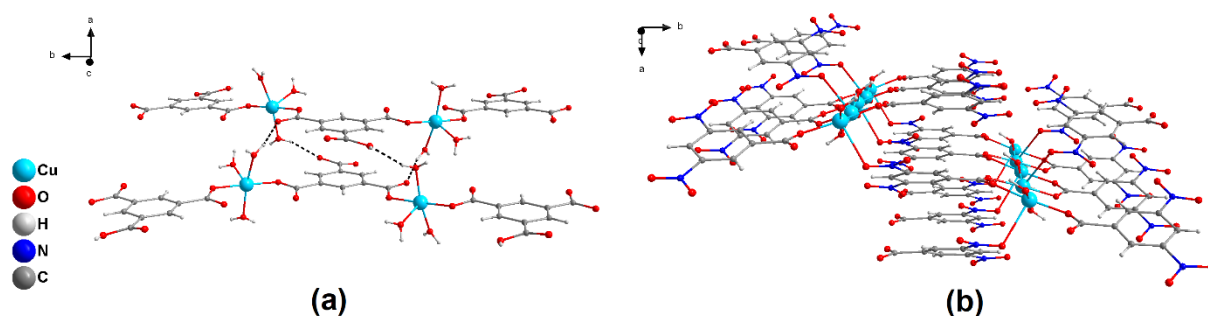


Figure 4.18. Crystal structure of (a) [Cu(Hbtc)(H₂O)₃] and (b) [Cu(dnb)(OH)].

4.4. Cu-H₂nip Metallogel as Metalloligand Precursor for La³⁺-Containing HMOFs

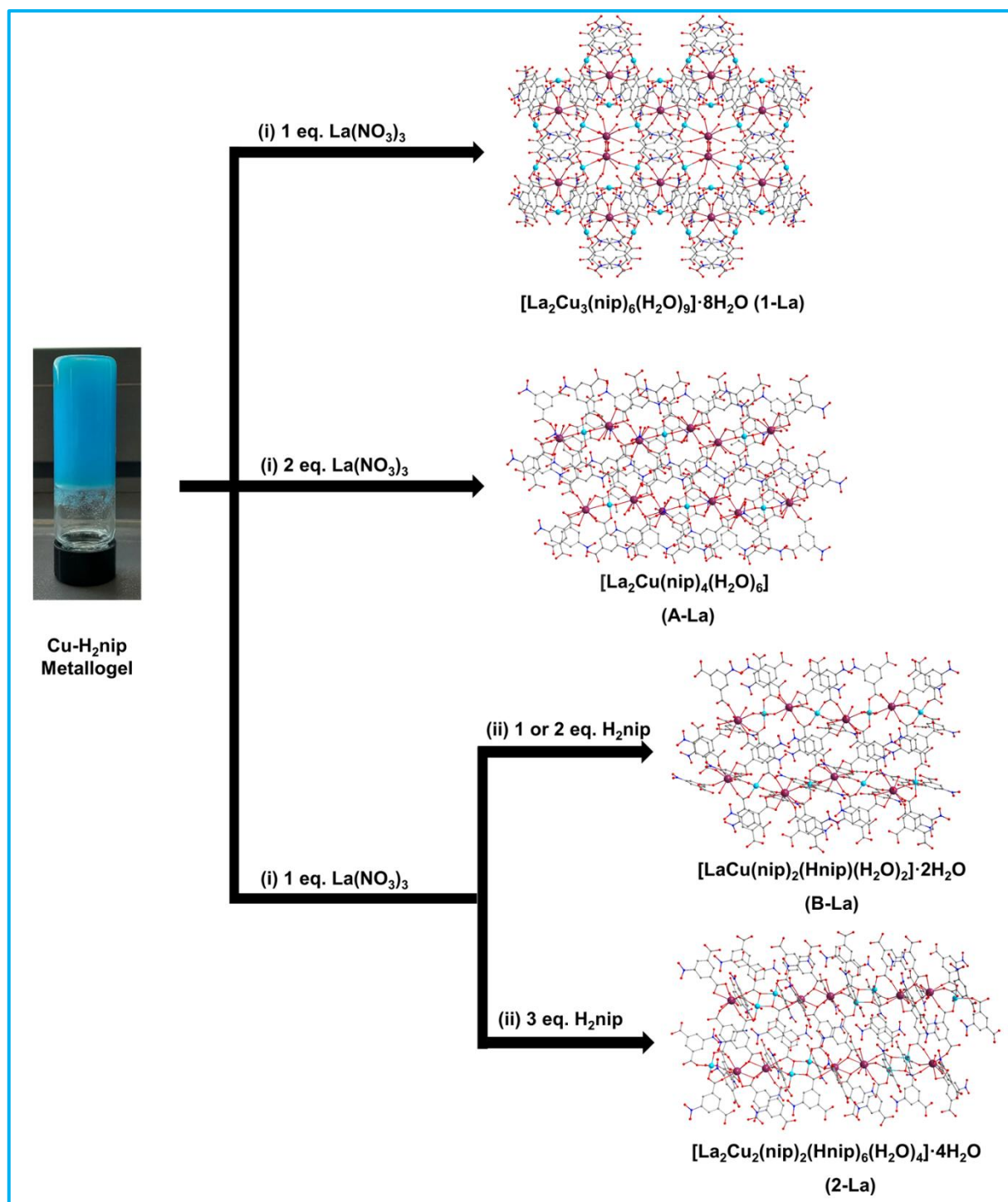


Figure 4.19. Metalloligand approach using Cu-H₂nip metallogel to incorporate La³⁺ ions.

The step-by-step procedure is the preferred methodology for synthesizing heterometallic metal-organic frameworks (HMOFs) containing lanthanide (Ln) and transition metal (TM) ions. As a general synthetic strategy, a single-metal metalloligand is first synthesized, followed by the introduction of Ln³⁺ ions into the target HMOFs.^[32]

In this case, the synthesis of Cu-Ln HMOF is achieved using Cu-H₂nip metallogel as the metalloligand precursor. After introducing additional reagents to the metallogel, the reaction mixtures were heated in an oven and monitored visually since the syntheses were performed using Wheaton vials. Initially, La(NO₃)₃ was used as the source of lanthanide ions. The synthetic strategy is outlined in Figure 4.19.

In the first experiment, one equivalent of La(NO₃)₃ was added to the Cu-H₂nip (1:1) metallogel, resulting in the formation of a new heterometallic MOF [La₂Cu₃(nip)₆(H₂O)₉]·8H₂O (**1-La**).

In the second reaction, higher equivalents of La(NO₃)₃ (e.g. 2 eq.) were added. Here [La₂Cu(nip)₄(H₂O)₆] (**A-La**) was isolated. This compound was previously reported by Junwei Ye *et al.*, but at a higher reaction temperature (170 °C) and using a different molar ratio of reagents.^[102]

In the next set of reactions, an equivalent of La(NO₃)₃ was added to the Cu-H₂nip (1:1) metallogel, followed by various equivalents (1, 2, 3 eq.) of H₂nip. For 1 and 2 eq. of H₂nip added, compound [LaCu(nip)₂(Hnip)(H₂O)₂]·2H₂O (**B-La**) was obtained and using 3 eq. of H₂nip, a new heterometallic MOF [La₂Cu₂(nip)₂(Hnip)₆(H₂O)₄]·4H₂O (**2-La**), was obtained. The compound **B-La** was also previously reported by Junwei Ye *et al.*, but at a higher reaction temperature in a one-pot reaction.^[102-103]

4.4.1. Addition of 1 Equivalent Lanthanum Nitrate: Synthesis of La₂Cu₃ (1-La) System

When one equivalent of La(NO₃)₃ was added to the blue Cu-H₂nip (1:1) metallogel, it gradually collapsed, forming a very pale blue colloidal mixture (Figure 4.20). The highly uniform mixture has a Cu : H₂nip : La ratio of 1 : 1 : 1 and this was then heated in an oven at 95 °C.

After about 2 hours, the mixture changes into a suspension where blue precipitate starts to settle on the bottom of the vial. After approximately 12 hours, tiny nucleation sites can be observed within the precipitate, which initiate the crystallization process. Blocks of long, dark blue crystals of [La₂Cu₃(nip)₆(H₂O)₉]·8H₂O (**1-La**) begin to grow, with crystallization via Ostwald ripening complete after approximately 64 hours (Figure 4.21c-g).

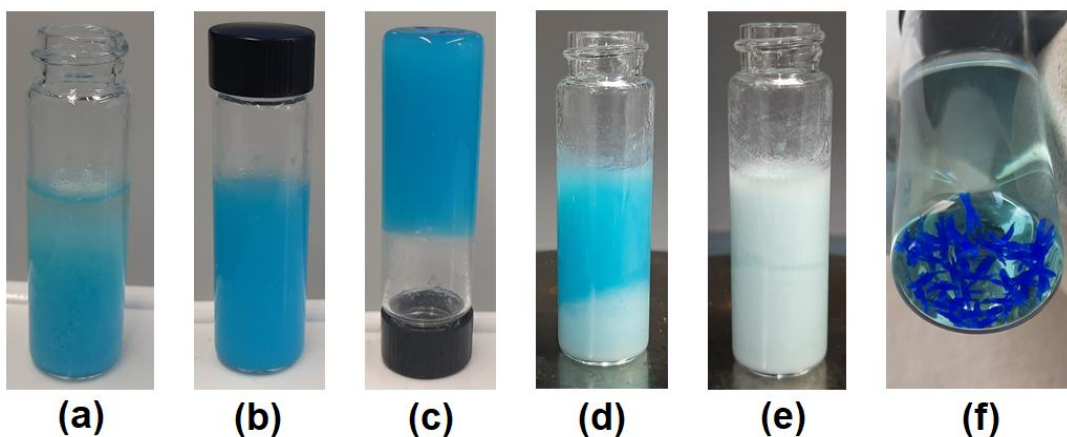


Figure 4.20. (a) Mixture of copper acetate, 5-nitroisophthalic acid and water evolving into gel over the course of 15 minutes; (b) Cu-H₂nip metallogel; (c) Inverted vial to show the stability of gel; (d) Blue gel collapsing into pale blue colloid after the addition of lanthanum nitrate; (e) Very pale-blue colloidal mixture; (f) Dark blue crystals of **1-La**.

Ostwald's rule states that crystallization typically proceeds through the formation of intermediate, less stable phases that gradually transform into larger, more stable crystals.^[97-98] From the starting materials, a kinetically metastable intermediate phase is initially formed, which then partially dissolves and transforms into a chemically and thermodynamically stable MOF.^[104]

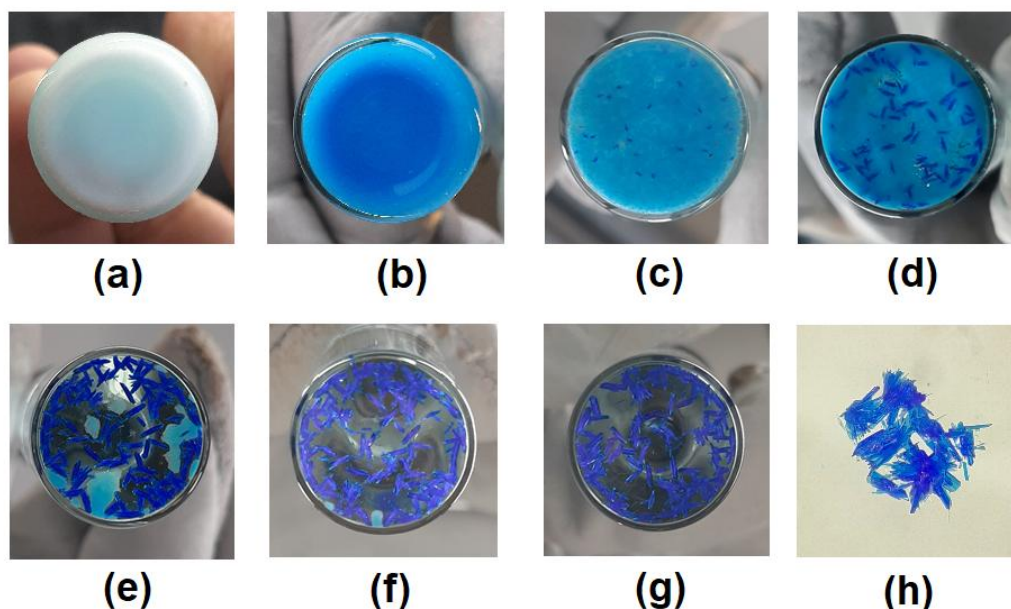
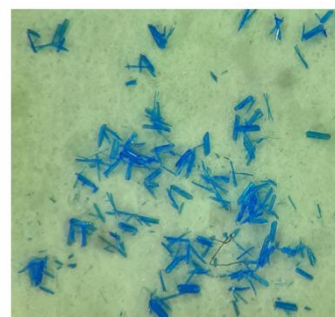
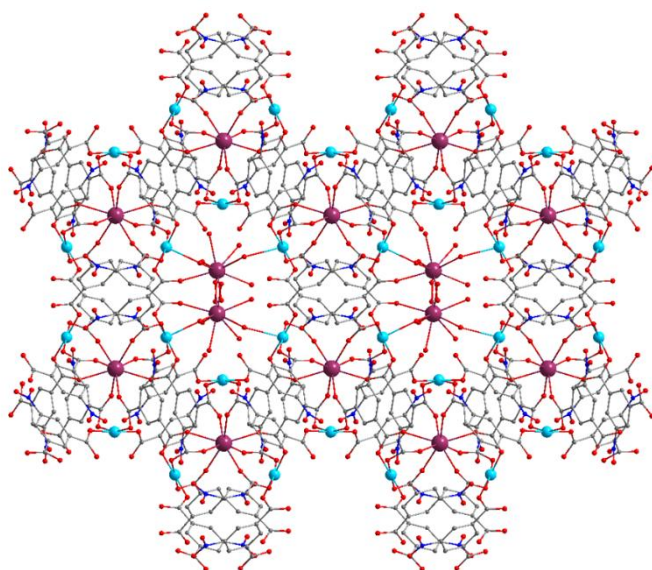


Figure 4.21. (a) Pale blue colloid reaction mixture before heating; (b) Blue precipitate of reaction mixture after 2 hours of heating in oven; (c)-(g) Crystal growth of compound **1-La** from precipitate through Ostwald ripening over 64 hours; (h) Dark blue crystals of **1-La**.

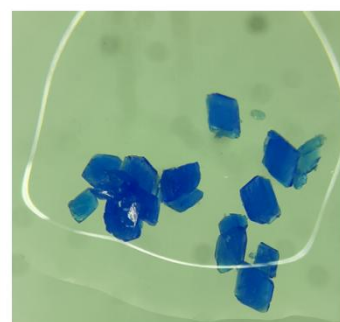
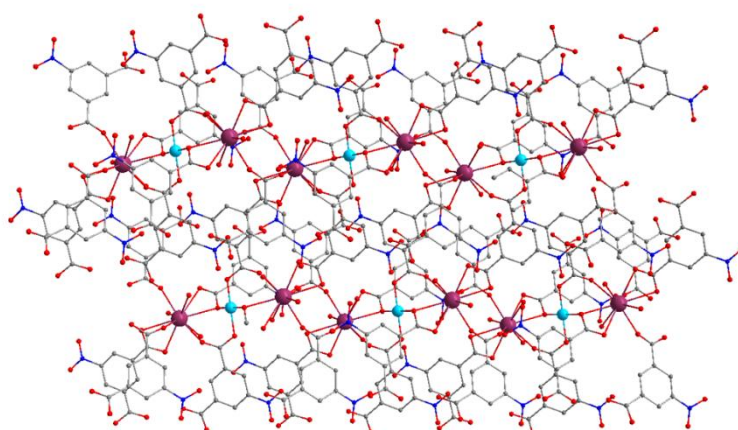


[La₂Cu₃(nip)₆(H₂O)₉]·8H₂O (1-La)

Figure 4.22. Crystal structure of **1-La** (left); Dark blue crystals of **1-La** (right).

4.4.2. Addition of Higher Equivalents of Lanthanum Nitrate: Synthesis of La₂Cu (A-La) System

When 2 equivalents of lanthanum nitrate are added to the Cu-H₂nip metallogel, the reaction mixture yields [La₂Cu(nip)₄(H₂O)₆] (**A-La**) within 24 hours of heating. This compound was first reported by Junwei Ye *et al.*¹⁴ in a one pot approach at 170 °C and with a different molar ratio. Since this compound is already known, only crystallographic structural evaluation and infrared spectroscopy were performed.



[La₂Cu(nip)₄(H₂O)₆] (A-La)

Figure 4.23. Crystal structure of **A-La** (left); Dark blue crystals of **A-La** (right).

4.4.3. Addition of Extra Equivalents of H₂nip: Synthesis of LaCu (B-La) and La₂Cu₂ (2-La) System

The amount and ratio of reagents in a reaction mixture can directly influence the yield and structure of the product obtained. In MOF synthesis, this is very important with regard to the amount of ligand in the system. To understand this scenario, the role of addition of extra amounts of H₂nip ligand in reaction mixture was investigated.

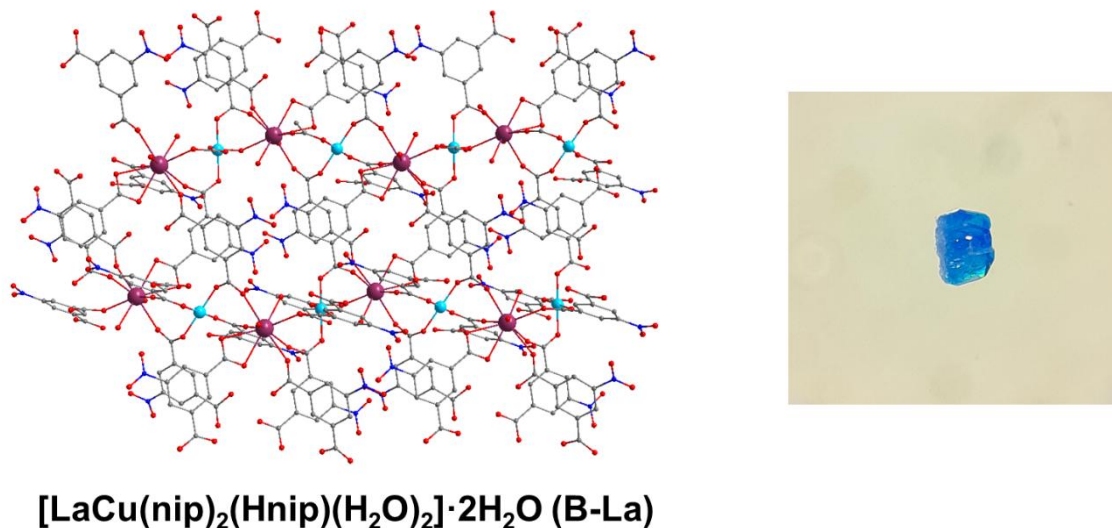


Figure 4.24. Crystal structure of **B-La** (left); Dark blue crystal of **B-La** (right).

As discussed in section 4.4.1, when 1 eq. La(NO₃)₃ was added to the Cu-H₂nip gel, a reaction mixture with Cu²⁺ : H₂nip : La³⁺ ratio of 1 : 1 : 1 was obtained, from which the compound **1-La** crystallizes. Considering this reaction as a reference, three Cu²⁺-H₂nip-La³⁺ mixtures with same molar ratio were prepared and extra 1, 2 or 3 equivalents of H₂nip ligands were added to these.

When 1 or 2 equivalents of extra H₂nip ligand were added to the Cu²⁺-H₂nip-La³⁺ (1-1-1) reaction mixture, the resultant ratio of reagents in the reaction mixture become Cu²⁺ : H₂nip : La³⁺ = 1 : 2 : 1 and 1 : 3 : 1 respectively. In both cases, after heating the reaction mixtures at 95 °C, the compound [LaCu(nip)₂(Hnip)(H₂O)₂·2H₂O] (**B-La**) was obtained. This compound was previously reported by Junwei Ye *et al.*,^{14,15} but by following a one-pot approach using a ratio of Cu²⁺ : H₂nip : La³⁺ = 1 : 2.5 : 1 and also for a ratio of Cu²⁺ : H₂nip : La³⁺ = 1 : 2 : 1, i.e., similar to the ratio used in this work.

Apparently, the optimum amount of H₂nip in the reaction mixture for which, the compound **B-La** is obtainable is 2-3 equivalents. This was confirmed with the case when 3 equivalents of extra ligand was added to the Cu²⁺-H₂nip-La³⁺ mixture, where the final

ratio is $\text{Cu}^{2+} : \text{H}_2\text{nip} : \text{La}^{3+}$ became 1 : 4 : 1, and resulted in a new compound $[\text{La}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**2-La**).

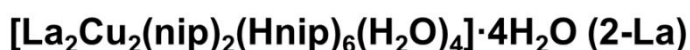
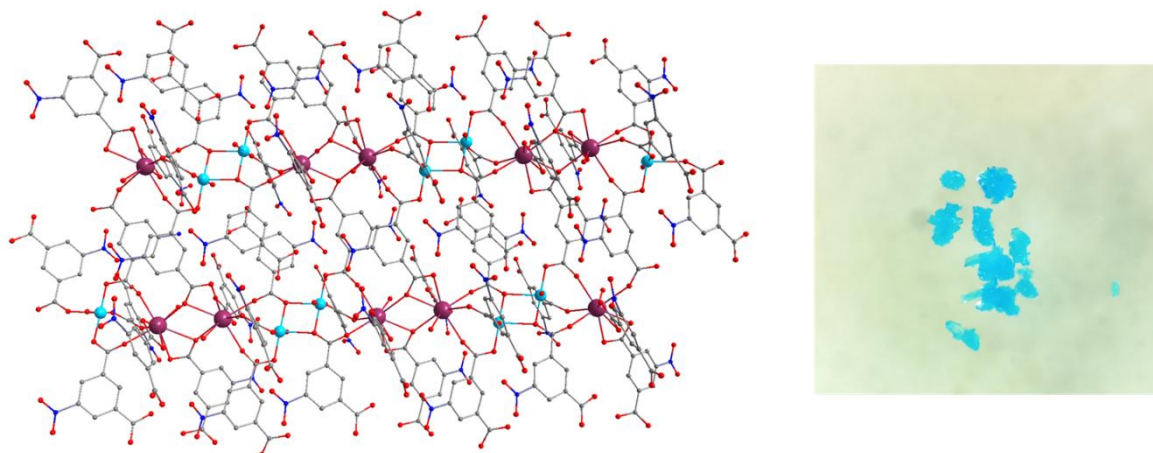


Figure 4.25. Crystal structure of **2-La** (left); Blue crystals of **2-La** (right).

The addition of more equivalents of ligand does not affect the outcome of the reaction, but rather, once the reaction mixture is removed from the oven and cooled to room temperature, the H_2nip ligand precipitates and forms colourless crystals within a few days. (Figure 4.26).

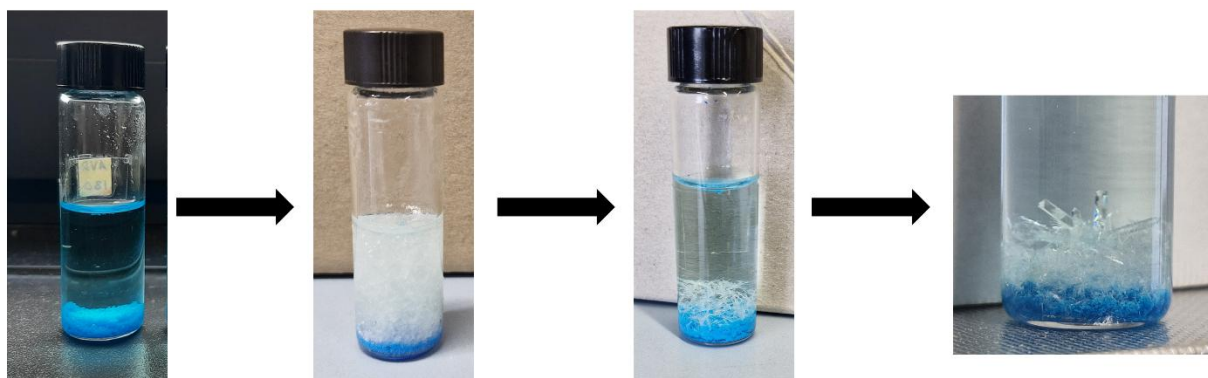


Figure 4.26. Crystallization of excess H_2nip from reaction mixture.

Furthermore, a metastable compound $[\text{La}_4\text{Cu}_{1.25}(\text{nip})_{4.5}(\text{Hnip})_{5.5}(\text{H}_2\text{O})_{8.5}] \cdot 12.5 \text{ H}_2\text{O}$ (**2-La-meta**) was also isolated during the initial phase of crystal growth in **2-La**. These were observed as pale blue crystals which then redissolve into the reaction mixture as the heating continued over 24-48 hours. During this time, an increase in the amount of the blue crystals of **2-La** was visible (Figure 4.27).

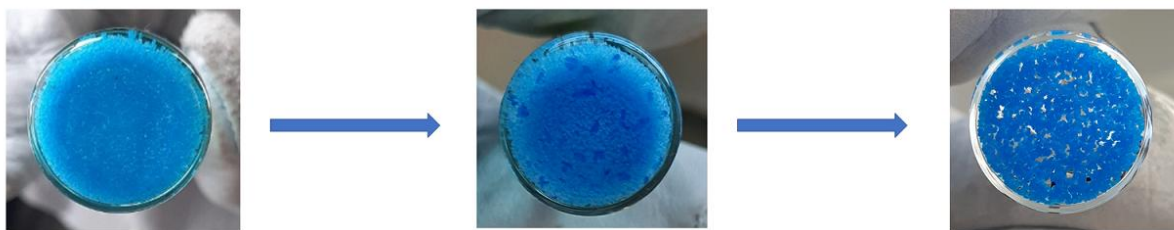


Figure 4.27. Crystal growth of **2-La** from **2-La-meta**.

4.5. Variation of the Anion of the La^{3+} Salt

As mentioned earlier, lanthanum nitrate was used for the synthesis of all the HMOFs. In the first example, when $\text{La}(\text{NO}_3)_3$ was introduced, the blue $\text{Cu-H}_2\text{nip}$ metallogel collapsed into a pale blue colloidal mixture. Upon heating, $[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$ (**1-La**) crystallized from this mixture. Another test reaction using LaCl_3 was performed using the same procedure as before. Here the compound **1-La** was obtained. This indicates that the presence of weaker conjugate bases such as $(\text{NO}_3)^-$ and Cl^- are favoured for the formation of **1-La** from the metallogel.

To substantiate this, the acetate (AcO^-) and carbonate ($(\text{CO}_3)^{2-}$) salts of La^{3+} were also tried under similar reaction conditions. Both these anions are stronger conjugate bases compared to nitrate and chloride ions. No crystals were formed in both cases, underlying the importance of having a weaker conjugate base to promote the formation of **1-La** from the metallogel.

4.6. Variation of Ln^{3+} Ion in the Nitrate Salt

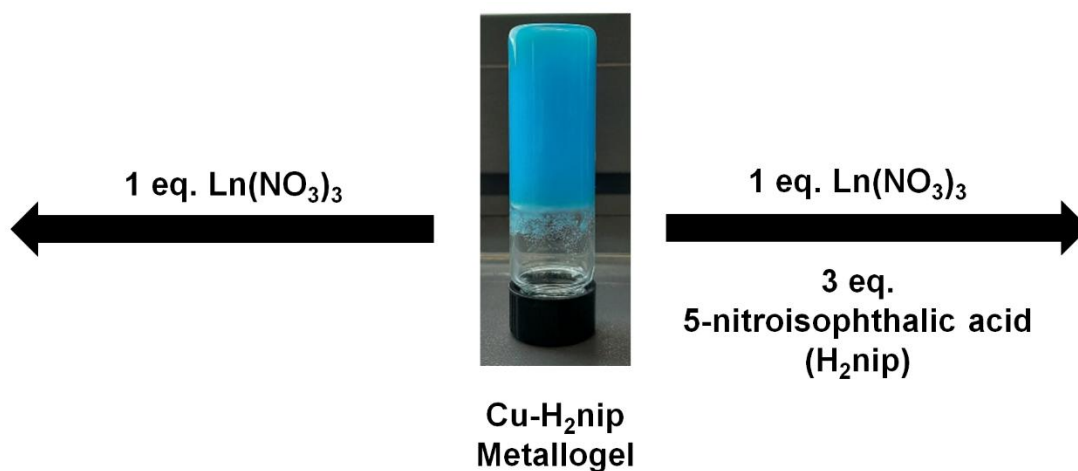


Figure 4.28. Metalloligand approach using $\text{Cu-H}_2\text{nip}$ metallogel to incorporate Ln^{3+} ions.

As described in section 4.4, two new types of HMOFs were obtained by following a metalloligand approach: $[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$ (**1-La**) through the addition of 1

equivalent $\text{La}(\text{NO}_3)_3$ and $[\text{La}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**2-La**) through the addition of 1 equivalent $\text{La}(\text{NO}_3)_3$ and 3 equivalents H_2nip to the Cu- H_2nip metallogel. Following the successful isolation of Cu^{2+} - La^{3+} HMOFs, different lanthanide (Ln^{3+}) variants were investigated for HMOFs using similar reaction conditions (Figure 4.28).

4.6.1. Addition of 1 Equivalent of $\text{Ln}(\text{NO}_3)_3$ to the Cu- H_2nip Metallogel

When 1 equivalent $\text{Ln}(\text{NO}_3)_3$ was added to the Cu- H_2nip metallogel, it was observed that the rate of collapse of the blue gel into the pale blue colloid decreases on moving from lighter to heavier lanthanides. For $\text{Ln}^{3+} = \text{Ce}^{3+}$, Pr^{3+} , Nd^{3+} , the reaction mixture formed an almost white, colloid-like suspension, similar to that observed with La^{3+} . For the heavier lanthanides, the mixture did not collapse into a colloid but remained thick and the blue colour intensifies, resembling the Cu- H_2nip metallogel. The hydrothermal reaction conditions over two days gave different results for different lanthanides as shown in Figure 4.29.

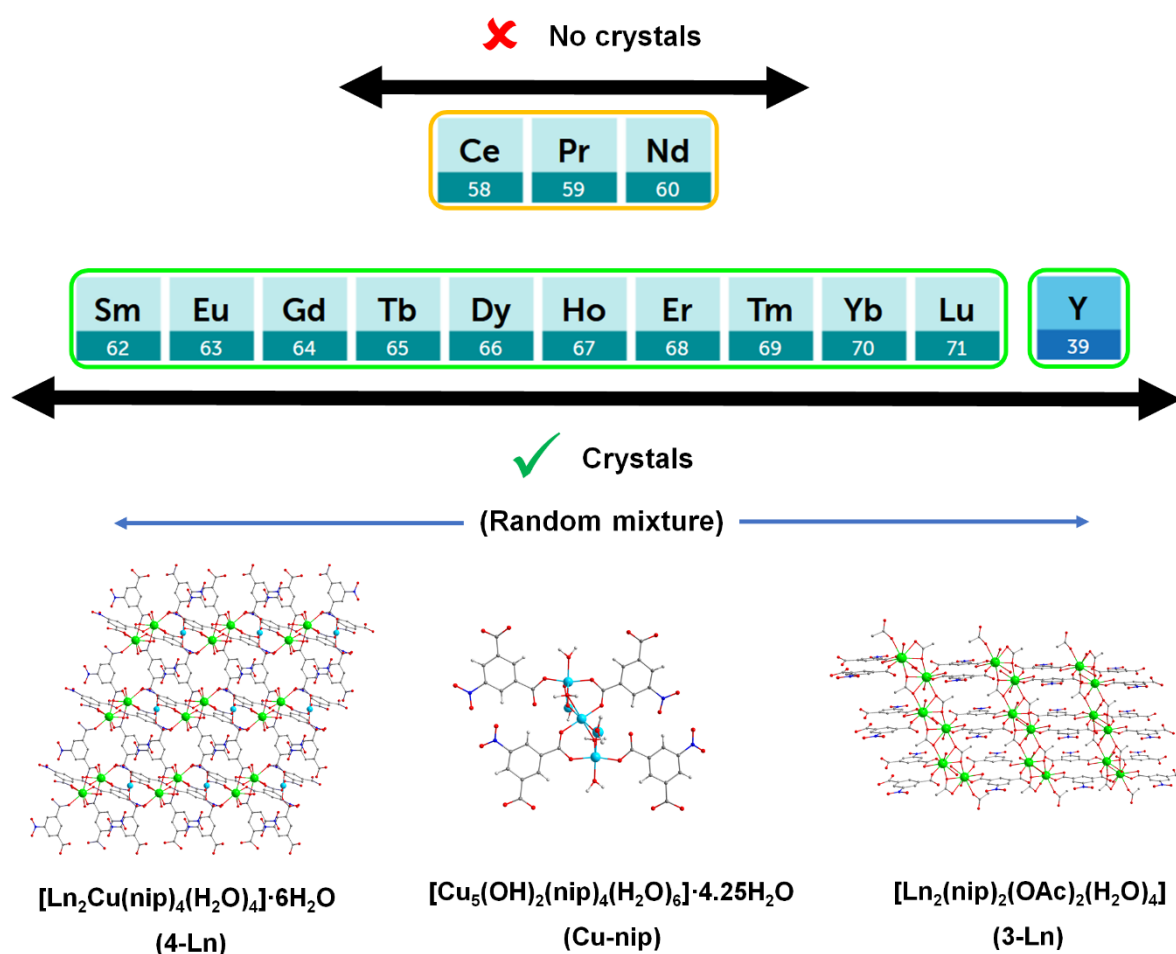


Figure 4.29. Compounds obtained by the metalloligand approach using Cu- H_2nip metallogel with 1 eq. Ln^{3+} nitrate

From Ce^{3+} to Sm^{3+} , no crystals were obtained. From Eu^{3+} onwards and including Y^{3+} which has an ionic radius close to that of Dy^{3+} , all behaved similarly. Mixtures of dark blue crystals of $[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**4-Ln**)^[103] were obtained along with blue crystals of the $[\text{Cu}_5(\text{OH})_2(\text{nip})_4(\text{H}_2\text{O})_6] \cdot 4.25\text{H}_2\text{O}$ (**Cu-nip**). In some cases, small amounts of colourless crystals of $[\text{Ln}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ (**3-Ln**) were also obtained. However, when these crystalline mixtures were continued heating for more than one week, the amount of crystals of **4-Ln** increased while that of **Cu-nip** and **3-Ln** decreased. This may be an indication that the thermodynamic stability of **Cu-nip** and **3-Ln** is low and it slowly dissolve into the reaction mixture and recrystallise into more stable compound **4-Ln**.

4.6.2. Addition of 1 Equivalent $\text{Ln}(\text{NO}_3)_3$ and 3 Equivalents H_2nip to Cu- H_2nip Metallogel

Similar to the case for the La^{3+} analogue described in section 4.4.3, 3 equivalents of H_2nip ligand were added after the addition of $\text{Ln}(\text{NO}_3)_3$ to the Cu- H_2nip metallogel and the reaction mixture was heated at 95 °C. Within 24 hours, blue crystals of $[\text{Ln}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**2-Ln**) were obtained for $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}$, but in the case of $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}$ and Gd^{3+} , a mixture of blue crystals of **2-Ln** and colourless crystals of homometallic Ln-MOFs $[\text{Ln}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**5-Ln**) were obtained (Figure 4.30).

Over a period of one week to four weeks, the colourless crystals in these examples slowly dissolved into the solution and further blue crystals of **2-Ln** are formed.

From Tb^{3+} to Er^{3+} , only crystalline phases of **5-Ln** were obtained which did not dissolve to form the blue crystals of **2-Ln**. Remaining lanthanides and yttrium were not tried as it can be safely assumed that it did not form HMOFs **2-Ln**, considering the smaller ionic radii of the Ln^{3+} .

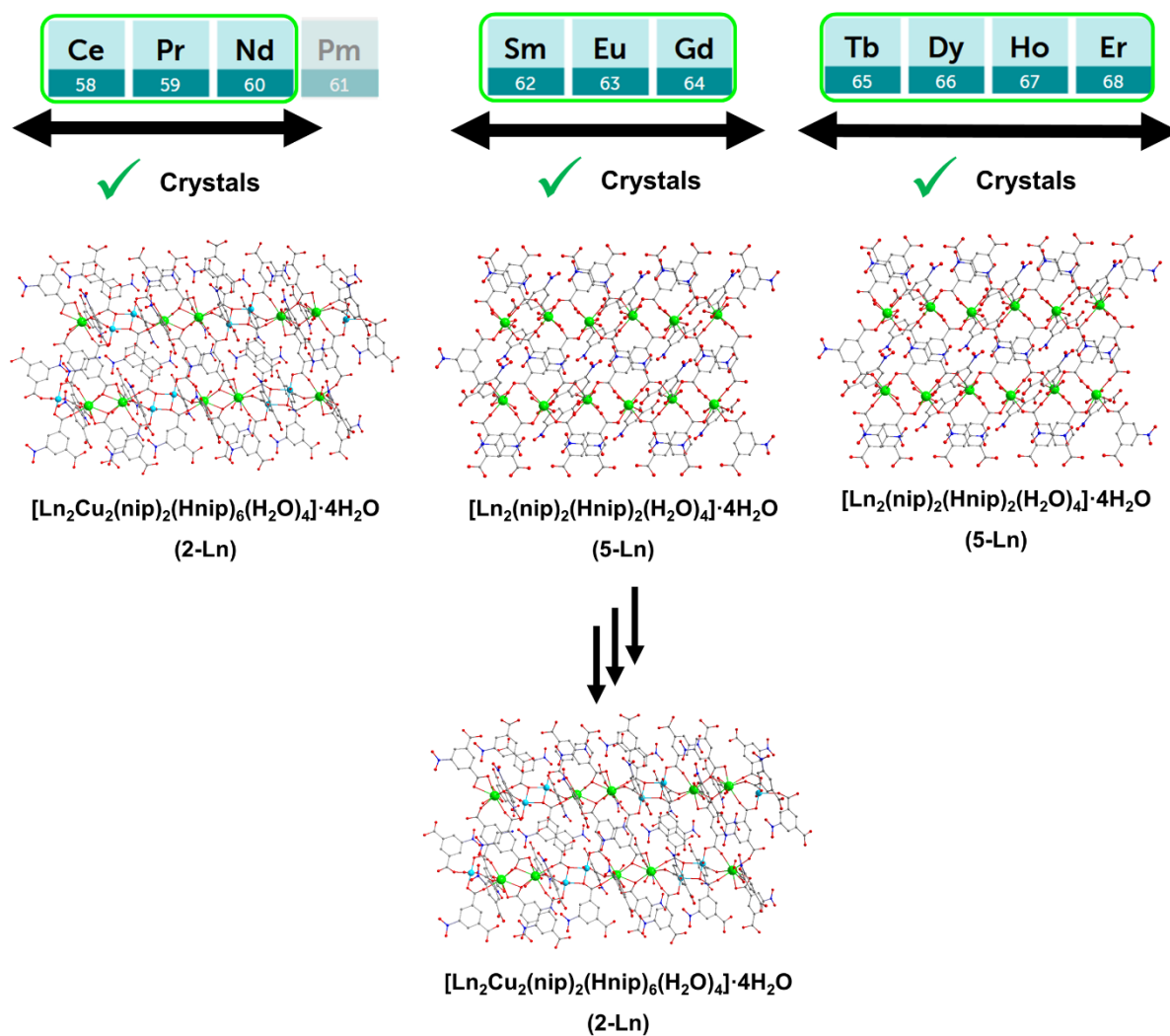


Figure 4.30. Compounds obtained by the metalloligand approach using Cu-H₂nip metallogel with 1 eq. Ln³⁺ nitrate and 3 eq. additional H₂nip ligand.

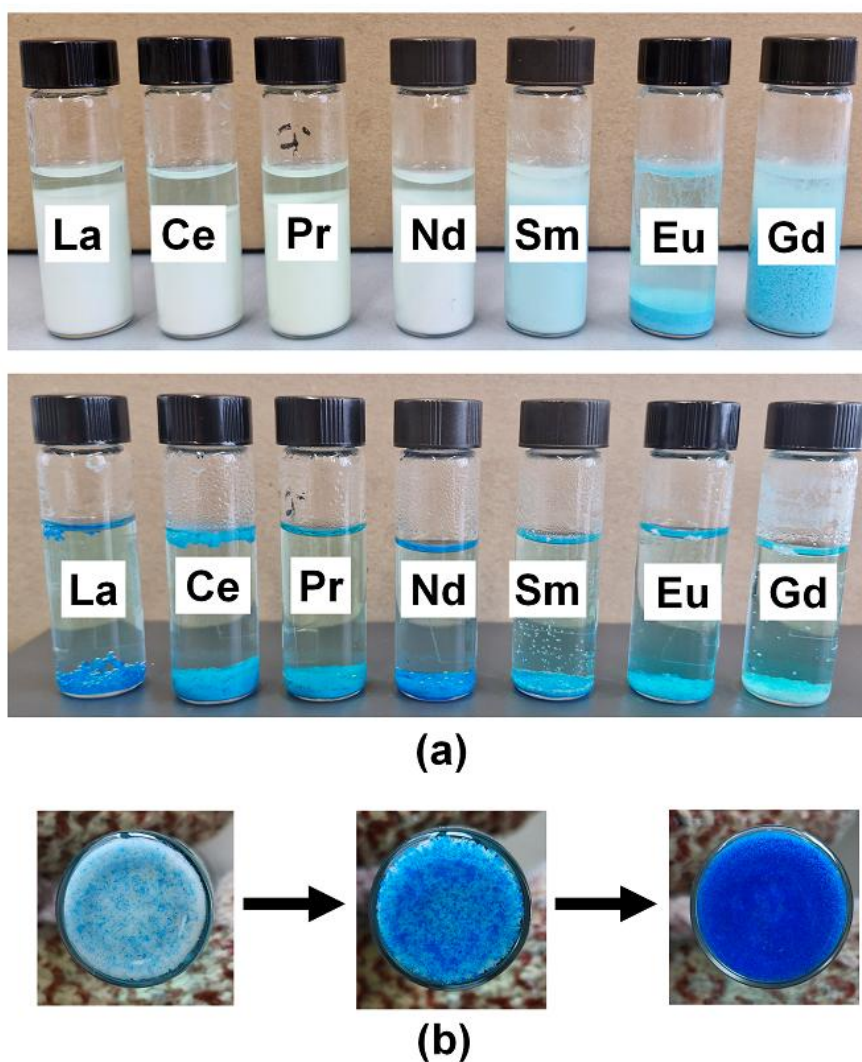


Figure 4.31. (a) Vials with reaction mixture for the synthesis of **2-Ln** for $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$ and Gd^{3+} before (top) and after (bottom) 24 hours of heating; (b) Crystal growth observed for **2-Gd** (blue) as the crystals of **5-Gd** (colourless) dissolve into the mixture over a period of 1 - 2 weeks.

4.7. Metastable Intermediate Compounds in $\text{Cu}^{2+}\text{-H}_2\text{nip-Ln}^{3+}$ System

As described in section 4.4.3 and 4.6.2, when an additional amount (3 eq.) of H_2nip ligand was added to the $\text{Cu}^{2+}\text{-H}_2\text{nip-La}^{3+}$ mixture to target HMOFs **2-Ln** ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$ and Gd^{3+}), some intermediate compounds were isolated as crystals (**2-La-meta** and **5-Ln**). These molecules underwent dissolution-recrystallisation processes until they reach a thermodynamically stable state, which is in this case **2-Ln**. The entire crystallisation process is evidence for the Ostwald ripening^[98] process.

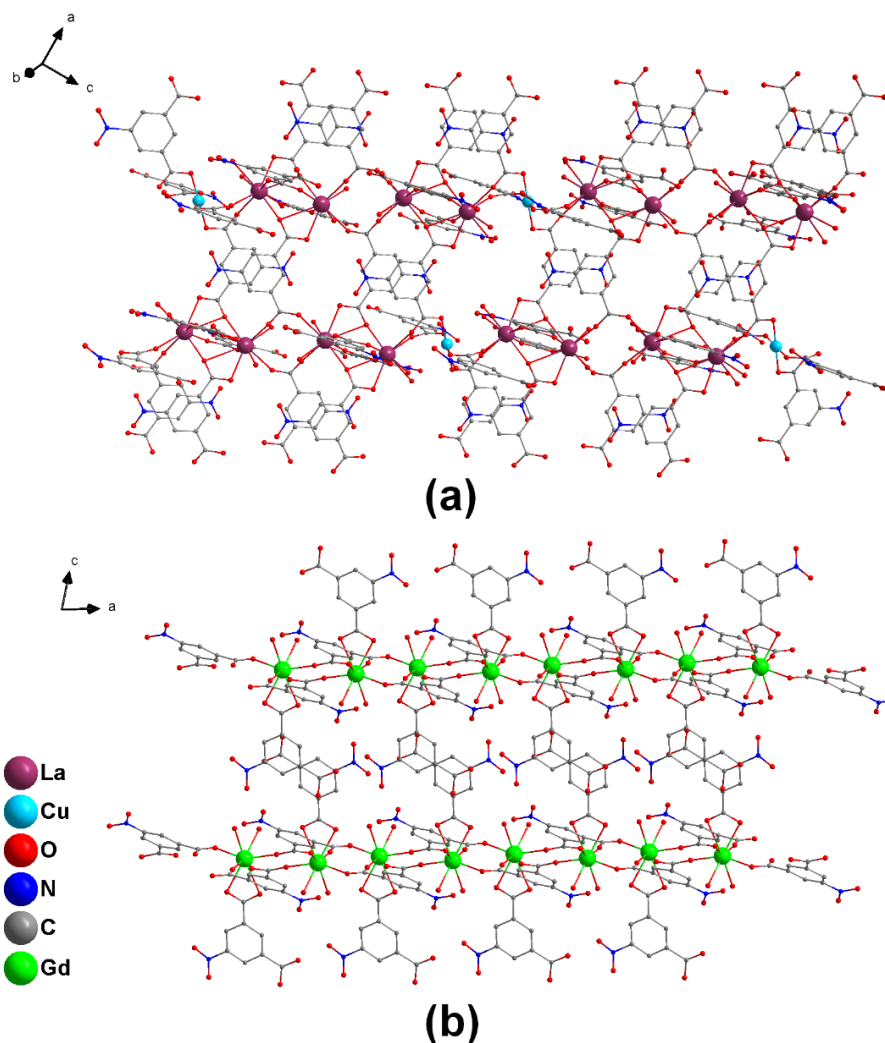


Figure 4.32. (a) Crystal structures of **2-La-meta** and (b) **5-Gd**.

In the case of **2-La**, the metastable compound **2-La-meta** was not very stable and dissolved into the reaction mixture within a few hours. On the other hand, the rate of dissolution of metastable compounds **5-Ln** was lower and took several days for completion. As the lanthanide got heavier from Sm^{3+} to Gd^{3+} , the dissolution of **5-Ln** and simultaneous crystallisation of **2-Ln** took about 1 to 4 weeks. The compounds **5-Ln** were colourless (without Cu^{2+} ions in the crystal structure) and when it undergoes dissolution and recrystallisation, the Cu^{2+} ions from the reaction media are taken up to form **2-Ln** (which has Cu^{2+} ions the crystal structure). For lanthanide ions beyond Gd^{3+} , the crystals of **5-Ln** are mostly inert toward such dissolution-recrystallisation processes and do not form any HMOFs with Cu^{2+} . The preference for a smaller coordination number (e.g., 8) for heavier (smaller) lanthanides could be a reason for the stability of the compounds **5-Ln** in the reaction mixture.

4.8. Significance of the Step-by-Step Metalloligand Approach for HMOF Synthesis

The step-by-step metalloligand approach is a powerful and versatile strategy for the design and synthesis of heterometallic metal-organic frameworks (HMOFs). One of the key benefits of the metalloligand strategy is the ability to pre-design coordination environments around the primary metal centre, ensuring compatibility with the secondary metal ions introduced during the synthesis. Additionally, this stepwise approach facilitates the isolation and characterization of intermediate phases, providing valuable insights into the mechanistic pathways of HMOF formation.

Step-by-step vs one-pot approach

By employing the metalloligand approach, a step-by-step methodology was used where a metalloligand (metallo-gel) was first made in order to synthesize the lanthanum-copper heterometallic MOFs. This method has demonstrated clear advantages over one-pot synthesis, particularly in improving control over the yield and purity of the desired compound. Considering the compound $[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$ (**1-La**) as the reference example, the reaction pathway can be visualized as follows:

When 5-nitroisophthalic acid (H_2nip) ligand is introduced to an aqueous solution of copper acetate, the Cu- H_2nip metallo-gel is formed. The AcO^- anions from copper acetate play a crucial role in facilitating the deprotonation of the carboxylate groups of the ligand. This process is accompanied by the coordination of Cu^{2+} ions, which results in the formation of the gel in water. Subsequently, when lanthanum nitrate is added, the $(\text{NO}_3)^-$ anions assist in breaking down the gel, and the lanthanum ions are incorporated into the Cu- H_2nip system, resulting in a pale blue gelatinous colloid. When the mixture is heated in an oven, it undergoes a transformation into a blue-coloured precipitate, from which compound **1-La** slowly crystallizes (in Figure 4.33a).

Another experiment was conducted with a slightly different procedure, by using copper nitrate and lanthanum acetate salts, i.e., by swapping the anions of Cu^{2+} and La^{3+} salts. When H_2nip ligand was stirred with copper nitrate dissolved in water, no gel was obtained. The addition of lanthanum acetate to this mixture resulted in a pale-blue suspension. The reaction mixture contains Cu^{2+} ions, AcO^- ions, La^{3+} ions, $(\text{NO}_3)^-$ ions, the H_2nip ligand along with its deprotonated forms, as in the former experiment.

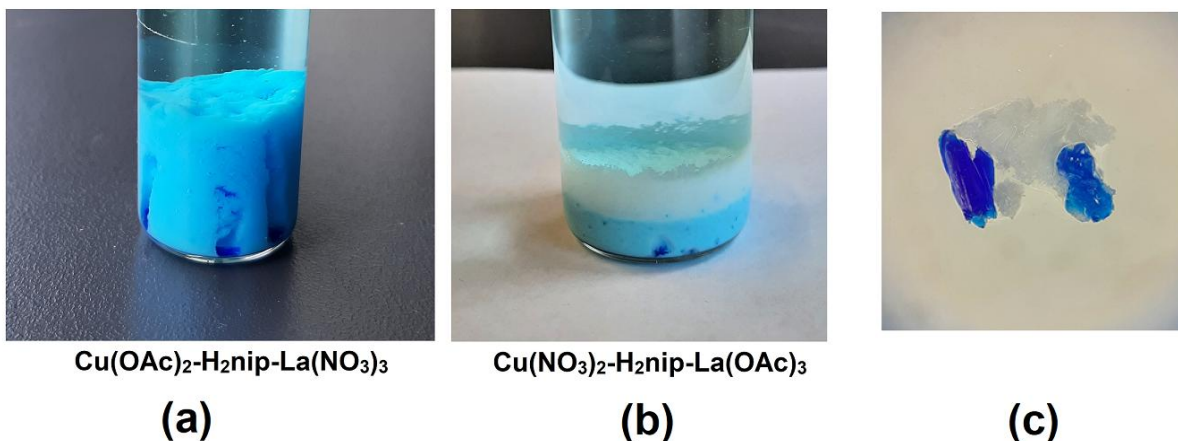


Figure 4.33. Crystal growth observed for compound **1-La** from precipitate for the system containing (b) Cu(OAc)_2 , H_2nip and $\text{La(NO}_3)_3$; (c) $\text{Cu(NO}_3)_2$, H_2nip and La(OAc)_3 ; (c) Mixture of crystals of **1-La** (dark blue, left), **A-La** (blue, right) and **3-La** (colourless, middle) obtained from the one-pot reaction of Cu(OAc)_2 , H_2nip and $\text{La(NO}_3)_3$ in water.

When this mixture was heated, a few dark blue crystals of **1-La** formed, but after a couple of hours the crystallization process stopped with a large amount of colourless crystals of $[\text{Ln}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_4]$ (**3-La**) and blue precipitate (as shown in Figure 4.33b). The one-pot reaction using the reagents copper acetate, H_2nip ligand and lanthanum nitrate in water resulted in a mixture of several compounds: **1-La** (dark blue crystals), **A-La** (blue crystals) and **3-La** (colourless crystals) (Figure 4.33c). This demonstrates that it is crucial to follow the step-by-step approach using the correct reagents to isolate the pure phases of HMOFs.

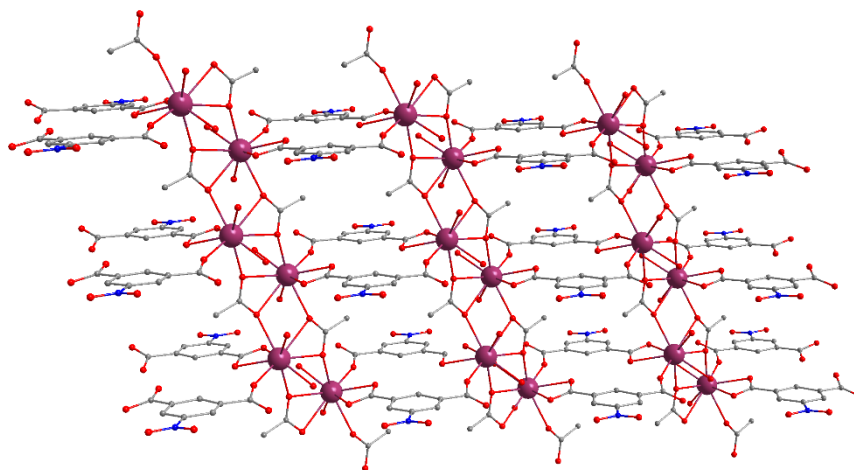


Figure 4.34. Crystal structure of **3-La**.

In conclusion, the step-by step method through a metalloligand approach was found to be an effective method to make heterometallic metal-organic framework (HMOF) molecules.

4.9. Cu-nip as the Functional Precursor for HMOFs

When 1 eq. $\text{Ln}(\text{NO}_3)_3$ was added to the Cu- H_2nip gel, a reaction mixture will have a $\text{Cu}^{2+} : \text{H}_2\text{nip} : \text{Ln}^{3+}$ ratio of 1 : 1 : 1. When the reaction mixture is heated in the oven, the stages of formation of HMOFs can be visualized as follows.

The blue precipitate formed during initial heating is mostly constituted by the pristine form of Cu_5 -cluster MOF compound **Cu-nip**, formed from the Cu- H_2nip gel. This slowly dissolves into the reaction mixture over the course of the heating and incorporate the Ln^{3+} ions from solution and crystallise through Ostwald ripening to yield the HMOFs. The Cu_5 -cluster MOF (**Cu-nip**) is the functional unit of the Cu- H_2nip metallogel that acts as the precursor of HMOFs. To verify this experimentally, two trial reactions were done using the preformed crystals of **Cu-nip** and nitrate salts of La^{3+} (large Ln^{3+}) and Tm^{3+} (small Ln^{3+}) (Figure 4.35).

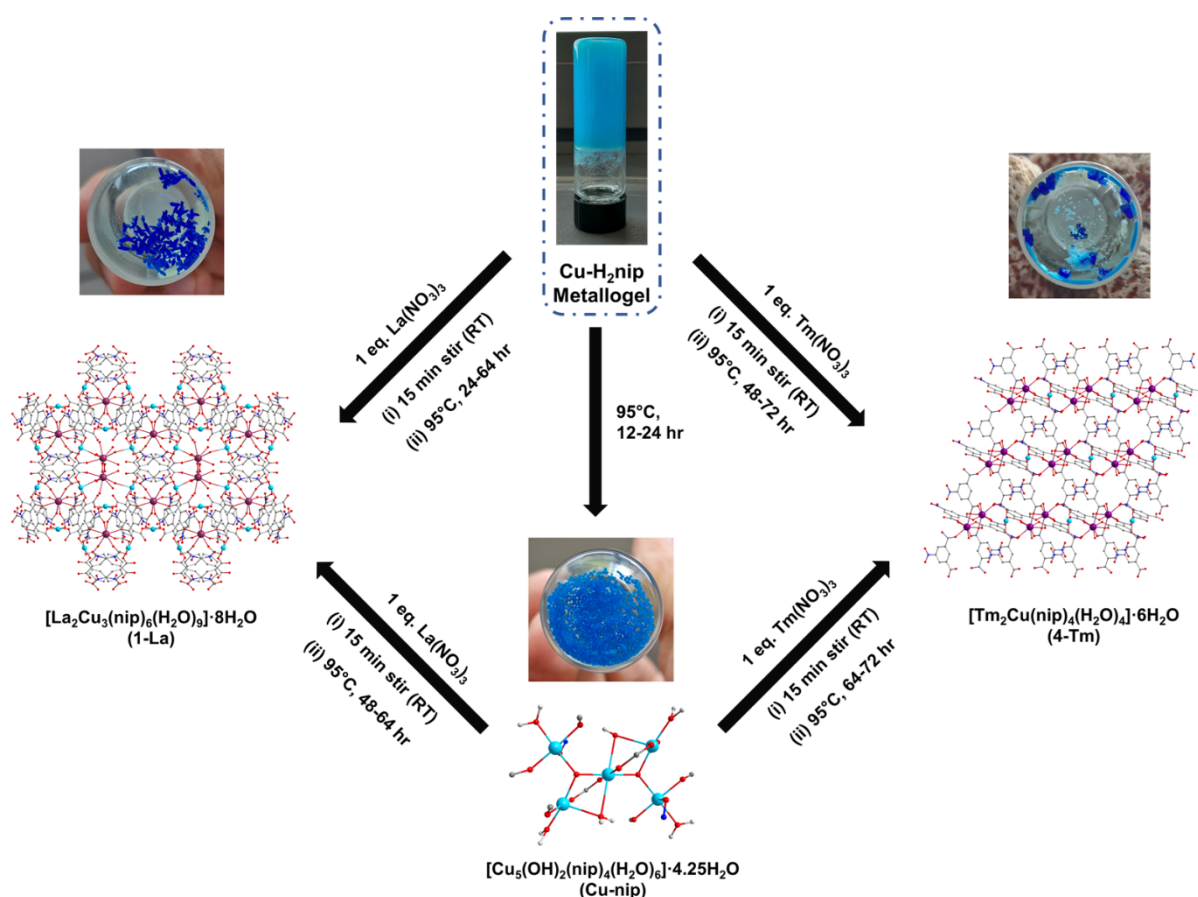


Figure 4.35. HMOFs obtained by the metalloligand approach using Cu- H_2nip metallogel and Cu-nip crystals to incorporate La^{3+} and Tm^{3+} ions.

The Cu- H_2nip metallogel was prepared in two vials by the reacting 1 eq. each of $\text{Cu}(\text{OAc})_2$ and H_2nip in 10 mL water. These vials were heated in an oven at 95 °C and

blue crystals of the **Cu-nip** were obtained over a period of 12-24 hours depending on the laboratory conditions in terms of temperature at which the gel was prepared. $\text{La}(\text{NO}_3)_3$ and $\text{Tm}(\text{NO}_3)_3$ were added to the first and the second vial respectively and both were stirred for about 15 minutes. During the stirring process, the crystals of **Cu-nip** disintegrated and resulted in pale blue suspensions in both cases. The heating of the reaction mixtures in the oven at 95 °C gave dark blue crystals as the major product, for the La^{3+} - variant, crystals of $[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9 \cdot 8\text{H}_2\text{O}]$ (**1-La**) and for the Tm-variant, $[\text{Tm}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (**4-Tm**) (Figure 4.35).

This experiment proves that the compound **Cu-nip** acts as the functional precursor for the HMOFs for the $\text{Cu}^{2+} : \text{H}_2\text{nip} : \text{Ln}^{3+}$ ratio of 1 : 1 : 1.

4.10. Characterizations of New MOFs

4.10.1. Crystallography

Crystal Structure Description of $[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$ (**1-La**)

The single-crystal X-ray diffraction analysis (SCXRD) of dark blue crystals of **1-La** revealed that it crystallizes in Cc space group of the monoclinic system. The La_2Cu_3 core consists of a lanthanum ion (La1) surrounded by crystallographically independent three Cu^{2+} ions (Cu1, Cu2 and Cu3), connected through the carboxylate groups of the 5-nitro-1,3-benzenedicarboxylate / 5-nitroisophthalate (nip^{2-}) ligands (Figure 4.36a).

The three Cu^{2+} ions form the vertices of a scalene triangle (distances $\text{Cu1-Cu2} = 6.70 \text{ \AA}$; $\text{Cu2-Cu3} = 7.09 \text{ \AA}$; $\text{Cu3-Cu1} = 7.21 \text{ \AA}$) and La1 is approximately in the middle of the triangle in the same plane. The second lanthanum ion (La2) exist outside and below the LaCu_3 triangular plane, near Cu1 (Figure 4.36c, d) and is connected via water ligand oxygen O40 (Figure 4.36e). The angle La1-Cu1-La2 is about 153.6° .

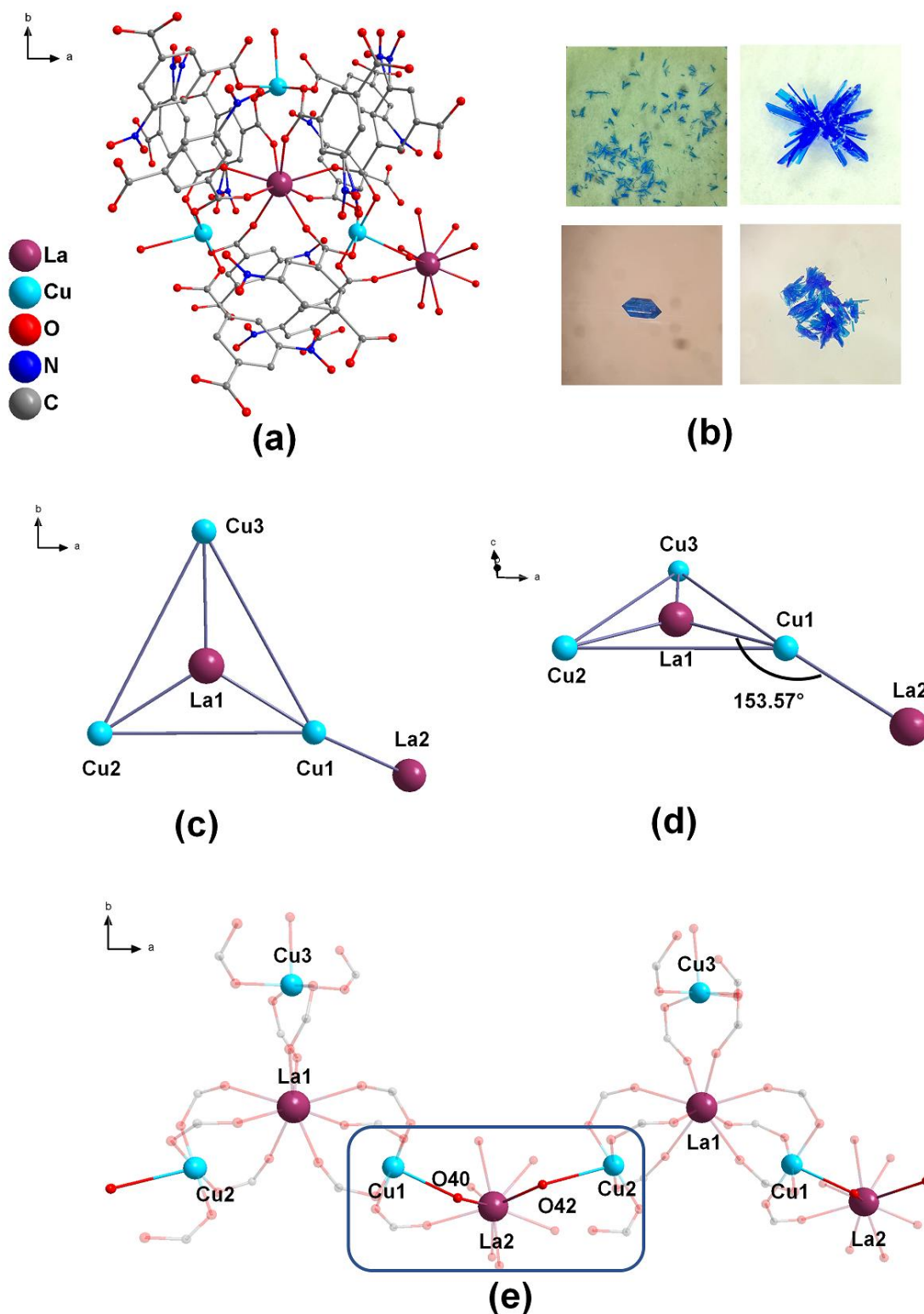


Figure 4.36. (a) Crystal structure of **1-La** depicting the La_2Cu_3 core along with the ligands; (b) Dark blue crystals of **1-La** with different size and shape, (c), (d) Positions of La1 and La2 with respect to the triangular Cu_3 core; (e) Water oxygen (O40 and O42) linking two La_2Cu_3 units via La2 (other non-metallic atoms shown as transparent).

In a La_2Cu_3 unit, La1 is 8-coordinated by oxygen atoms from the carboxylate group of eight nip^{2-} ligands. The 9-coordinated La2 is surrounded by a carboxylate oxygen of nip^{2-} ligand, six water ligands ($\mu_1\text{-O}$), and two bridging water oxygen atoms ($\mu_2\text{-O}$). One of the bridging water molecules, O40 is linked to Cu1 of the same unit as described above and the other water (O42) to Cu2 of the next unit (Figure 4.36e). All Cu^{2+} ions are penta-coordinated, where the equatorial plane is formed by four $\mu_1\text{-O}$ from carboxy groups of nip^{2-} ligands and apical sites are occupied by oxygen atoms from water.

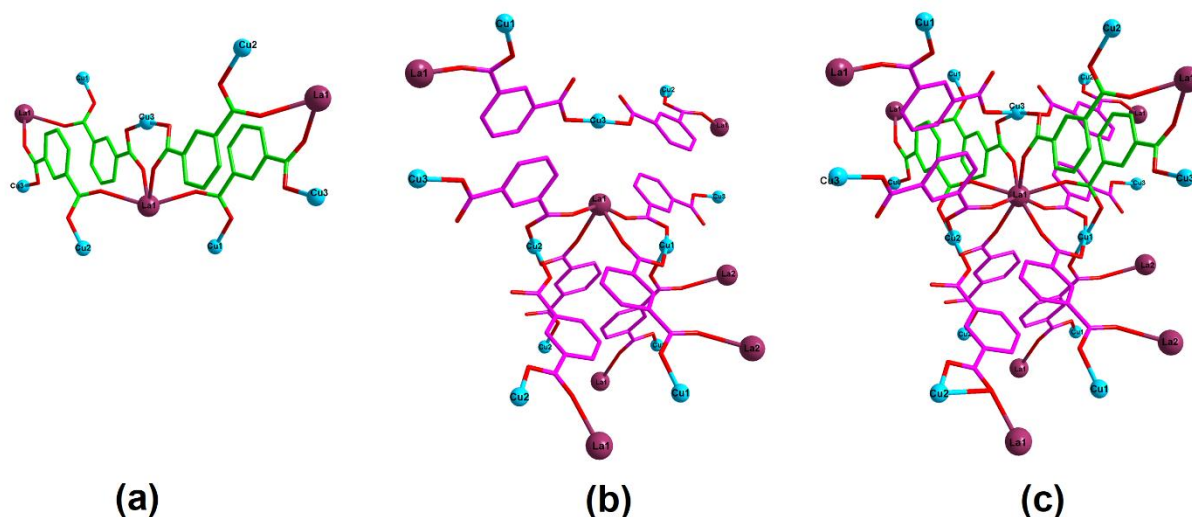


Figure 4.37. (a) First set of parallel nip^{2-} ligands where all the four carboxylate oxygen atoms are coordinated to metal ions; (b) Second set of parallel nip^{2-} ligands where three out of four carboxylate oxygen atoms are coordinated to metal ions; (c) Both (a) and (b) around the La_2Cu_3 core. Carbon atoms of aromatic rings and carboxylate groups of the nip^{2-} ligands are represented in green and pink color to distinguish them. Nitro groups and hydrogen atoms on the ligand are omitted for clarity.

In the three-dimensional network of **1-La**, the metal ions are predominantly interconnected through sets of almost parallelly arranged 5-nitro-1,3-benzenedicarboxylate (nip^{2-}) ligands. By considering a group of these parallel nip^{2-} ligands, these can be differentiated into two types: In the first set, all four carboxylate oxygen atoms of each ligand (resulting in a total of 8 oxygen atoms) are coordinated either to La^{3+} or Cu^{2+} . This coordination involves bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn*) binding of both carboxylate groups (Figure 4.37a). The nitro groups (O14–N3–O13) and (O19–N4–O20) of these nip^{2-} ligands are disordered. They are disordered between two crystallographic sites with occupancy of 60% and 40%. For the other set of nip^{2-} ligands, the four carboxylate oxygen atoms from one molecule and three from other (so, total 7 oxygen atoms) are coordinated with the metal ions (bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn*) and

monodendate κ^1 - κ^0 - μ_1 respectively). One remaining carboxylate oxygen exist as O^- (Figure 4.37b). The $-NO_2$ groups (O8–N2–O7), (O25–N5–O26), (O1–N1–O2), (O31–N6–O32) in these sets of ligands are not disordered in the crystal structures. The central La_2Cu_3 unit is surrounded by a total of 12 nip^{2-} ligands and each pair of these are shared between two adjacent units (Figure 4.26c). Consequently, each La_2Cu_3 units are associated with six nip^{2-} ligands. Among these ligands, two belong to the first type, while the remaining four belong to the second type, as previously mentioned.

The continuous shape measures (CShM)^[105-106] on the 8-coordinated La1 describes it as a square antiprism with minor distortion (SAPR-8, CShM = 2.27) and on the 9-coordinated La2 describes it as a capped square antiprism (CSAPR-9, CShM = 0.52). All three Cu atoms are five coordinated and have square pyramid geometry (SPY-5, CShM = 1.14 for Cu1, CShM = 2.29 for Cu2, CShM = 1.17 for Cu3).

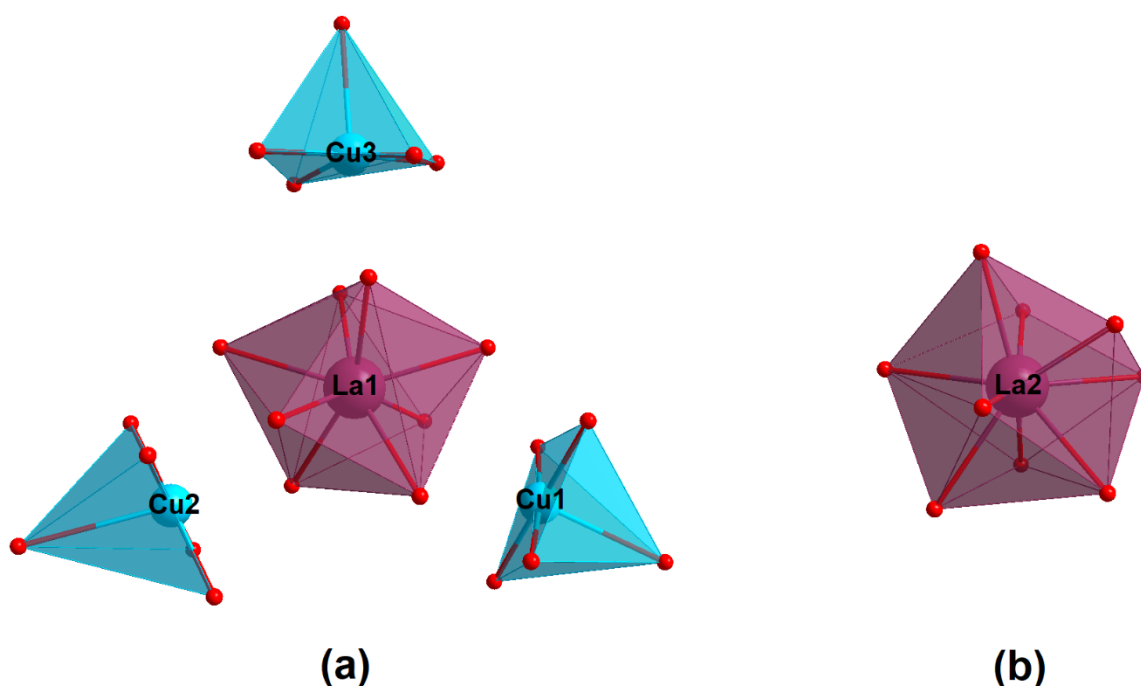


Figure 4.38. Coordination polyhedral representation for (a) La1, Cu1, Cu2 and Cu3 and (b) La2 in **1-La**.

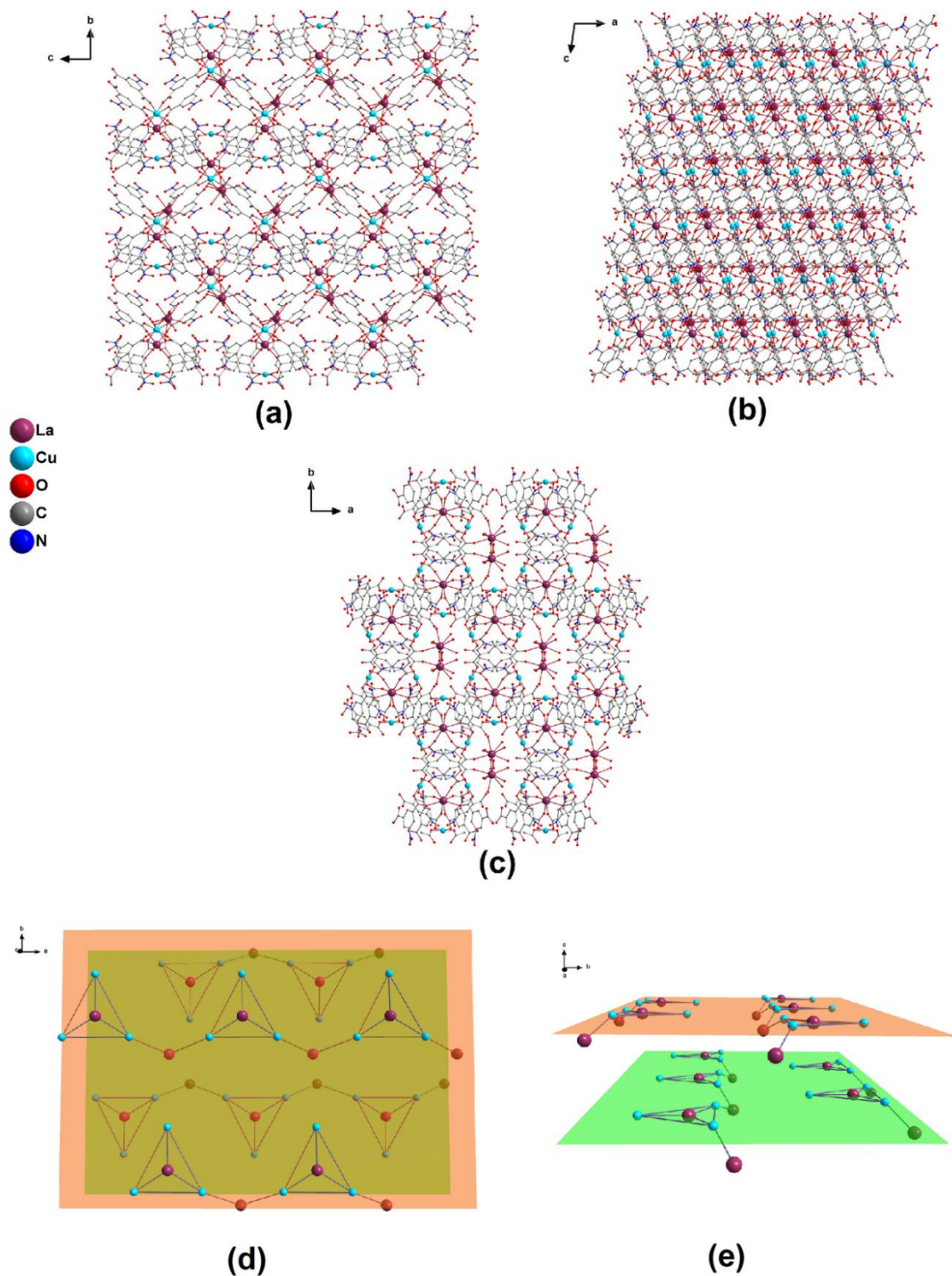


Figure 4.39. (a), (b), (c) Three-dimensional structure of **1-La** when viewed along *a*, *b*, *c* axes; (d), (e) The simplified representation of La_2Cu_3 cores of **1-La** in two different planes when viewed along different directions (All ligands removed for clarity).

The three-dimensional network structure in **1-La** is shown in Figure 4.39. Here, the alternating layers of La_2Cu_3 cores are arranged on parallel planes in a zig-zag fashion.

The planes are about 7.5-8 Å far apart (Figure 4.39e).

Even though the compound **1-La** has a three-dimensional structure, it is non-porous (Figure 4.39a, b, c). When La1 atoms (in the central LaCu_3 triangular core) are solely considered for topological understanding, the structure has a hexagonal **acs** topology^[107] (Figure 4.40).

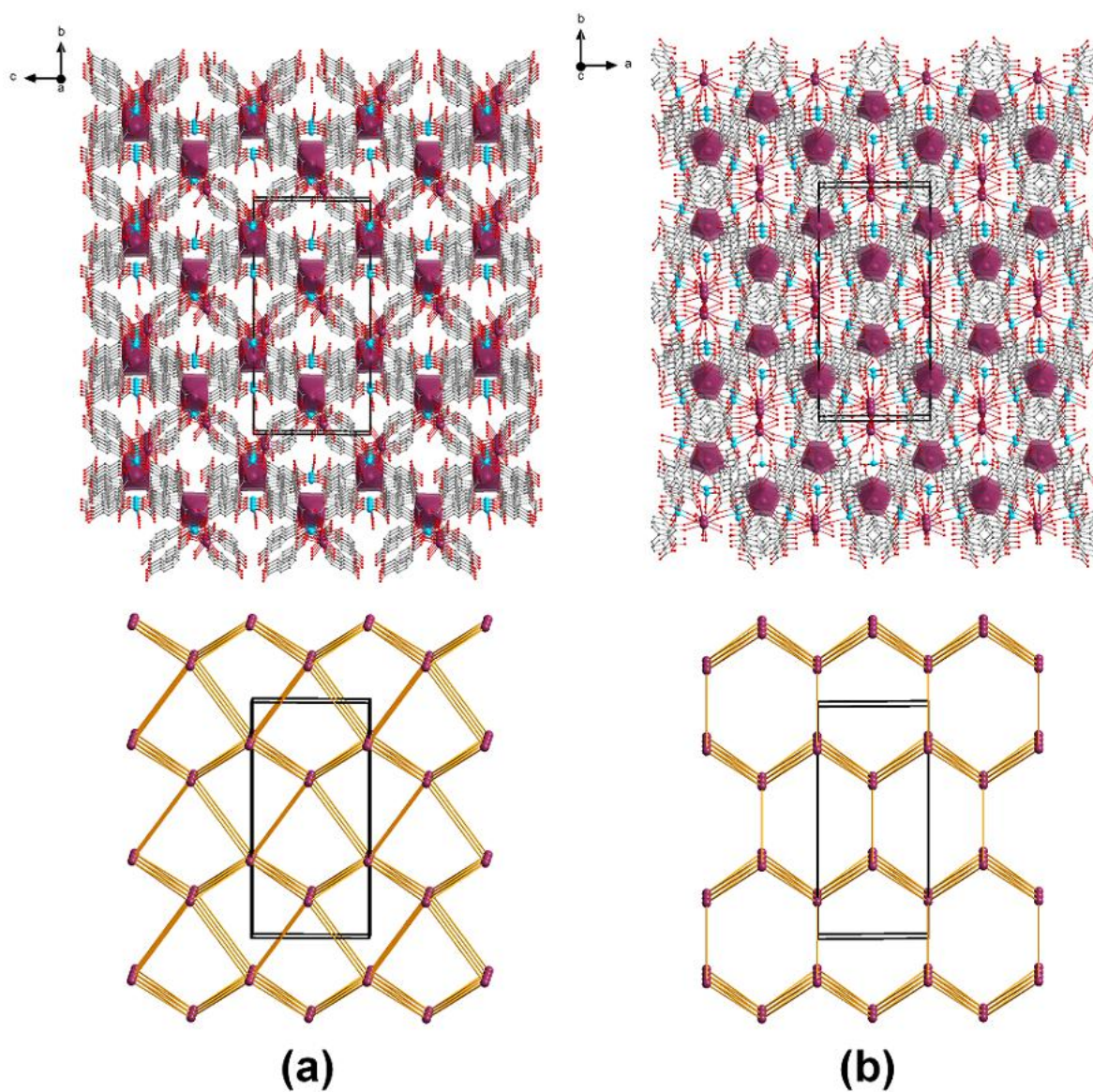


Figure 4.40. Atoms with unit cell in the three-dimensional structure of **1-La** viewed along (a) a-axis and (b) c-axis. (La1 atoms are shown as coordination polyhedra) (top) and topological representation showing only La1 atoms (bottom).

Crystal Structure Description of $[\text{La}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_6]$ (**A-La**)

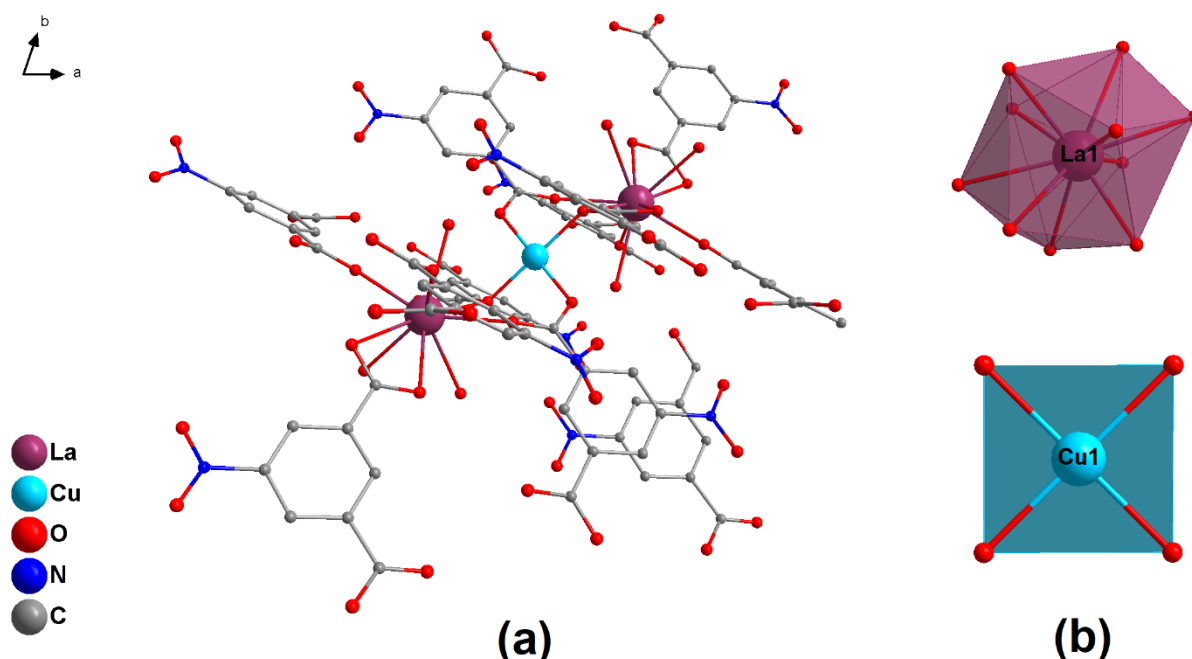


Figure 4.41. (a) The core structure of **A-La**; (b) Coordination polyhedral representation of La and Cu.

The single-crystal X-ray analysis reveals that compound **A-La**^[102] crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains $1/2 \text{ Cu}^{2+}$, 1 La^{3+} ions and 2 nip^{2-} ligands and 3 water ligands. The three-dimensional network structure is formed from 4-coordinated square planar Cu^{2+} ions which lie on inversion centres and 10-coordinated La^{3+} ions. Another inversion centre lies at the middle of line joining two La^{3+} ions. The carboxylate groups of nip^{2-} ligand bridges or chelates the metal ions via tridentate $\kappa^2\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn, anti*), bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn*) coordination modes.

The SHAPE^[105-106] analysis on the 10-coordinated La1 describes it as bicapped square antiprism (JBCSAPR-10; CShM = 3.06), and the 4-coordinated Cu1 as a square (SP-4 CShM = 0.003).

Crystal Structure Description of [LaCu(nip)₂(Hnip)(H₂O)₂]₂·2H₂O (**B-La**)

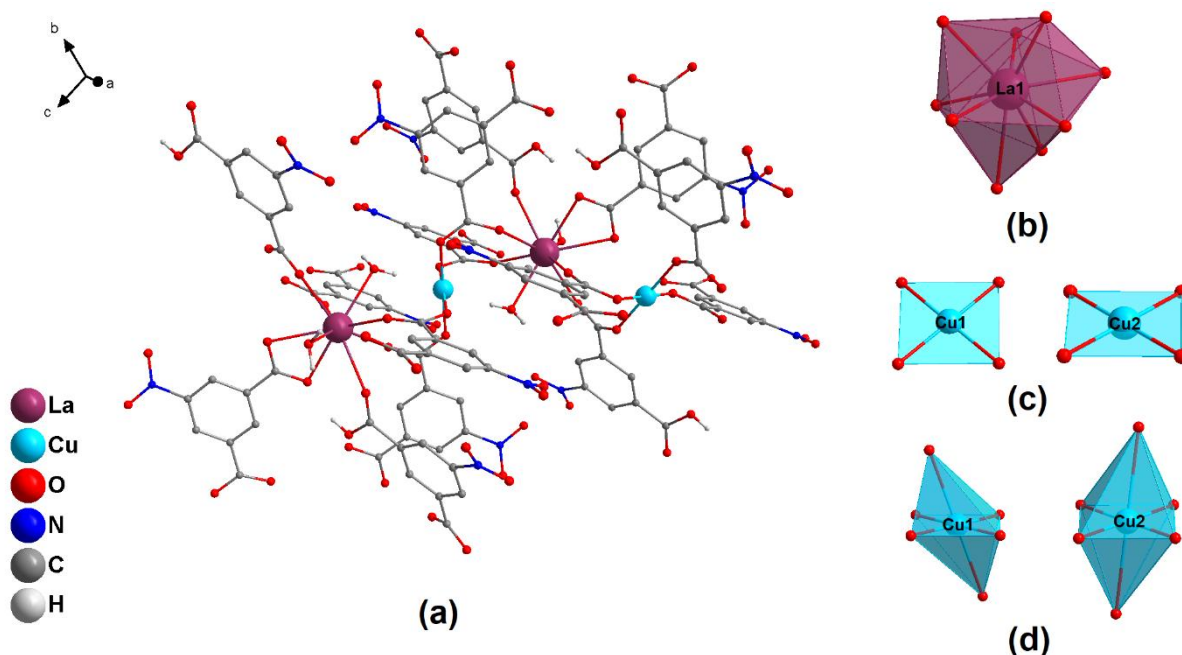


Figure 4.42. (a) The core structure of **B-La** (Hydrogen atoms on benzene ring and lattice solvent omitted for clarity); Coordination polyhedral representation of (b) La1 (capped square antiprism) and Cu ions (c) as square plane and (d) octahedra.

The compound **B-La**^[102] crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two Cu²⁺, one La³⁺ and three nip²⁻ ligands two coordinated water (on La³⁺) and two uncoordinated water. The three-dimensional network structure is formed from 9-coordinated La³⁺ ions and 4-coordinated square planar Cu²⁺ ions which lie on inversion centres (Figure 4.42a). Coordination environment of La³⁺ ions is described by seven oxygen atoms from four nip²⁻ and two Hnip⁻ ligands and two oxygen atoms from the coordinated water molecules. The coordination modes of nip²⁻ with metal ions are tridentate $\kappa^2\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn, anti*), bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn*) and that of Hnip⁻ is monodentate $\kappa^1\text{-}\kappa^0\text{-}\mu_1$. The SHAPE analysis^[105-106] on the 9-coordinated La1 describes it as capped square antiprism (CSAPR-9, CShM = 1.62) (Figure 4.42b).

Each of the Cu atoms, Cu1 and Cu2 are coordinated by four carboxylic oxygen atoms of nip²⁻ and Hnip⁻ ligands. The SHAPE analysis on the 4-coordinated Cu1 and Cu2 describe them as a square (SP-4, CShM = 0.13 for Cu1 and CShM = 0.03 for Cu2) as shown in Figure 4.42c. Very weak interactions from two water molecules at a distance of 2.7 Å for Cu1 and two carboxylate oxygen atoms at a distance of 2.8 Å for Cu2 can be considered to assume the coordination number for both Cu atoms as 6. However, these are too far away and highly disoriented to be considered as an octahedral

coordination environment for Cu1 and Cu2 (Figure 4.31d). The SHAPE analysis also shows a deviation from perfect octahedral coordination environment. According to the analysis, the CShM values for 6-coordinated Cu1 and Cu2 for Octahedron (OC-6) are 4.71 and 4.46 respectively.

Crystal Structure Description of $[\text{Ln}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (2-Ln, $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$)

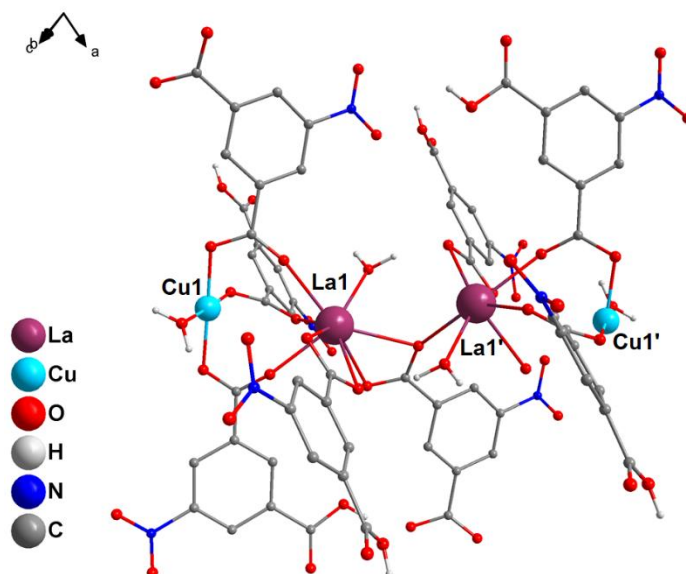


Figure 4.43. The core structure of **2-La**.

Single crystal X-ray diffraction analyses reveal that **2-Ln** (where $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) crystallizes in $P\bar{1}$ of triclinic space group. Since all the lanthanide analogues crystallize as isomorphous compounds, only the La^{3+} analogue is discussed here. In the asymmetric unit of **2-La** there are La^{3+} , Cu^{2+} ions, a nip^{2-} , three Hnip^- and two water ligands which are all inversion-related (Figure 4.43). In addition, there are two lattice water molecules.

The two La^{3+} ions are connected via a pair of two carboxylate oxygen atoms (O15, O16) from two symmetrically equivalent nip^{2-} ligands in a bridging-chelate tridentate $\kappa^2-\kappa^1-\mu_2$ (syn, syn, anti) fashion (Figure 4.44a) and the La-La distance is 4.39 Å. The two Cu^{2+} ions are 3.30 Å far apart and are bridged by carboxylate oxygen atoms (O1 and O1') of two symmetrically equivalent Hnip^- ligands in a double bridge mode bidentate $\kappa^1-\kappa^1-\mu_2$ (syn, syn) (Figure 4.44b). Each pair of the La^{3+} and Cu^{2+} ions are 3.90 Å apart and are bridged by a nip^{2-} and two Hnip^- ligands, with bidentate $\kappa^1-\kappa^1-\mu_2$ (syn, syn) coordination modes (Figure 4.44c).

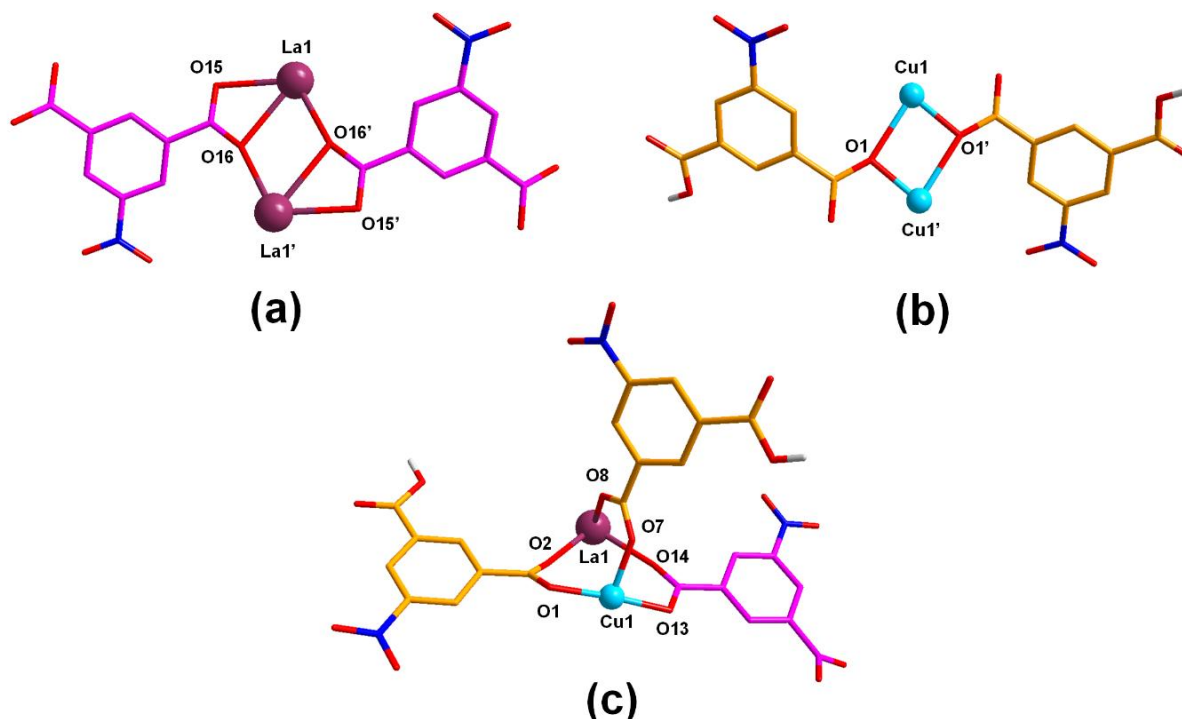


Figure 4.44. Bridging modes of ligands in **2-La**. (a) nip²⁻ ligands in between two La³⁺ ions; (b) Hnip⁻ in between two Cu²⁺ ions; (c) nip²⁻ and Hnip⁻ in between a La³⁺ ions and a Cu²⁺. Carbon atoms of aromatic rings and carboxylate groups of nip²⁻ and Hnip⁻ are represented in pink and orange respectively. The hydrogen atoms on benzene ring, and other coordinating atoms/groups including coordinated water molecules are omitted for clarity.

The La₂Cu₂ metal ion cores are interconnected via the carboxylate groups of nip²⁻ and Hnip⁻ ligands forming one dimensional chain (Figure 4.45a). Each of the one-dimensional chains of Ln₂Cu₂ cores are interconnected via pairs of quasi parallel nip²⁻ ligands leading to a two-dimensional structure (Figure 4.45b).

The SHAPE analysis^[105-106] on the 9-coordinated La1 describes it as bicapped square antiprism (CSAPR-9; CShM = 1.42). The 5-coordinated Cu1 as a vacant octahedron (vOC-5; CShM = 1.13) (Figure 4.46), and also close to square pyramid (SPY-5, CShM = 1.50).

For the **2-Ln** series, the Ln-Ln and Ln-Cu distances decreases while the Cu-Cu distance increases as the Ln³⁺ ions get bigger as shown in Table 4.2.

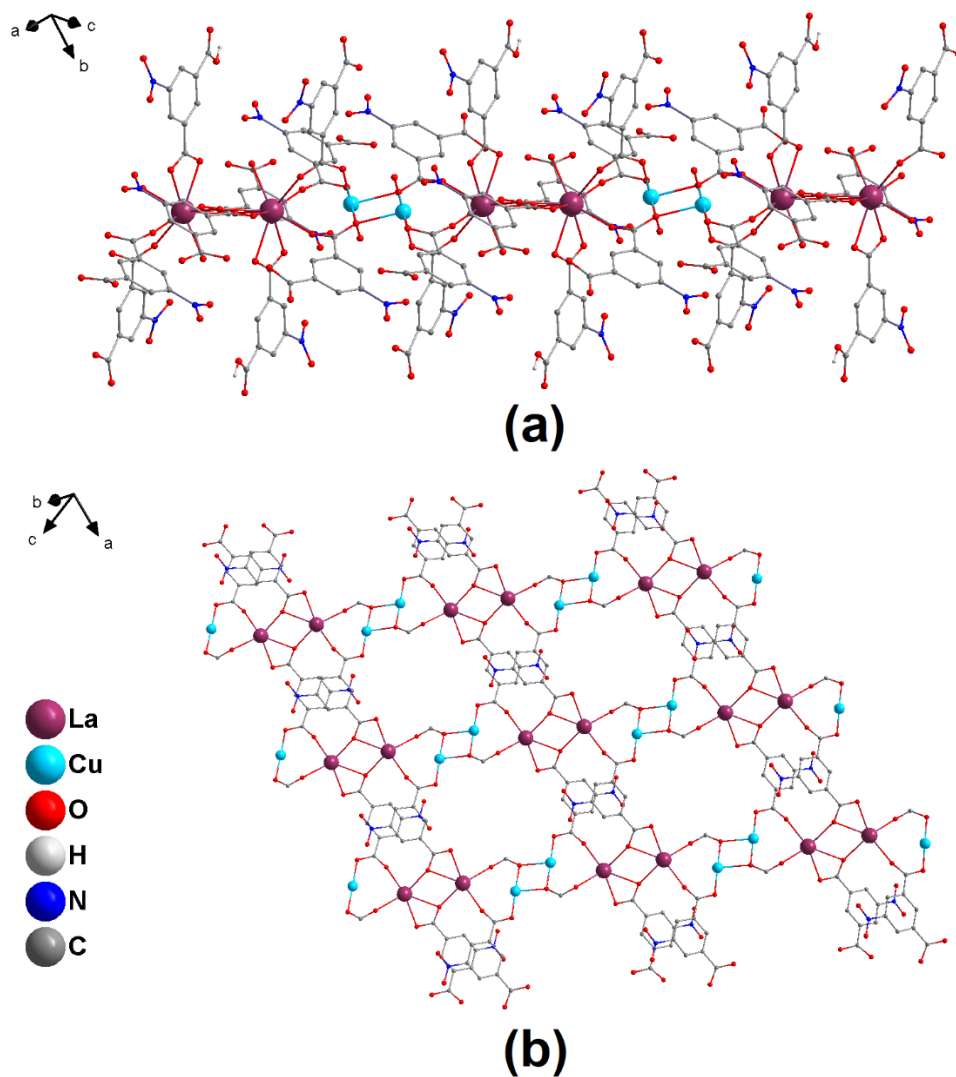


Figure 4.45. (a) One-dimensional chains of La_2Cu_2 in **2-La**; (b) One-dimensional chains interconnected by nip^{2-} ligands in **2-La**. The ligands that are not involved in this linking are not shown. Hydrogen atoms on aromatic carbon are ignored for clarity.

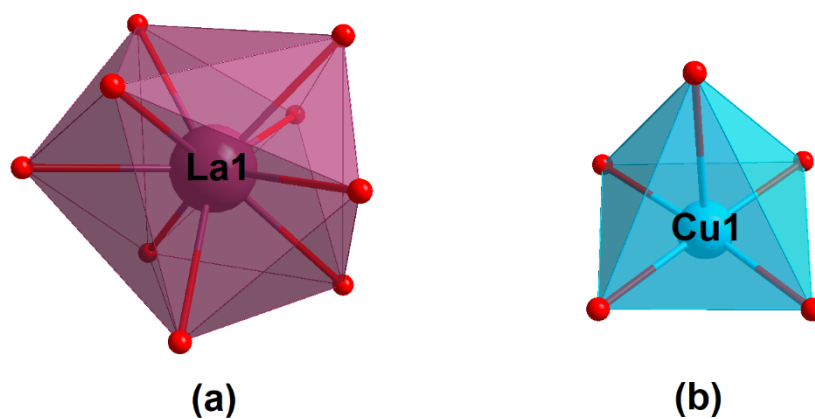
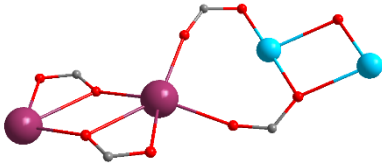
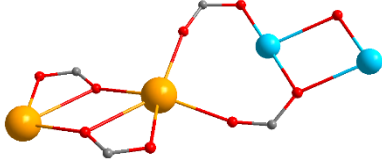
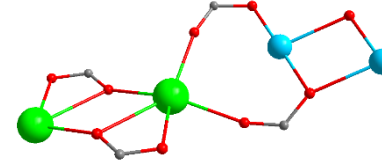
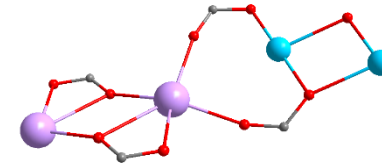
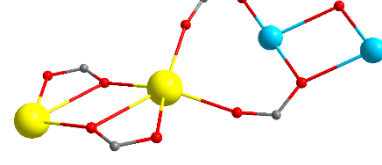
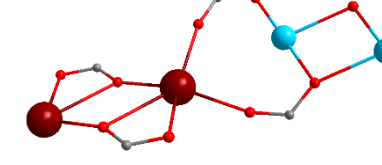
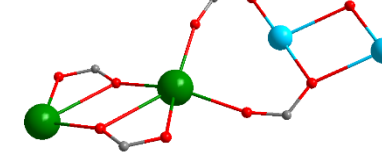


Figure 4.46. Coordination polyhedral representation of La and Cu in **2-La**.

Table 4.2. List of Ln-Ln and Ln-Cu and Cu-Cu distances in **2-Ln**.

Compound	Ln ₂ Cu ₂ Core	Distance (Å)		
		Ln-Ln	Ln-Cu	Cu-Cu
2-La		4.3926	3.9034	3.3006
2-Ce		4.3827	3.8823	3.3101
2-Pr		4.3676	3.8718	3.3191
2-Nd		4.3579	3.8600	3.3240
2-Sm		4.3467	3.8173	3.3371
2-Eu		4.3533	3.8100	3.3445
2-Gd		4.3506	3.7907	3.3524

Crystal Structure Description of 2-La-meta and 5-Ln

[La₄Cu_{1.25}(nip)_{4.5}(Hnip)_{5.5}(H₂O)_{8.5}] $\cdot$ 12.5 H₂O (2-La-meta)

The pale blue crystals of **2-La-meta** were isolated from the reaction mixture within 24 hours since the start of reaction and were subjected to X-ray analysis. The single-crystal data reveals that the compound crystallises in $P\bar{1}$ space group. The core structure consists of La₄Cu units consisting of La1, La2 and Cu1, where Cu1 is on an inversion centre, and there is a further inversion centre between La2 and La2' at the mid-point of the La₄ unit. The metal cations are bridged by carboxylate groups of nip²⁻ and Hnip⁻ ligands forming a one-dimensional chain (Figure 4.47).

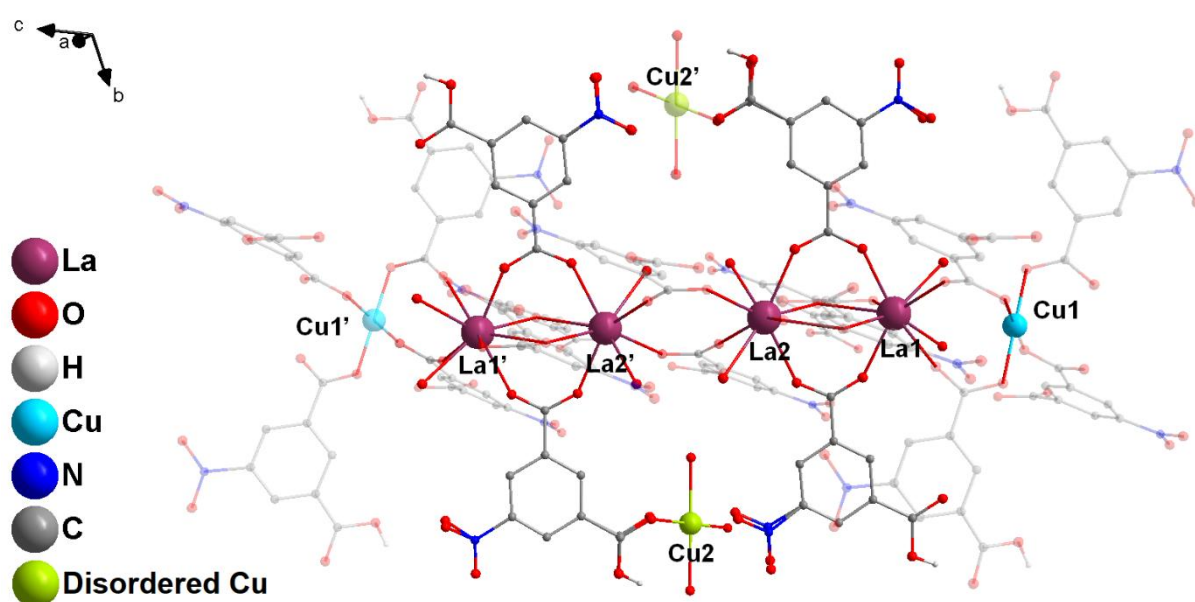


Figure 4.47. La₄Cu - unit interconnected by Hnip⁻ ligands and nip²⁻ in **2-La-meta**. The disordered ligands are highlighted and the ordered ligands and metal atoms from adjacent units are shown as transparent. Hydrogen atoms on aromatic ring and water are ignored for clarity.

The one-dimensional chains of La₄Cu units are interconnected by nip²⁻ ligands to form a two-dimensional sheet-like structure (Figure 4.48). At the same time, the remaining nip²⁻ and Hnip⁻ ligands from different sheets are arranged in quasi-parallel fashion (Figure 4.49a, b). Furthermore, there is an unusual disorder involving the carboxylate group of the ligand containing O3 and O4. In 75% of these sites in the crystal these groups are protonated -CO₂H groups, but in 25% of sites a pair of such groups are deprotonated and coordinated to a Cu²⁺ (Cu2) which also has 25% occupancy (Figure 4.49c).

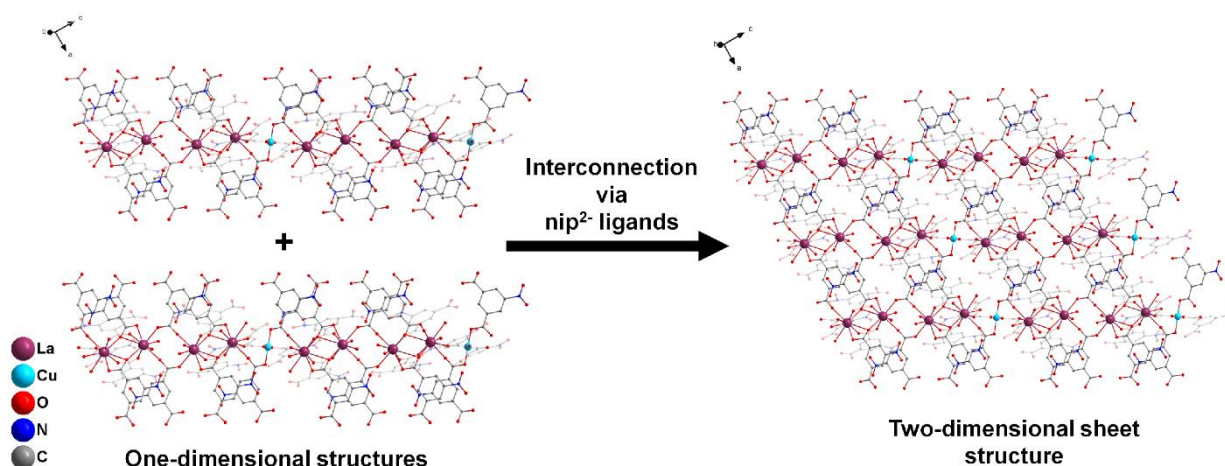


Figure 4.48. One-dimensional chains interconnected by nip²⁻ ligands in **2-La-meta**. The ligands that are not involved in this linking are shown as transparent. Hydrogen atoms are ignored for clarity.

The main disorder in the crystal lies at the degree of protonation of the carboxylate groups of a pair of inversion-related 5-nitroisophthalic acid ligands and the associated absence or presence of a Cu²⁺ (Cu2) in the lattice (Figure 4.49d). One of the carboxylate groups of the ligand always bridges La1 and La2 (Figure 4.49c), but the other group (containing O3 and O4) exists either as -COOH in Hnip⁻ (75 %) or -COO⁻ in nip²⁻ (25 %) (Figure 4.49d). When this group together with its inversion-related counterpart are protonated (Hnip⁻ form) they are linked via hydrogen bonds to the lattice waters O47 and O47' (Figure 4.49e). The remaining 25% of the carboxylate groups are deprotonated (form nip²⁻) and now coordinate to a Cu²⁺ ion (Cu2) with 25% occupancy which lies on the inversion centre (Figure 4.49f). The two lattice water molecules (O47 and O47') are now also coordinated to the copper ion.

The disorder is thus between a Cu²⁺ cation and a pair of protons, and so does not affect the overall charge. When the Cu2 is present 25% of the time in the lattice site, the two lattice waters become aquo ligands. Hence over the crystal as a whole these two waters now become 0.5 ligand water and 1.5 lattice water.

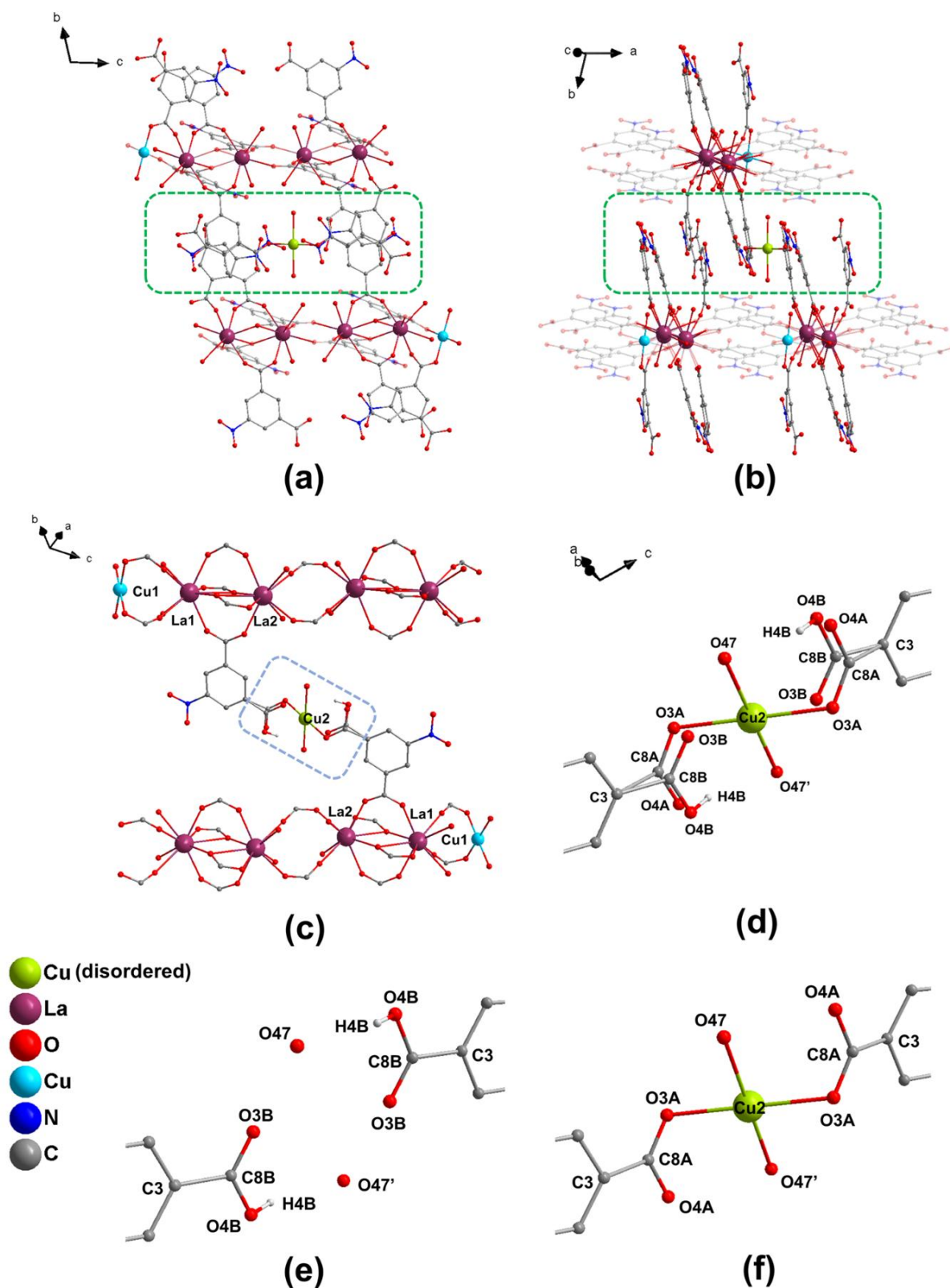


Figure 4.49. (a), (b) Quasi-parallel arrangement of disordered ligands in **2-La-meta**; (c) Disordered atoms in between the two-dimensional layers; (d) Enlarged view of the disordered atoms; (e) Atoms with higher occupancy (75%) with prefix B; (f) Atoms with lower occupancy (25%) with prefix A.

The part of the framework independent of this disorder corresponds to a $[\text{La}_4\text{Cu}(\text{nip})_4(\text{Hnip})_4(\text{H}_2\text{O})_8]^{2+}$ unit and 11 lattice waters. When the disordered pair of 5-nitroisophthalic acid ligands and Cu^{2+} (Cu_2) ion are considered along with their respective occupancies, there are in addition alternative units $[(\text{Hnip})_2 \cdot 2\text{H}_2\text{O}]_{0.75}$ and $[\text{Cu}(\text{nip})_2(\text{H}_2\text{O})_2]_{0.25}$, each with 2- charge. Hence the total formula for **2-La-meta** is $[\text{La}_4\text{Cu}(\text{nip})_4(\text{Hnip})_4(\text{H}_2\text{O})_8] \cdot 11\text{H}_2\text{O} \cdot [(\text{Hnip})_2 \cdot 2\text{H}_2\text{O}]_{0.75} \cdot [\text{Cu}(\text{nip})_2(\text{H}_2\text{O})_2]_{0.25}$, or simply $[\text{La}_4\text{Cu}_{1.25}(\text{nip})_{4.5}(\text{Hnip})_{5.5}(\text{H}_2\text{O})_{8.5}] \cdot 12.5 \text{H}_2\text{O}$.

Thus, the entire structure can be considered as a three-dimensional structure formed from the two-dimensional sheets by the bridging Cu^{2+} ions at some sites in the lattice (Figure 4.50).

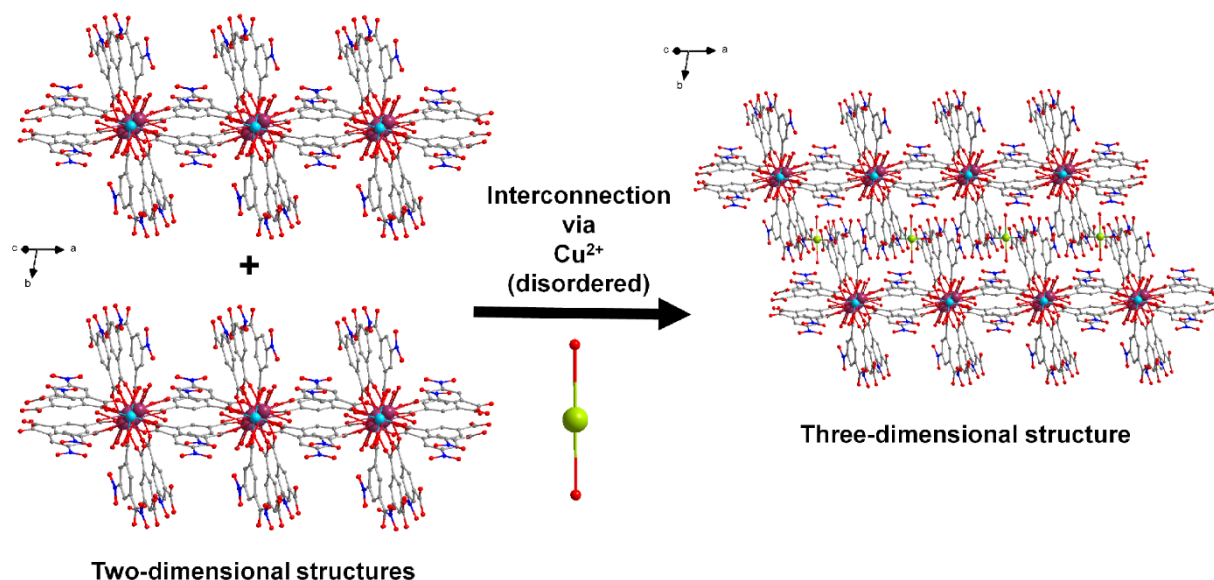


Figure 4.50. Two-dimensional chain interconnected by Cu^{2+} ions (disordered) in **2-La-meta**.

$[\text{Ln}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (5-Ln, $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$)

Single crystal X-ray diffraction analyses reveal that **5-Ln** (where $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$) crystallizes in $P\bar{1}$ of triclinic space group. Since all the lanthanide analogues crystallize as isomorphous compounds, only the Gd^{3+} analogue is discussed here.

The structure of the colourless crystals of $[\text{Gd}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**5-Gd**) was investigated using SCXRD. Some structural features are similar to that in **2-La-meta**, but differs in some aspects as there is no Cu^{2+} in the structure and the disorder of 5-nitroisophthalic acid ligands as $\text{Hnip}^- / \text{nip}^{2-}$ couple is thus also absent.

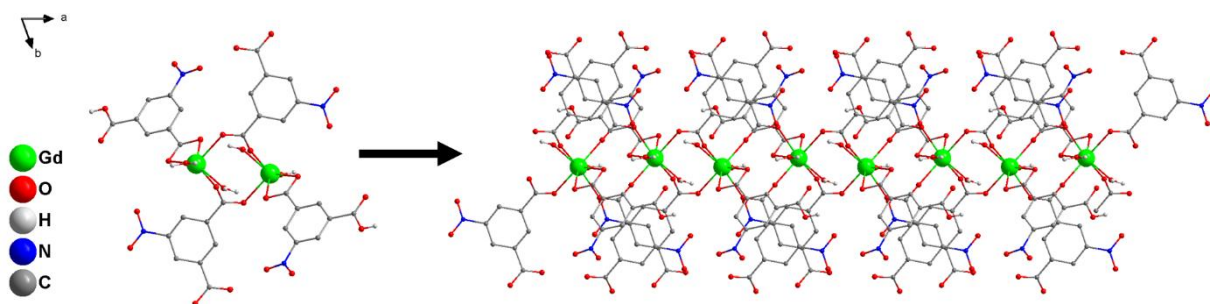


Figure 4.51. Core Gd_2 unit in **5-Gd** unit interconnected by Hnip^- and nip^{2-} ligands, forming a one-dimensional chain.

The compound crystallises in $P\bar{1}$ space group and the asymmetric unit consists of Gd_2 -units with two water ligands coordinated per Gd^{3+} ion. There are a pair of nip^{2-} and Hnip^- ligands per core unit which interconnect the Gd_2 -units by their carboxylate groups forming a one-dimensional chain (Figure 4.51). There are four lattice water molecules in the asymmetric unit.

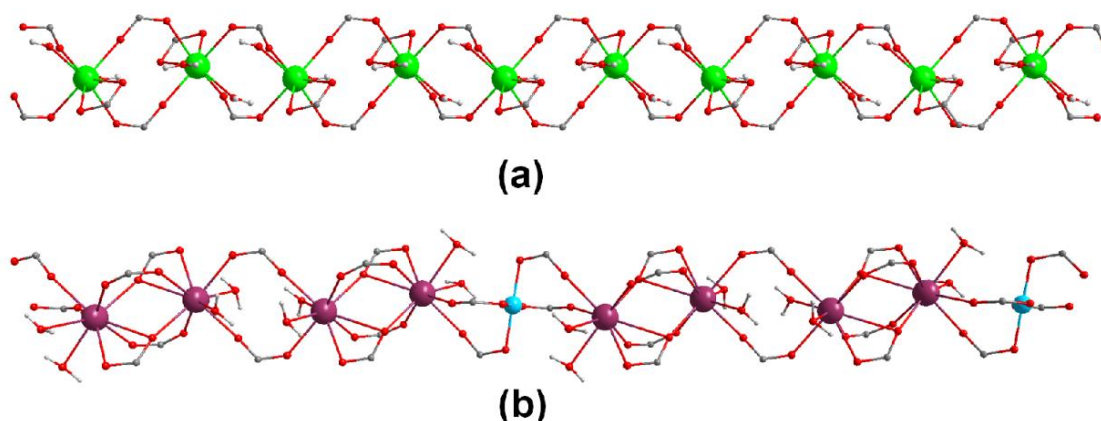


Figure 4.52. One-dimensional chain formed by the metal ions with coordinated water ligands and carboxylate groups of nip^{2-} ligands in (a) **5-Gd** and (b) **2-La-meta**.

The structure of the metal chains in **5-Gd** was compared with those in **2-La-meta** in Figure 4.32 (section 4.7). In **5-Gd**, the Gd_2 units form a one-dimensional chain, whereas a Cu^{2+} (Cu1) is present at every fifth site instead of the La^{3+} after each La_4 units in **2-La-meta** (Figure 4.52).

Each of the one-dimensional chains are interconnected via the nip^{2-} ligands, forming two-dimensional sheet-like structure (Figure 4.53). The crystal lattice of **5-Gd** has parallel arrangement of such sheets, but they are not interconnected as in the case of **2-La-meta** (Figure 4.54). There is quasi-parallel arrangement of the Hnip^- ligand in **5-Gd**, similar to the $\text{Hnip}^- / \text{nip}^{2-}$ disordered ligand system in **2-La-meta**. (Figure 4.55)

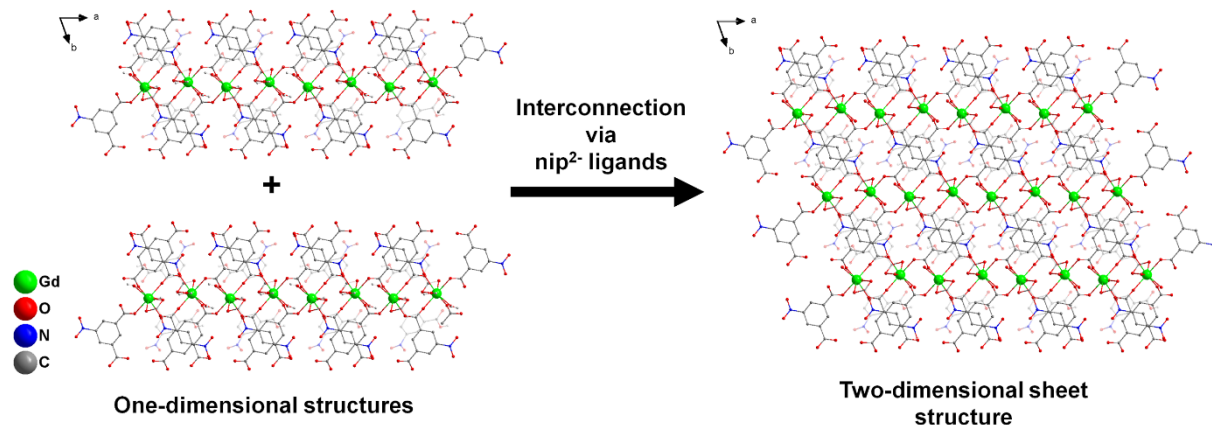


Figure 4.53. One-dimensional chain interconnected by nip²⁻ in **5-Gd** forming a two-dimensional sheet.

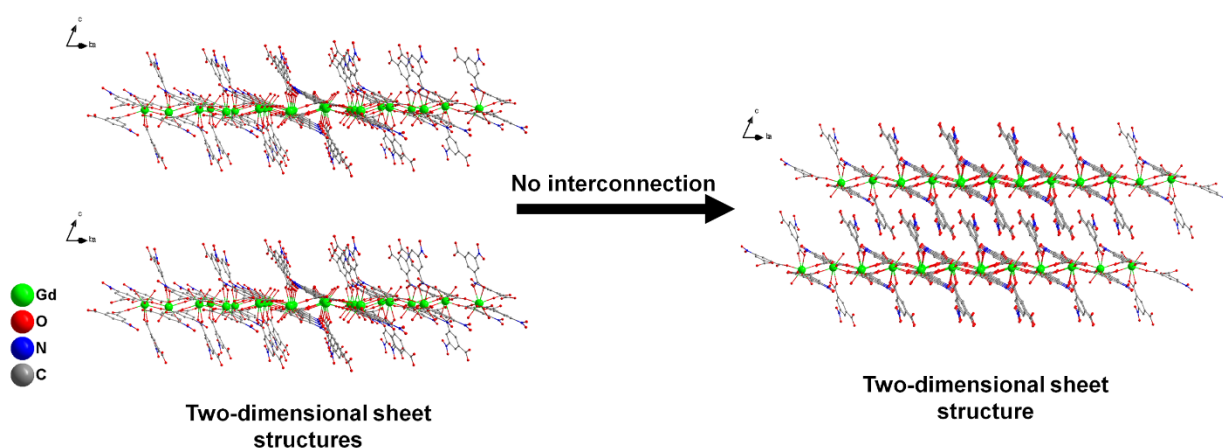


Figure 4.54. Arrangements of two-dimensional sheets in the crystal lattice of **5-Gd**. Note that there is no connection between the sheets.

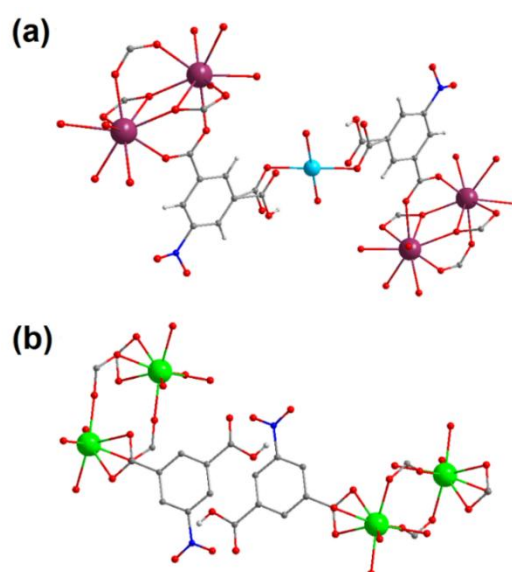


Figure 4.55. The quasi-parallel arrangement of ligands in (a) **2-La-meta** and (b) **5-Gd**.

Crystal Structure Description of $[\text{Ln}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$ (3-Ln**, $\text{Ln}^{3+} = \text{La}^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Y^{3+})**

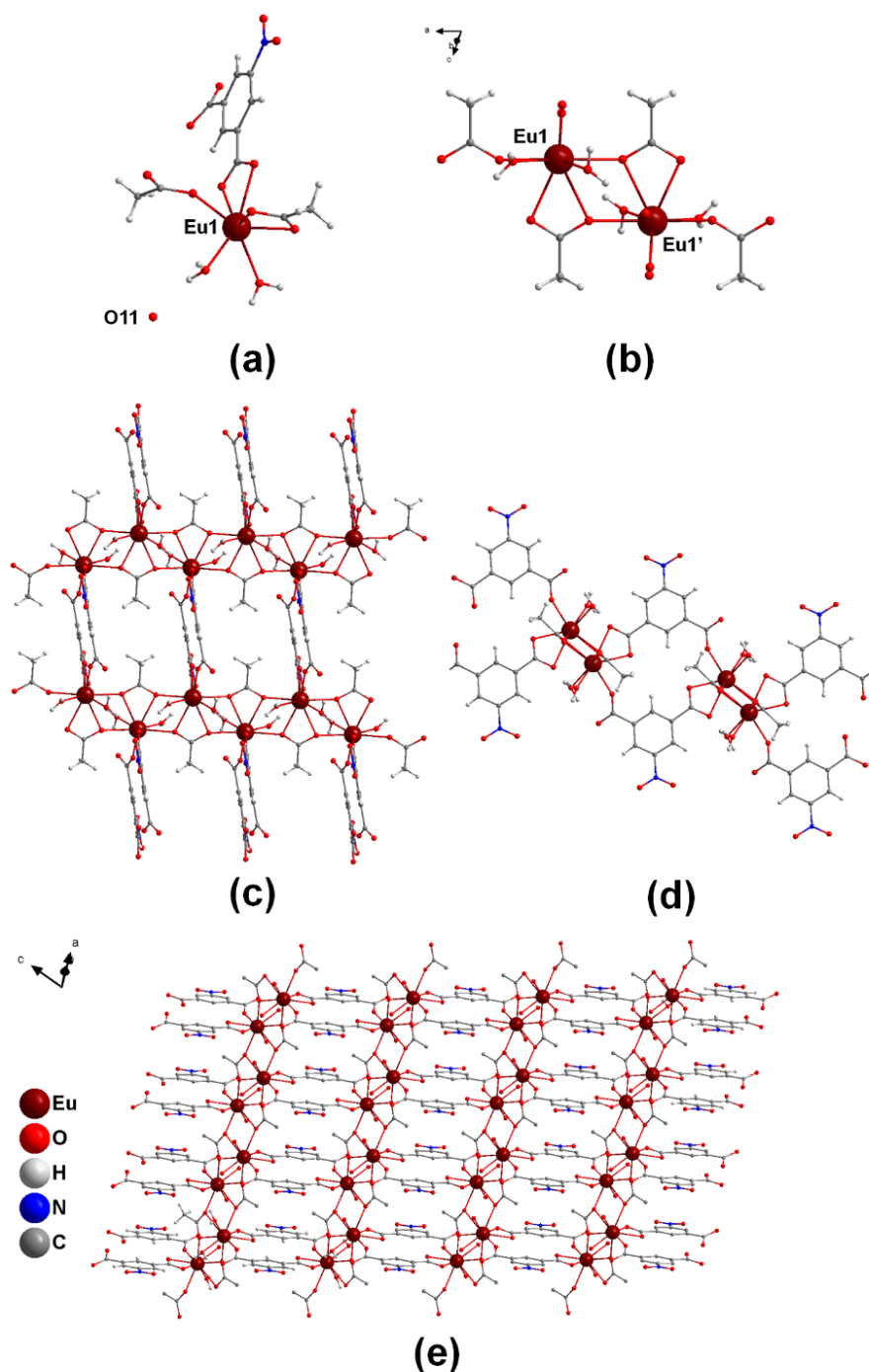


Figure 4.56. (a) Asymmetric unit in **5-Eu** including disordered lattice water (O11); (b) acetate bridges across Eu³⁺ ions; (c) zig-zag chains of Eu₂ core; (d) and (e) one-dimensional chains interconnected by nip²⁻ ligands to form the two-dimensional sheet structure in **5-Eu**.

Single crystal X-ray diffraction analyses reveal that **3-Ln** (where $\text{Ln}^{3+} = \text{La}^{3+}$, Eu^{3+} , Gd^{3+} , Tm^{3+}) crystallizes in $P\bar{1}$ of triclinic space group. All the lanthanide analogues crystallize as isomorphous compounds as confirmed with PXRD and FT-IR spectroscopy. In the

asymmetric unit, there was a disordered lattice water in the lattice. The occupancy varied from 56% in **3-La**, 26% in **3-Eu**, 24% in **3-Gd** and 15% in **3-Tm**. Apart from that, the structural details are same for all compounds. The structural details of **3-Eu** are described below.

In the asymmetric unit, there is a Eu^{3+} ion coordinated with a nip^{2-} , acetate and two water ligands and a disordered lattice water. The acetate groups bridge two Eu^{3+} ions in tetradentate $\kappa^2-\kappa^2-\mu_3$ (*syn, syn, anti, anti*) fashion to form alternating zig-zag chains of Eu_2 central cores. Each of these chains are interconnected by nip^{2-} ligands to form a two-dimensional sheet structure.

4.10.2. FT-IR Spectroscopy

The FT-IR spectra of the crystals of HMOFs **1-La**, **A-La**, **B-La**, **2-La** show characteristic signals, in particular the contributions from the organic ligand 5-nitroisophthalic acid which are visible in the 1800 to 900 cm^{-1} region (Figure 4.57a).

In addition to the broad IR band at 3600 cm^{-1} to 3400 cm^{-1} region which can be attributed to the (O–H) stretching vibration coming from water molecules, sharp bands corresponding to C–H stretch are seen at 3080–2070 cm^{-1} region. The strong bands in the 1650–1500 cm^{-1} , 1470–1420 cm^{-1} and 1350–1300 cm^{-1} regions correspond to the asymmetric and symmetric vibrations from the carboxylate groups are visible in all these compounds.^[108-110] A sharp band near 1350–1340 cm^{-1} and 1540–1530 cm^{-1} regions correspond to symmetric stretching and asymmetric stretching of $-\text{NO}_2$ groups of the ligand.^[111]

The FT-IR spectra HMOFs **1-La** and **2-La** are compared it with that of $\text{Cu-H}_2\text{nip}$ gel, which was used as the starting material for their synthesis (Figure 4.57b). The strong absorption between 1650 cm^{-1} and 1600 cm^{-1} can be assigned to the $\nu(\text{C}=\text{O})$ stretching vibration and is visible in all three spectra. A strong band at 1445 cm^{-1} in the gel is visible in **1-La** and **2-La**, which accounts for various monodentate and bidentate modes of carboxylate groups of the ligand molecules when it is coordinated with two different metal ions (Cu^{2+} and La^{3+}) in the these HMOFs.

It is worth mentioning about the strong band at 1710 cm^{-1} in the gel and 1703 cm^{-1} in **2-La** which accounts for the protonated carboxylate group, which is absent in **1-La**.

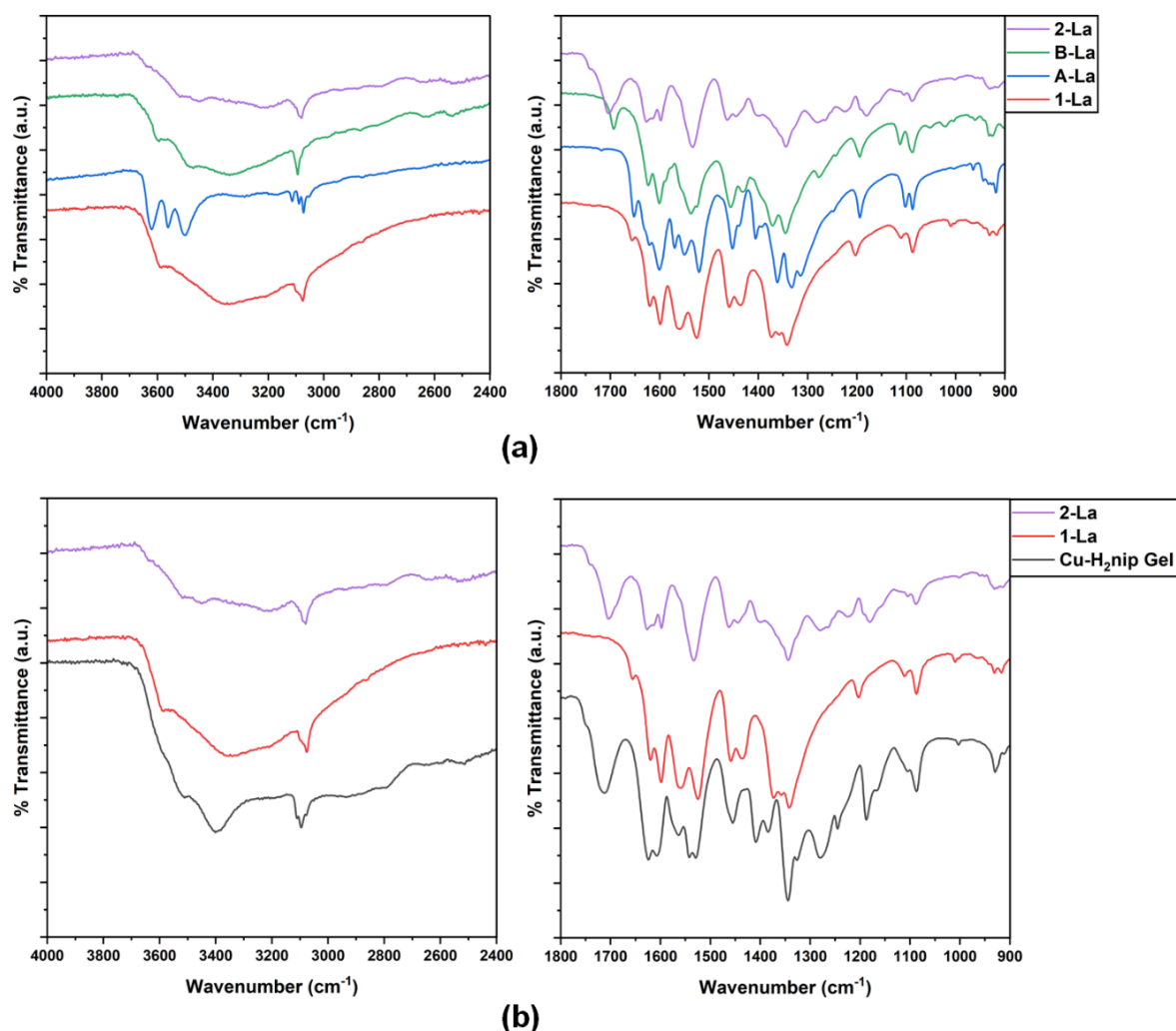


Figure 4.57. Comparison of major peaks in the FT-IR spectra (two regions) for (a) HMOFs **1-La**, **A-La**, **B-La**, **2-La**; (b) HMOFs **1-La**, **2-La** and Cu-H₂nip gel.

4.10.3. Thermogravimetric Analysis (TGA)

The thermal stability of compounds **1-La** and **2-Ln** (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) was investigated by TG analysis under air in the range of temperature 30–700 °C (Figure 4.58a). In **1-La**, two weight losses of about 4-13% from 70 °C up to around 130 °C corresponding to loss of water molecule. In the case of **2-Ln**, the weight loss due to water starts at about 160 °C and continue till 260 °C (8% weight loss).

The H₂nip ligand decomposition in **2-Ln** start at about 275 °C and after about 410 °C only 20-25% weight remains which could be due to the formation mixture of oxides of copper and various lanthanides.^[112]

The lanthanum compounds **1-La** and **2-La** shows similar thermal decompositions above 300 °C. A drop in temperature was observed for some compounds between 345 °C and

365 °C as the heating continued (Figure 4.58b). Similar behaviour has been seen in some MOF compounds, but has not been conclusively explained.^[113-114]

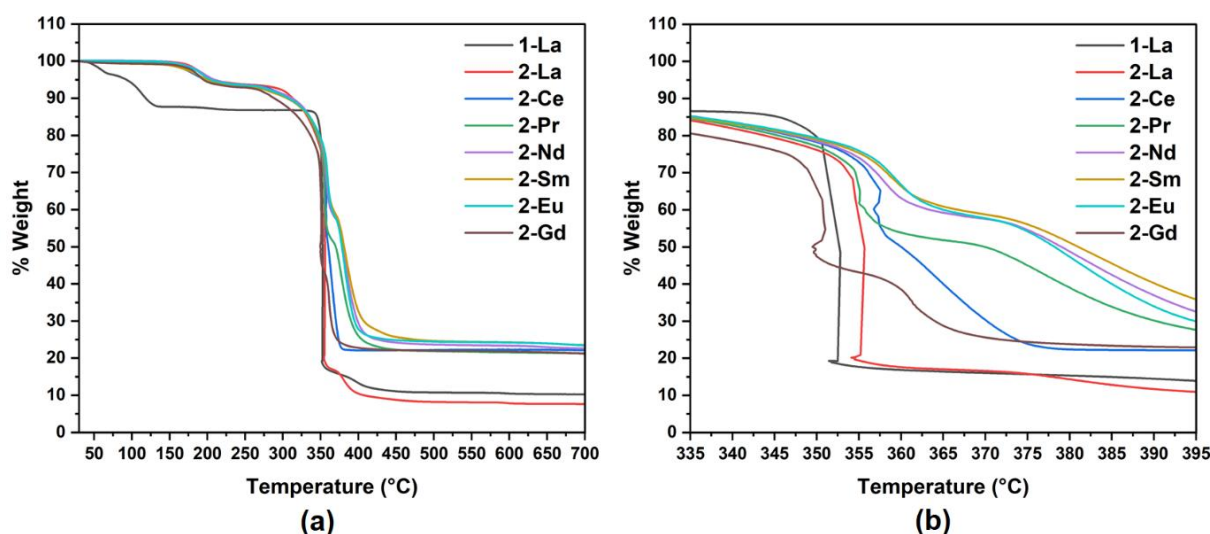


Figure 4.58. (a) TGA analysis of **1-La**, **2-Ln**. (b) Region between 320 °C and 420 °C shown as enlarged.

4.10.4. Solid-State UV-Vis Spectroscopy

The solid-state UV-Vis absorption spectroscopy of compounds **1-La** and **2-Ln** (**Ln** = **La**, **Ce**, **Pr**, **Nd**, **Sm**, **Eu**, **Gd**) were performed on crushed crystals. The dark blue colour in **1-La** is due to the absorption by three Cu^{2+} ions and this is visible as the broad peak from 500 to 800 nm. Similarly for **2-La**, a similar band with a slightly different intensity (Figure 4.60a) explain the blue colour of the crystals (Figure 4.59).

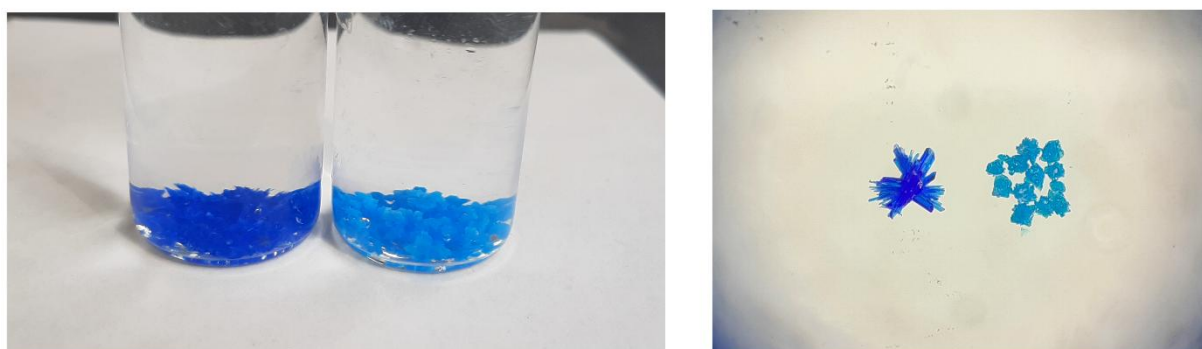


Figure 4.59. Crystals of **1-La** (dark blue) and **2-La** (blue).

For the **2-Ln** series, the absorption peaks corresponding to the f-f transitions (in the visible region) are also additionally visible (Figure 4.60b). Pr, Nd, Sm and Eu-analogues shows very sharp absorption signals for these transitions and are listed in the Table 4.3. Since, La, Ce, Gd- analogues do not show these transitions in visible region, the spectra for these are similar and only accounts for the absorption by Cu^{2+} ions.

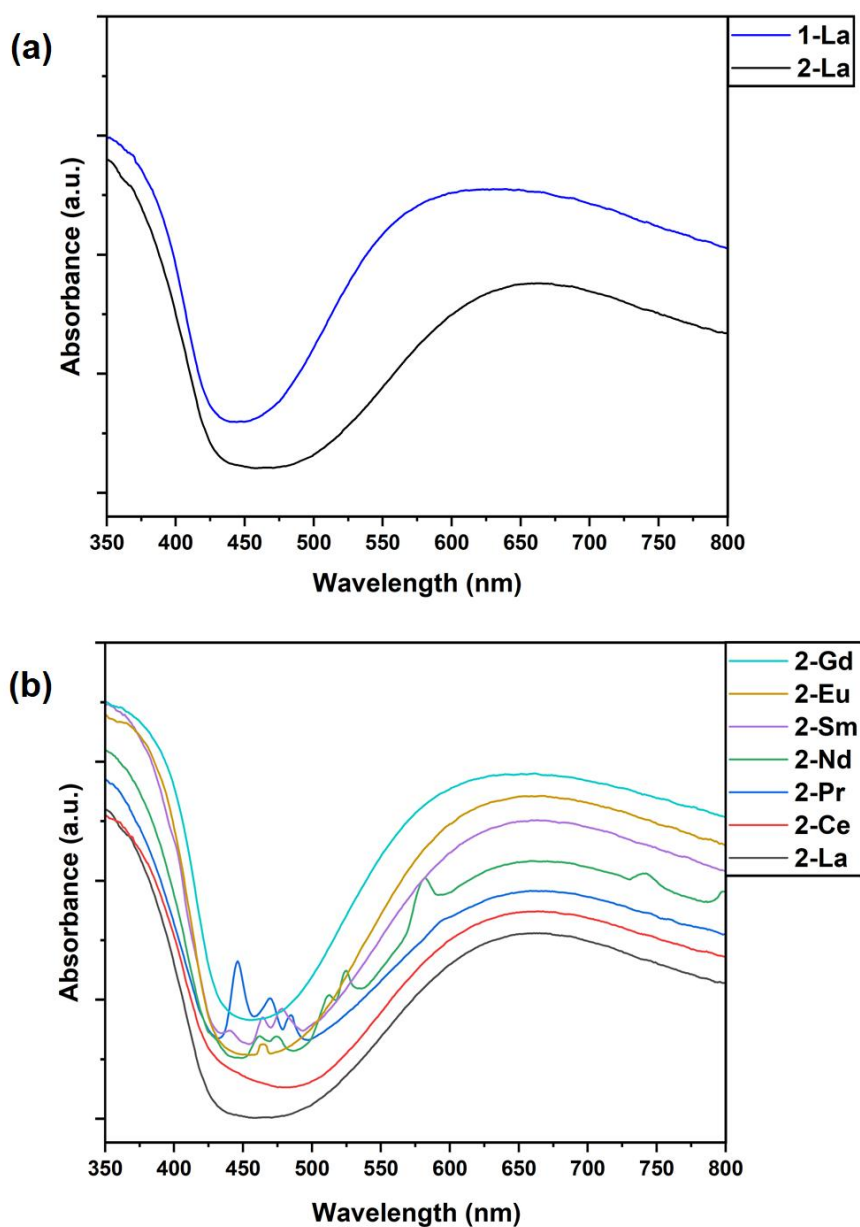


Figure 4.60. Solid state UV-Vis absorption spectra in the range of 350 to 800 nm for (a) 1-La & 2-La and (b) 2-Ln (for Ln = La, Ce, Pr, Nd, Sm, Eu, Gd).

Table 4.3. List of absorption maxima corresponding to f-f transitions of Ln^{3+} ions in 2-Ln.

<u>Compound</u>	<u>Ln</u>	<u>Absorption Maxima from f-f Transition (nm)</u>
2-Pr	Pr	446, 469, 484
2-Nd	Nd	461, 474, 512, 524, 581, 742, 800
2-Sm	Sm	441, 464, 478, 502
2-Eu	Eu	465

4.10.5. Solid-State Photoluminescence Spectroscopy

For the compound **2-Eu**, the solid-state photoluminescence (PL) spectra were measured to investigate its emission properties. An emission spectrum was measured first by exciting the sample at an arbitrary wavelength of 375 nm within the estimated region of the ligand's absorption (in UV region). A maxima in emission was observed around 612 nm, which is the typical finger print for Eu^{3+} emission for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition.^[115-116] Next, an excitation spectrum was recorded by setting the detector to the wavelength where the maximum emission was observed, i.e., 612 nm. Here, absorption maxima were found at 394 nm and 465 nm. By exciting the sample using these as excitation wavelengths, new emission spectra were recorded (Figure 4.61a).

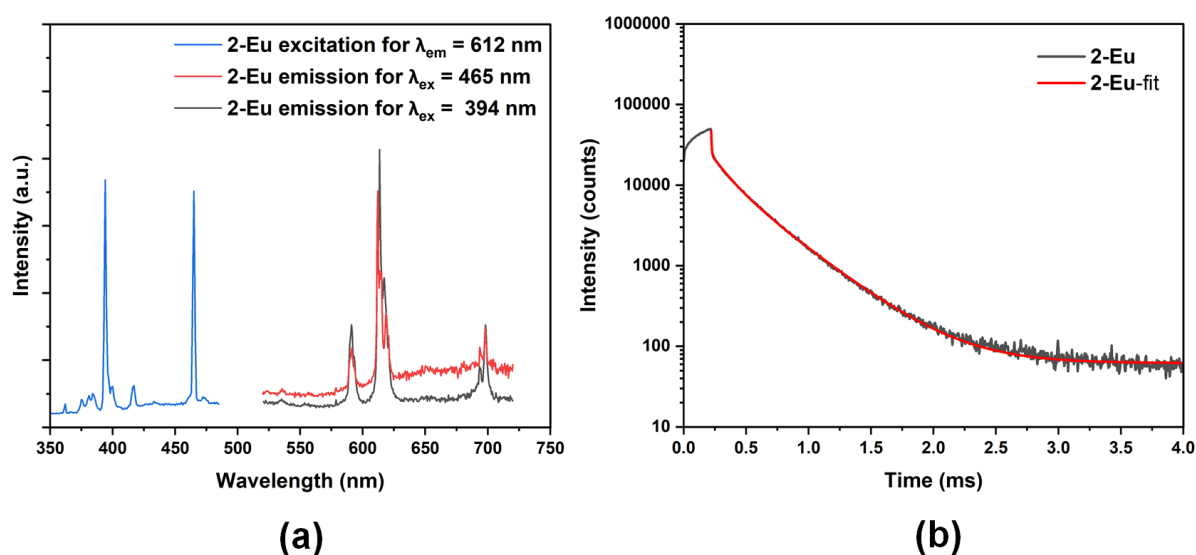


Figure 4.61. (a) Excitation and emission spectra of **2-Eu** measured in the solid-state; (b) Luminescence decay profile of **2-Eu** measured in the solid-state at RT ($\lambda_{\text{ex}} = 378$ nm). The decays (black) can be fitted with a bi-exponential function.

The $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions of the Eu^{3+} centre in the 520-720 nm region, reveal the emissive nature of the **2-Eu**. However, the emission intensity was low and the average lifetime was found to be 0.31 ms by fitting the decays with a bi-exponential function.

The efficiency of photoluminescence can be affected by the non-radiative decay via vibronic relaxations.^[117] This is usually the case when C-H, N-H and O-H oscillators are coordinated to an emissive Ln^{3+} ion which act as non-radiative relaxation channels, leading to a quenching of the luminescence. Since the Eu^{3+} centres in **2-Eu** have coordinated water ligands (Figure 4.62), this could be one of the factors causing fast decay of the $^5\text{D}_0$ state, leading to a lower emission intensity and lifetime.

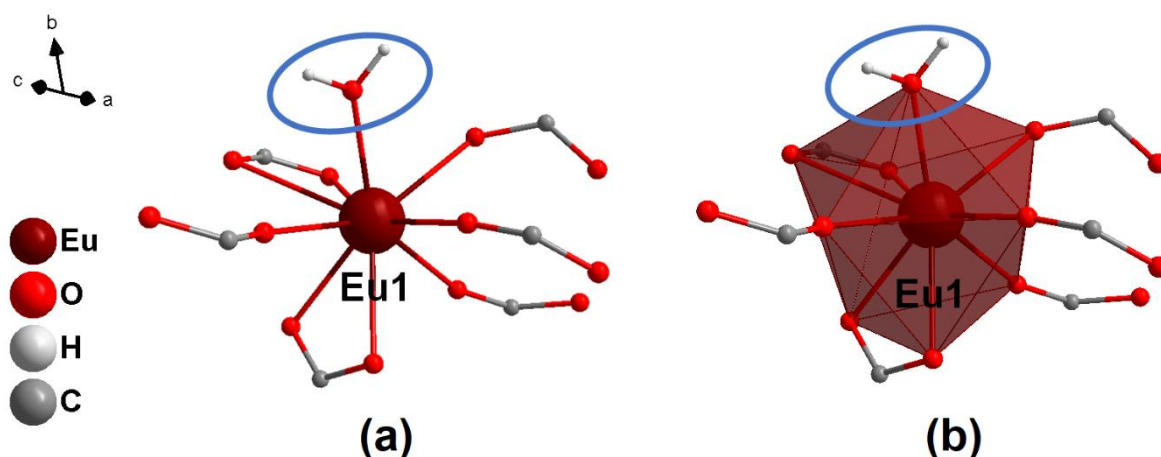


Figure 4.62. Coordination environment of Eu^{3+} ion in **2-Eu** showcasing coordinated water ligand.

Photoluminescence spectra of **2-Nd** and **2-Sm** were too weak to be quantified.

4.10.6. Magnetic Properties

Magnetic measurements under an applied dc field of 0.1 T were performed on a powder sample prepared from the crystals of **2-La**, **2-Nd** and **2-Gd**. The magnetic susceptibility was measured in the temperature range between 2 and 300 K and the $\chi_{\text{M}}T$ vs T plots are shown in the Figure 4.63.

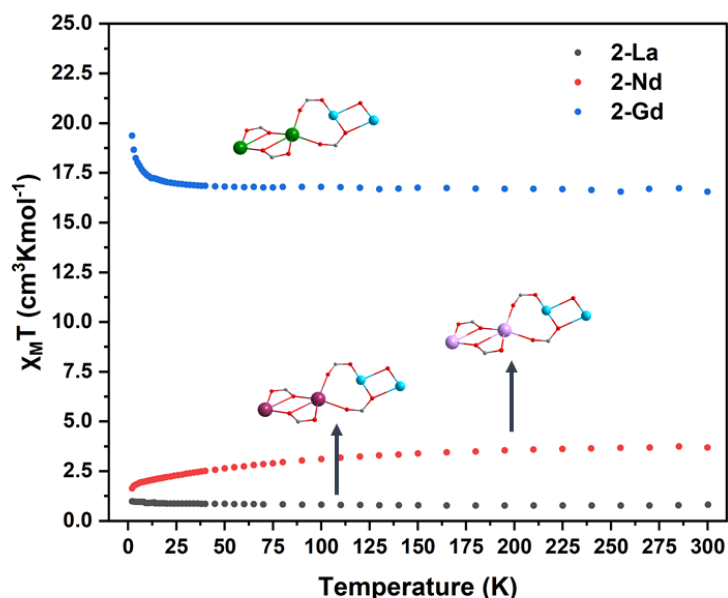


Figure 4.63. $\chi_{\text{M}}T$ vs T plot of **2-Ln** (for $\text{Ln}^{3+} = \text{La}^{3+}$, Nd^{3+} and Gd^{3+}).

For compound **2-La** that has two Cu^{2+} ions and two La^{3+} ions, the $\chi_{\text{M}}T$ value at room temperature (300 K) was found to be of $0.80 \text{ cm}^3 \text{mol}^{-1} \text{K}$ (Figure 4.63). This is in good agreement with the theoretical value of $0.75 \text{ cm}^3 \text{mol}^{-1} \text{K}$ for two non-interacting Cu^{2+} ions. At low temperatures a slight increase of the $\chi_{\text{M}}T$ value is detected indicating weak

ferromagnetic interactions between the Cu^{2+} ions and resulting in a value of $0.98 \text{ cm}^3\text{mol}^{-1}\text{K}$ at 2 K. Similar magneto-structural correlations in Cu-dimers bridged by alkoxo-groups that form Cu_2O_2 cores has been previously investigated.^[118-119]

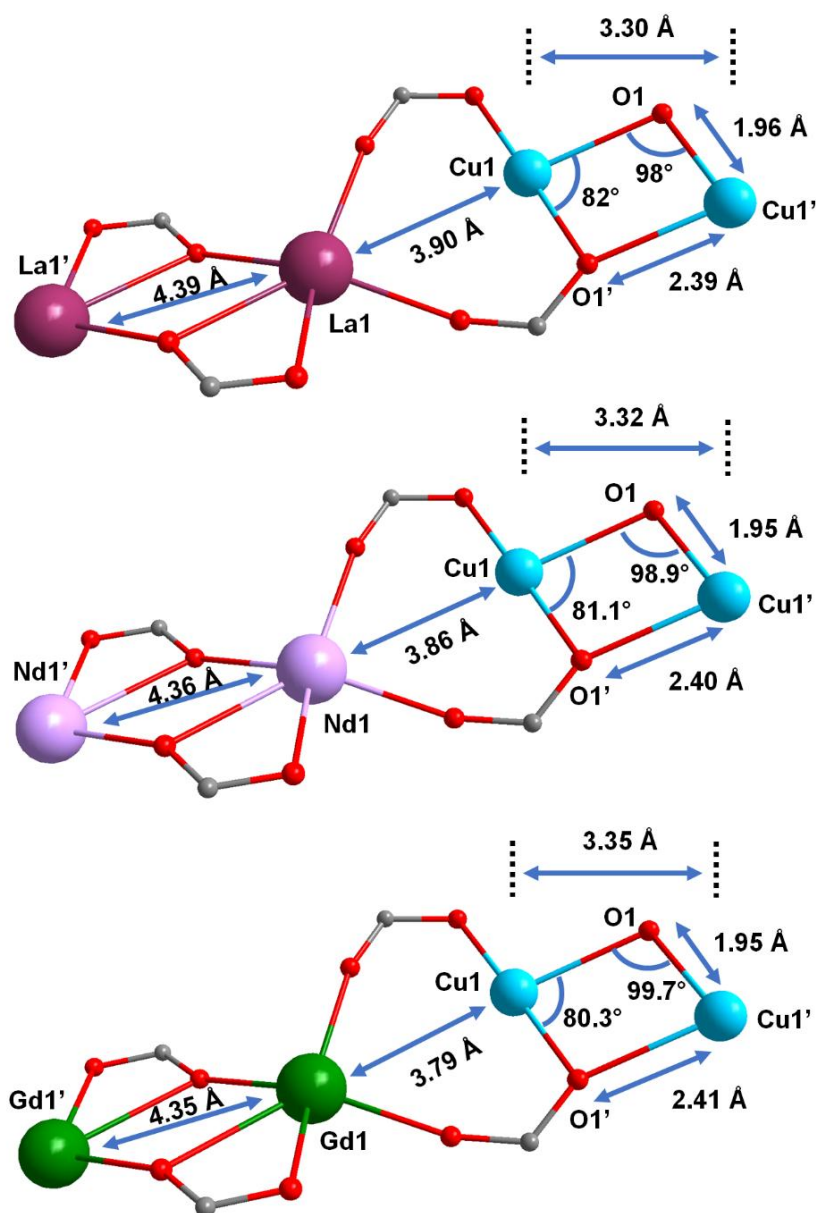


Figure 4.64. Relevant bond angles and distances between atoms in **2-La**, **2-Nd** and **2-Gd**.

Having established the nature of the Cu-Cu coupling, the compound **2-Nd** was investigated which has a χ_{MT} value of $3.68 \text{ cm}^3\text{mol}^{-1}\text{K}$ at room temperature (300 K) (Figure 4.63), significantly lower than the theoretical value of $4.55 \text{ cm}^3\text{mol}^{-1}\text{K}$ for two non-interacting Cu^{2+} ions and two Nd^{3+} ions. With decreasing temperature, the χ_{MT} values also decreases which could be the result of depopulation of excited states and potential antiferromagnetic interactions. Given that 4f-4f coupling is usually at least one order of magnitude weaker than coupling between 3d and 4f ions, this antiferromagnetic

interaction can likely be attributed to the Cu-Nd interaction outweighing the weak ferromagnetic Cu-Cu interaction.

For **2-Gd**, the $\chi_{\text{M}}T$ value at room temperature is 16.76 cm³mol⁻¹K (Figure 4.63) which excellently reproduces the theoretical value of 16.50 cm³mol⁻¹K for two non-interacting Cu²⁺ ions and two Gd³⁺ ions. As the temperature is decreased, the $\chi_{\text{M}}T$ product remains essentially constant up to ca. 50 K. Below that the value increases resulting in $\chi_{\text{M}}T$ = 20.6 cm³mol⁻¹K at 2 K. This behaviour suggests the presence of ferromagnetic Gd-Cu exchange interactions in addition to the weakly ferromagnetic interaction between the Cu²⁺ ions in this system (Figure 4.63). The change in sign of the overall magnetic interaction in **2-Nd** to **2-Gd** is likely a result of the anisotropic nature of the Nd³⁺ ions. This could lead to non-negligible antiferromagnetic dipolar interactions between the Nd³⁺ and Cu²⁺ ions. The behaviour of **2-Gd** is thus likely a result of the isotropic Gd³⁺ ions which may show weak ferromagnetic Gd-Cu exchange interactions^[120] in addition to the effect from the established Cu-Cu superexchange.

The Cu-O-Cu and the O-Cu-O angles of the Cu₂O₂ unit in **2-La**, **2-Nd** and **2-Gd** and the Ln-Ln, Ln-Cu and Cu-Cu distances in each case are illustrated in Figure 4.64.

4.11. Conclusion and Outlook

In this chapter, several HMOFs were successfully synthesized via a metalloligand approach in aqueous media. The metalloligand was prepared from copper acetate and 5-nitroisophthalic acid (H₂nip), resulting in the formation of a Cu-H₂nip metallogel. This metallogel was thoroughly characterized using rheological analysis, microscopy, and infrared spectroscopy. Detailed studies of the synthetic components, Cu²⁺ ions, acetate ions, and H₂nip, showed that the acetate anion is essential for deprotonating the H₂nip ligand, which is critical for gel formation. Among various transition metal acetate salts tested, only Cu²⁺ formed the gel. The 5-nitro substituent (-NO₂) acts as a strong hydrogen bond acceptor and activates the aromatic ring, facilitating the deprotonation of the carboxylic acid groups and enhancing ligand solubility in water, which is essential for aqueous-phase reactions. Additionally, the presence of two carboxylic acid groups in H₂nip makes it an excellent multidentate ligand candidate. The Ostwald ripening mechanism, supported by the ligand's solubility at elevated temperatures, guided the crystal growth of **Cu-nip** from the gel.

The latter part of the chapter focused on synthesizing La^{3+} -containing HMOFs using the Cu- H_2nip metallogel as a precursor. The influence of varying molar ratios of lanthanum nitrate and ligand excess was systematically examined, leading to the formation of new HMOFs (**1-La** and **2-La**) alongside known MOF compounds (**A-La** and **B-La**).

The synthesis protocols developed for La^{3+} -based HMOFs were extended to other lanthanides. While no analogues of **1-La** were obtained for other lanthanides, crystalline mixtures of **Cu-nip**, **3-Ln**, and previously reported MOFs **4-Ln** were isolated for $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$ and Y^{3+} . For the **2-La** system, isomorphous compounds **2-Ln** were isolated with $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$ and Gd^{3+} . During crystallization of **2-Ln**, colourless homometallic MOFs **5-Ln** ($\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) formed initially but dissolved back into solution over time. For heavier lanthanides beyond Gd^{3+} , homometallic MOFs remained in solution, and the corresponding HMOFs did not form.

Metastable intermediates, **2-La-meta** and **5-Ln** ($\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$), were isolated as crystals, enabling their structural characterization. Notably, **2-La-meta** exhibited unusual crystallographic disorder, which was analysed and explained. These findings support Ostwald ripening as a key process during HMOF crystallization.

Finally, selected compounds were characterized using thermogravimetric analysis, solid-state absorption spectroscopy, photoluminescence spectroscopy, and magnetic measurements to assess their physical properties.

This work reveals key factors in the formation of Cu-Ln MOFs and their structural diversity, providing a basis for exploring their properties and applications. It also shows that using the metalloligand method in aqueous media offers new ways to create a wider variety of HMOFs. Future work will involve detailed studies of properties like luminescence, magnetism and catalysis to better understand and utilize their potential.

5. Copper-Lanthanide Heterometallic Metal-Organic Frameworks Synthesized in Water-DMF Media

5.1. Introduction

Topotactic reactions have been observed frequently in MOFs and coordination networks. This solid-state transformation usually involves stimulus like removal of solvent or guest molecules in the lattice without collapsing the structure.^[121-124] The structural transformation opens possibilities for new materials with new properties, such as adsorption, magnetic properties etc. In topotactic processes, the crystal structure of the product maintains specific crystallographic orientation(s) relative to the crystal structure for the starting material.^[125] This is a particular area of interest as it can provide a pathway to obtain unique compounds that cannot be obtained by direct reaction.^[126]

Topotactic transformations are also called as single-crystal-to-single-crystal (SC–SC) transformations in many contexts. The SC–SC processes usually involve changes in host–guest behaviour, exchange of coordinated metal ions or counterions which are triggered by external stimuli such as heat, light, solvent molecules, anions, metal cations.^[127] The structural integrity of the framework and crystallinity are usually retained.^[128-129]

Apart from these solid-state transformations, there are also solvent-mediated structural transformations where the dissolution of one crystalline phase and subsequent formation of another occurs. This can happen as a result of external stimuli such as temperature and solvents. Usually, the crystals lose their crystallinity and form a new phase.^[130] Studies on structural transformation are important in order to understand the factors that influence crystal nucleation and growth and thereby the development of new functional materials.^[131]

In the previous chapter, the synthesis of Heterometallic Metal-Organic Frameworks (HMOFs) focused on using aqueous media. Classic MOF syntheses usually involve solvothermal methods and polar, high-boiling solvents such as N,N'-dimethylformamide (DMF), N,N'-dimethylacetamide (DMA), N,N'-diethylformamide (DEF) are used. These solvent systems have the ability to dissolve a wide range of metal salts and organic linkers. In this chapter, the metallogel approach is once again used for the HMOFs, with a small amount of DMF in the reaction mixture. Since the H₂nip ligand is soluble in DMF, it is of interest to find out how the dissolution of the solid reactants into the solution and

crystallisation as MOFs (Ostwald ripening)^[97-98] will be different compared to the case when water was used as the solvent. Here as in Chapter 4, the La^{3+} system was first studied for the formation of HMOFs. Different factors like temperature, rate of heating was found to have effect on the structure of HMOFs. For these HMOFs, the structural transformations were observed visually over a period of 10 days with continuous heating. This approach was also applied to all the other lanthanides.

5.2. Cu-H₂nip-La in a H₂O/DMF (10:2) Solvent System

5.2.1. Overview

The Cu-H₂nip metallogel discussed in chapter 4 was used as the metalloligand in this work. This study led to the isolation of both heterometallic and homometallic MOFs.

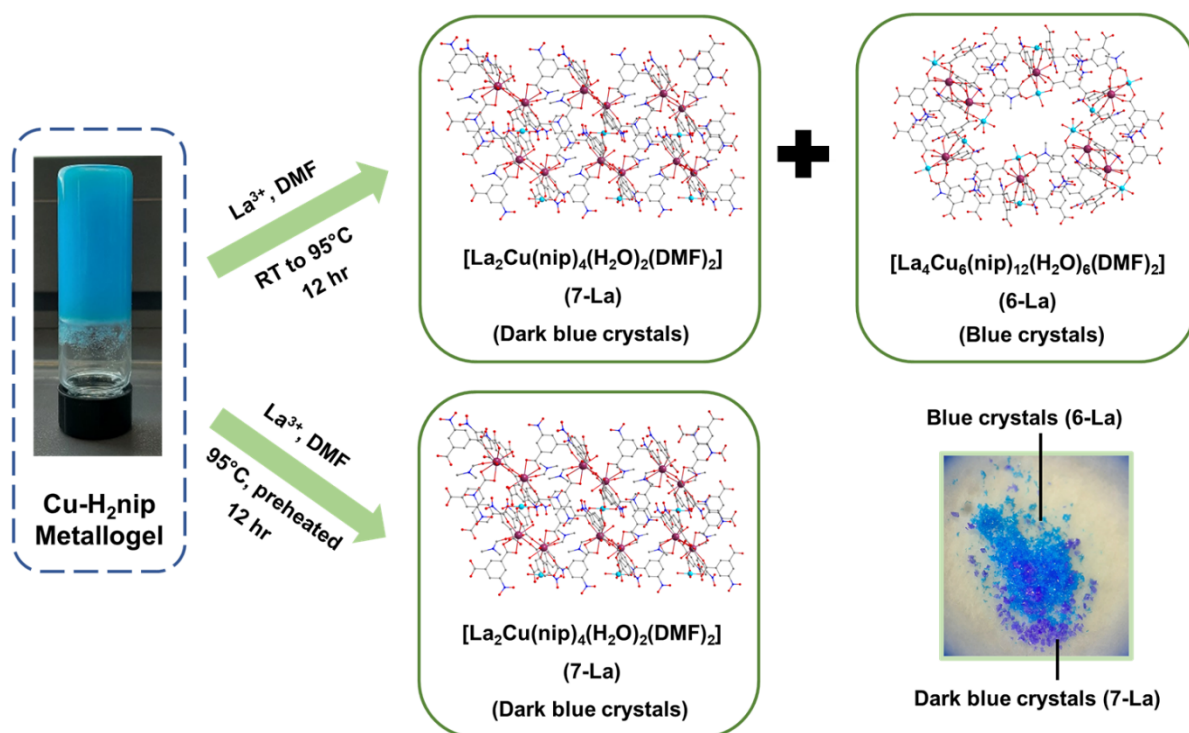


Figure 5.1. Reaction pathways at different heating conditions.

In the first set of studies, an optimized reagent ratio of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{La}(\text{NO}_3)_3 = 1 : 1 : 1.5$ in a solvent system $\text{H}_2\text{O} : \text{DMF}$ (v : v / 10 mL : 2 mL) was used. Various crystal transformations were observed for this system depending on the reaction temperatures and rate of heating. Experiments were conducted at 95 °C and 75 °C either with heating starting from room temperature to 95 °C (or 75 °C) or directly heating at 95 °C (or 75 °C) in a preheated oven over 10 days.

When the heating was done from room temperature to 95 °C, a mixture of blue crystals of $[\text{La}_4\text{Cu}_6(\text{nip})_{12}(\text{H}_2\text{O})_{10}(\text{DMF})_2]$ (**6-La**) and dark blue crystals of $[\text{La}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$ (**7-La**) were obtained within 12 hours. Over 48 hours, the crystals of **6-La** eventually dissolved and more crystals of **7-La** were formed. In contrast, directly heating the reaction mixture in a preheated oven at 95 °C yielded pure **7-La** within 12 hours (Figure 5.1). Similar trends were observed at 75 °C, although transformations occurred slowly.

A notable structural transformation was observed when dark blue crystals of **7-La** were heated at 95 °C over about 10 days, leading to the formation of pale-yellow $[\text{La}_2(\text{nip})_2(\text{HCOO})_2(\text{H}_2\text{O})_4]$ (**8-La**), Cu_2O particles, and colourless fibrous solids of lanthanum formate (Figure 5.2). This entire process can be considered as a temperature-induced and solvent-mediated structural transformation. A similar transformation was not observed at 75 °C.

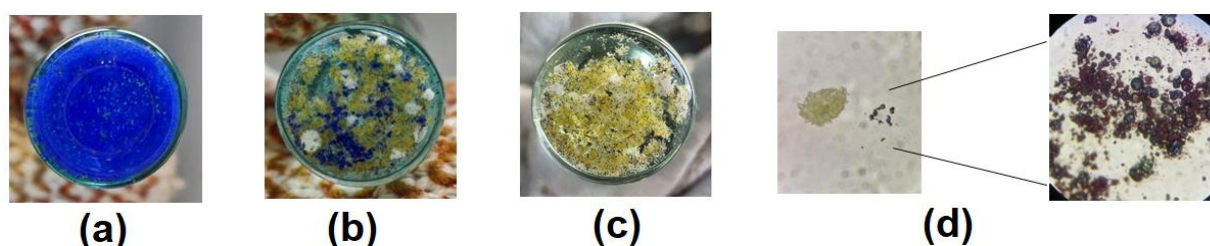


Figure 5.2. (a)-(c) Transformation of **7-La** into **8-La** over ten days; (d) Optical microscope images of **8-La** and Cu_2O formed.

The initial findings during the solvothermal reaction of Cu- H_2nip -La- H_2O -DMF system led to the following questions:

- How does temperature and heating rate affect the rate of crystallization and stability of the resulting compounds?
- What is the mechanism for the conversion of heterometallic MOF $[\text{La}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$ (**7-La**) into homometallic MOF $[\text{La}_2(\text{nip})_2(\text{HCOO})_2(\text{H}_2\text{O})_4]$ (**8-La**)?
- How the leaching of Cu^{2+} from **7-La** results in **8-La**?
- How did Cu_2O particles form in the reaction mixture?

Another interesting crystal transformation was observed when the reaction mixture was stored at room temperature after the complete crystallization of **7-La** from the reaction mixture. Over several weeks, the amount of dark blue crystals of **7-La** decreased and a

blue crystalline phase formed:
 $[\text{La}_4\text{Cu}_{2.35}(\text{nip})_{6.7}(\text{Hnip})_{1.3}(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_6(\text{H}_2\text{O})_{16.7}]^+ \cdot 8.3\text{H}_2\text{O}$ (**9-La-A**).

In the second part of the studies, the effect of additional amounts of H₂nip in reaction mixture with respect to the optimized stoichiometry was considered. Another series of reactions with Cu(OAc)₂·H₂O : H₂nip : La(NO₃)₃ : H₂nip = 1 : 1: 1.5 : 2 were performed. Here the crystals of **7-La** were obtained even with the addition of extra ligand. Upon prolonged heating, the crystal transformation of **7-La** into **8-La** was not observed until the reaction was done for about 2 weeks at 95 °C and for about a month at 75 °C. In both cases, the crystals decomposed and amorphous materials were isolated. The similar crystal transformation in **7-La** at room temperature was observed here as well. However, the crystals here were dichroic green-blue coloured (**9-La-B**).

5.2.2. Optimization of Molar Ratio

To begin with, the reagent ratio for **1-La**, as in Chapter 4, was followed (Cu : H₂nip : La = 1 : 1 : 1). 1 equivalent of La(NO₃)₃ was added to the Cu-H₂nip metallogel followed by DMF and the resulting pale-blue colloidal reaction mixture was heated in an oven. The reaction temperature was kept fixed as 95 °C (preheated oven). Initially, a blue suspension formed and the growth of dark blue crystals from the blue precipitate occurred as the heating continued. This was accompanied by the formation of a blue amorphous powder (Figure 5.3a), likely due to side products from mismatched stoichiometry.

Table 5.1. Stoichiometries of the starting materials considered for the reaction optimization.

Trial	Equivalent of Cu(OAc) ₂ ·H ₂ O	Equivalent of H ₂ nip	Equivalent of La(NO ₃) ₃	Observation
(a)	1	1	1	Mixture of dark blue crystals and greenish blue amorphous solids
(b)	1	1	1.5	Dark blue crystals
(c)	1	1	2	Dark blue crystals

Optimization trials (Table 5.1) with varying La(NO₃)₃ ratios with respect to the constituents of gel (Cu(OAc)₂·H₂O and H₂nip) were performed. In all the cases, the volume of solvent system (H₂O : DMF = 10 : 2 / v : v) was kept fixed. The best conditions required an addition of at least 1.5 equivalents of La(NO₃)₃ yielding pure **7-La** crystals

after 48 hours (Figure 5.3b). Hence the reagent ratio $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{La}(\text{NO}_3)_3$ of 1 : 1 : 1.5 was used for all subsequent reactions.

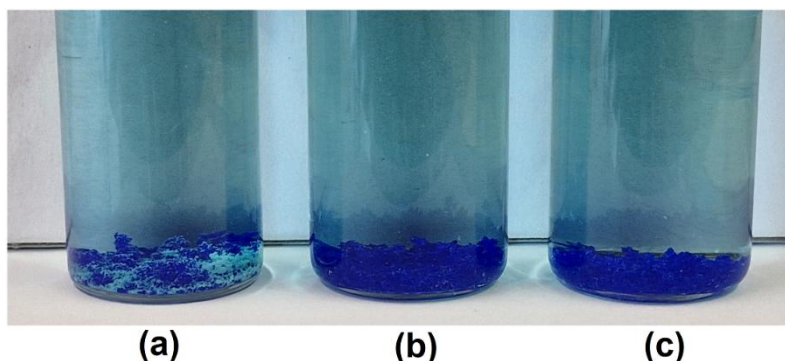


Figure 5.3. Reaction mixtures from each trials (described in Table 5.1) obtained after 48 hours of heating at 95 °C.

5.2.3. Structural Transformation During Crystallization

A typical reaction was done at 95 °C in oven, and it is registered as complete when the transformation of the entire blue precipitate into dark blue crystals of **7-La** has occurred. This crystallization from the precipitate becomes visible within 2 hours and typically takes 24-48 hours to form into single crystals. Since the H_2nip ligand has higher solubility in DMF, the dissolution and recrystallization occur quickly, leading to small adjunct crystals with many defects (Figure 5.4). The crystals of La-HMOFs (**1-La** and **2-La**) obtained in Chapter 4, where water was used as the solvent, were of higher quality compared to these.

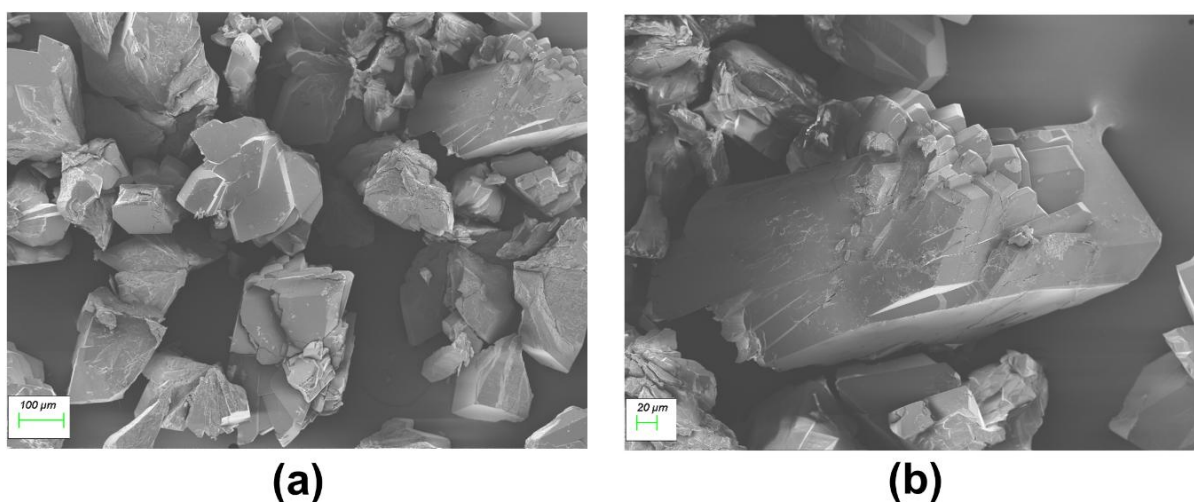


Figure 5.4. SEM Images of joint crystals of **7-La** showcasing defects.

To control the rate of crystallization, the heating process and the temperature were monitored. Thus, the heating of the reaction mixture could be performed in two ways:

1) Heating from room temperature to 95 °C

In this method, the crystallisation is slower and within 12 hours, a mixture of blue crystals (**6-La**) and dark blue crystals (**7-La**) are formed (Figure 5.5.a). As the heating is continued for another 36 hours, the blue crystals dissolve and more dark blue crystals are formed (Figure 5.5b-d).

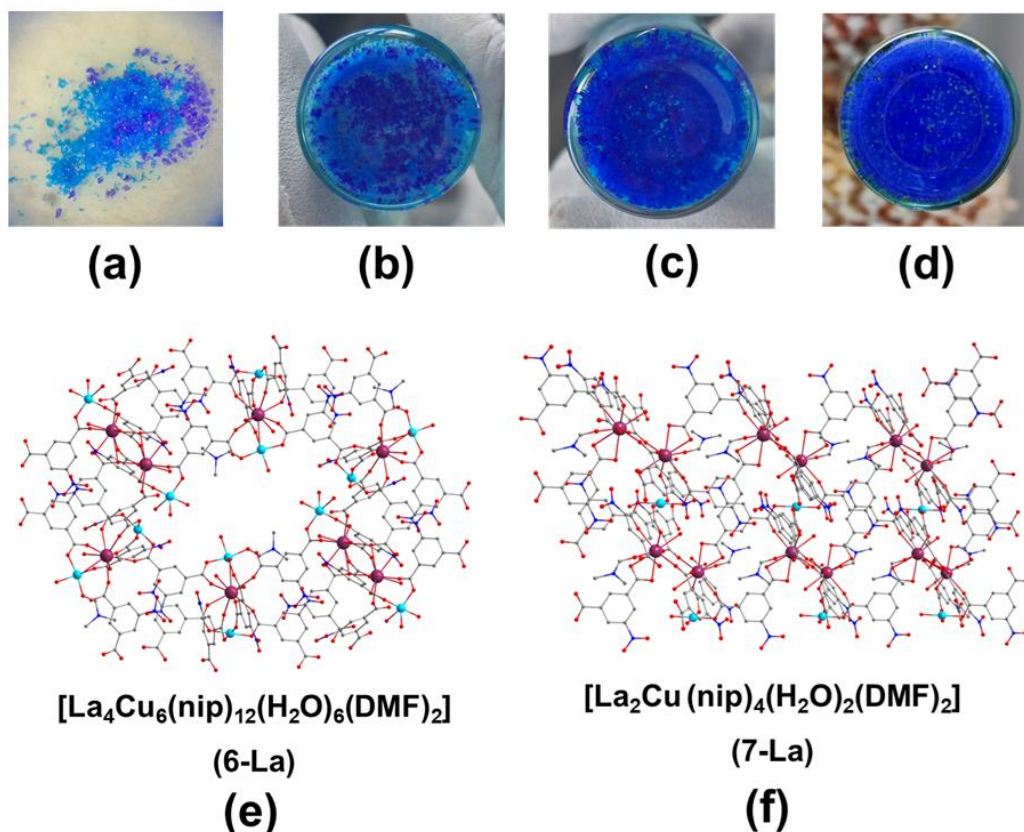


Figure 5.5. (a) Mixture of blue crystals of **6-La** and dark blue crystals of **7-La** viewed under optical microscope; (b)-(d) Structural transformation from **6-La** to **7-La** over 48 hours; (e) Crystal structure of **6-La**; (f) Crystal structure of **7-La**.

2) Heating in a preheated oven at 95 °C

This method exclusively yields dark blue of **7-La** crystals after 12 hours (Figure 5.1), without the formation of crystals of **6-La**.

When the reaction mixture was heated from room temperature to 75 °C, a similar crystalline mixture of **6-La** and **7-La** was obtained, but the quantity of blue crystals of **6-La** was higher. The transformation from blue to dark blue crystals in this case occurs at a slower rate (about twice as long) compared to the reaction at 95 °C. Since the transformation process involve the dissolution of crystals of **6-La** into the solution and recrystallisation of dark blue crystals of **7-La** with a different topology. This Ostwald

ripening can be considered as temperature-induced, solvent-mediated structural transformation during the crystallization process.^[132]

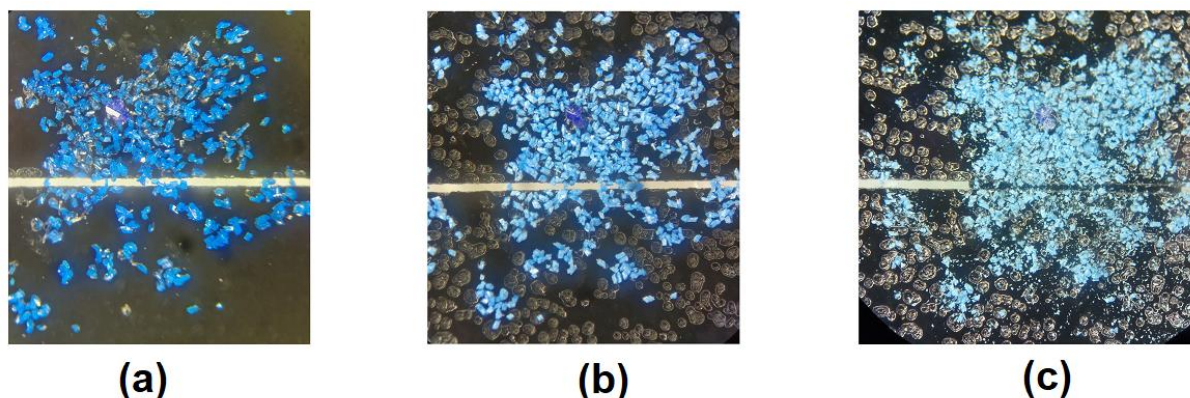


Figure 5.6. The crystalline mixture of **6-La** (blue crystals, majority) and **7-La** (dark blue crystals, minority) (a) freshly applied on the carbon tape for SEM imaging; (b) After drying in vacuum for 15 minutes; (c) After SEM imaging.

During the structural transformation involving **6-La** and **7-La**, the formation of crystals of homometallic MOF $[\text{La}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_2] \cdot 0.56\text{H}_2\text{O}$ (**3-La**) were also observed. The crystals of **6-La** and **3-La** dissolved as the reaction progressed towards **7-La** indicating that the transformation is a complex process involving many intermediate compounds. At the end the thermodynamically stable product **7-La** is that all remains.

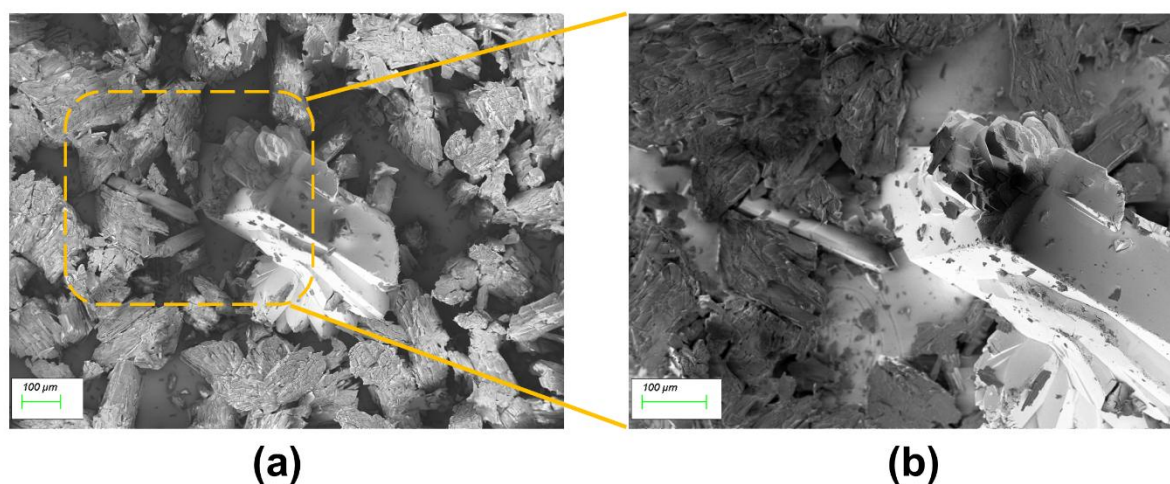


Figure 5.7. SEM images showing the cracked crystals of **6-La** surrounding a few uncracked crystals of **7-La**.

The SEM imaging of the crystalline mixture of the blue crystals of **6-La** and dark blue crystals of **7-La** was performed, before which the crystals were applied on a carbon tape and kept in vacuum for about 15 minutes to dry. It was observed that the blue colour of crystals of **6-La** became pale (Figure 5.6a and b). The blue colour became even paler after the imaging was done (Figure 5.6c).

The crystals of **6-La** cracked under the vacuum conditions during SEM imaging and this is visible in the images (Figure 5.7). This is likely due to solvent loss and collapse of the crystal structure.

5.2.4. Structural Transformation Post-Crystallization

After 48 hours, the crystallization of compound **7-La** is complete and leaves the pale-blue mother liquor. This system can undergo two identifiable transformations, depending on the temperature at which the vials are stored, which is explained below for the two cases: (1) 95 °C and (2) room temperature.

5.2.4.1. At 95 °C

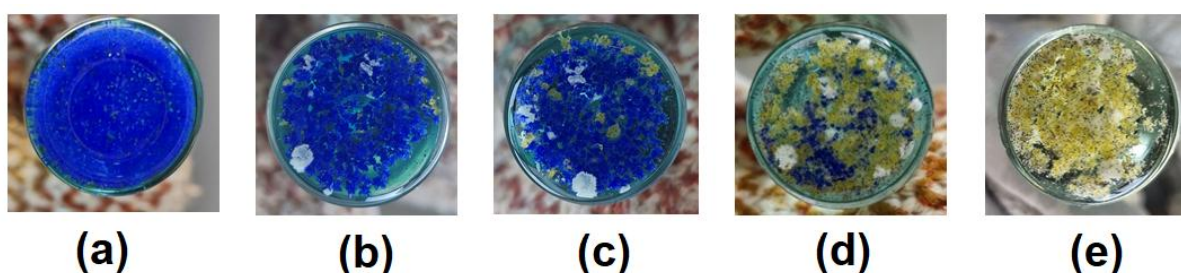


Figure 5.8. Transformation of dark blue crystals of **7-La** into pale yellow crystals of **8-La** over 10 days.

When the reaction mixture of dark blue crystals **7-La** and mother liquor was subjected to continued heating at 95 °C, it was observed that after about 4 days, a few colourless fibrous solids begin to form (Figure 5.8b). Afterwards, a pale-yellow crystalline material begins to form along with dark reddish-brown particles, especially on the walls and the bottom of the vial. As the heating was continued for about 5-10 days, it was clear that the amount of dark blue crystals of **7-La** has decreased (Figure 5.8d-e).

The pale-yellow crystals were found to be $[\text{La}_2(\text{nip})_2(\text{HCOO})_2(\text{H}_2\text{O})_4]$ (**8-La**) (Figure 5.9a, b) from SCXRD data. The reddish-brown particles and the colourless fibrous solids (Figure 5.9c) were analysed by PXRD and these were matching with the PXRD pattern of copper (I) oxide (cuprous oxide, Cu_2O) and of lanthanum formate respectively (Figure 5.9d, e).

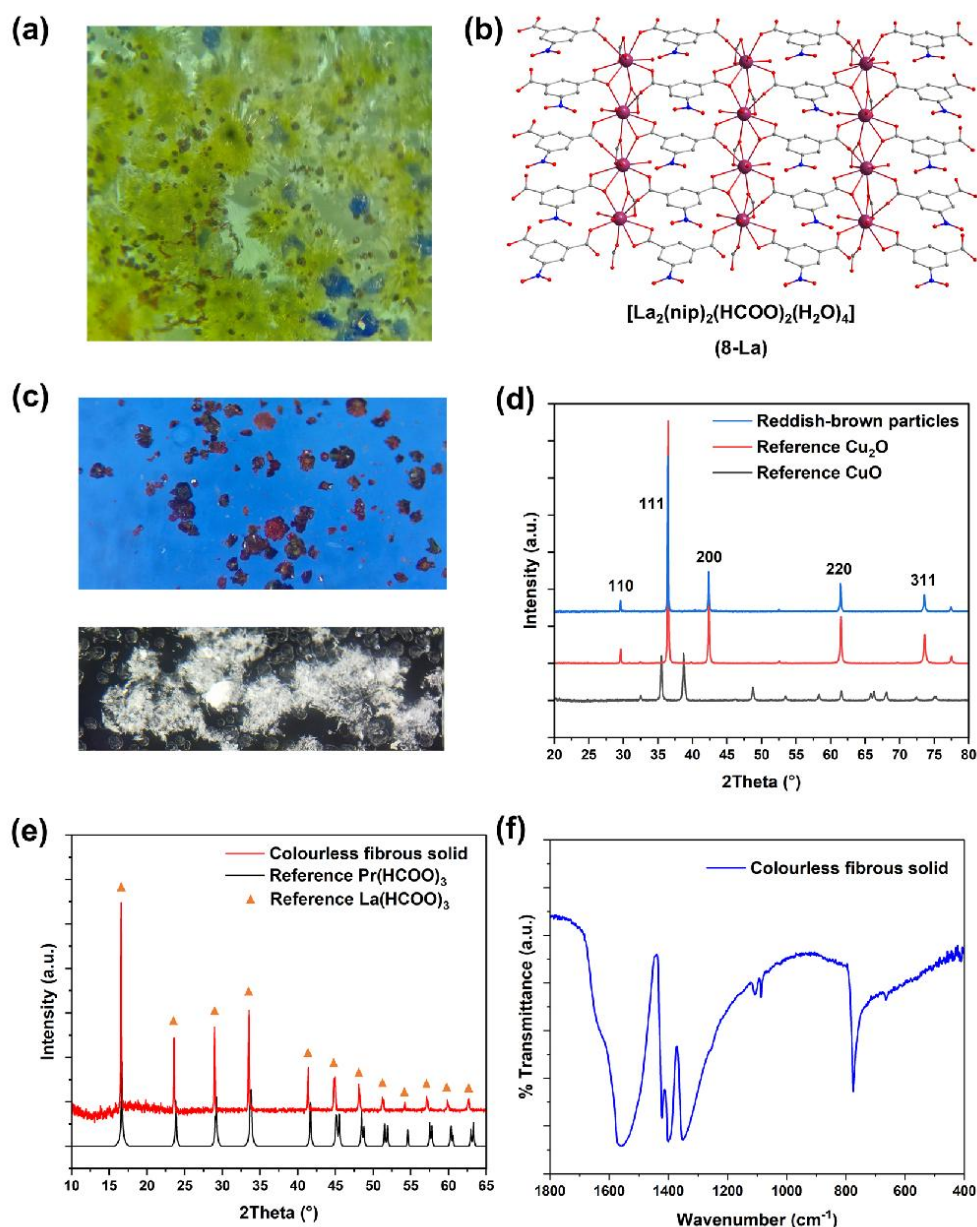


Figure 5.9. (a) Mixture of pale-yellow crystals of **8-La**, dark blue crystals of **6-La**, reddish brown particles and colourless fibrous solids; (b) Crystal structure of **8-La**; (c) Reddish-brown particles on a blue background (top) and colourless fibrous solids on a black background (bottom) viewed under optical microscope; (d) Comparison of PXRD pattern of the reddish-brown particles with reference Cu_2O and CuO , showing matching facets of the Cu_2O crystals; (e) PXRD pattern of the colourless fibrous solids compared with reference lanthanide formate; (f) FT-IR spectrum of colourless fibrous solids.

In addition, the FT-IR spectrum of the colourless solids (Figure 5.9f) shows a characteristic IR fingerprint of lanthanum formate as reported in the reference.^[133] Strong bands at 1560 and 1400 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of the carboxylate group. The C-O symmetric stretching vibration

is observed at 1350 cm^{-1} . The strong sharp band at 775 cm^{-1} possibly indicate the vibration in La-O bond.

In conclusion, the dark blue crystals $[\text{La}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_2(\text{DMF})_2]$ (**7-La**) underwent a solvent-mediated transformation process where it dissolved into mother liquor and recrystallised as a mixture of pale-yellow crystals of $[\text{La}_2(\text{nip})_2(\text{HCOO})_2(\text{H}_2\text{O})_4]$ (**8-La**), along with the formation lanthanum formate and Cu_2O .

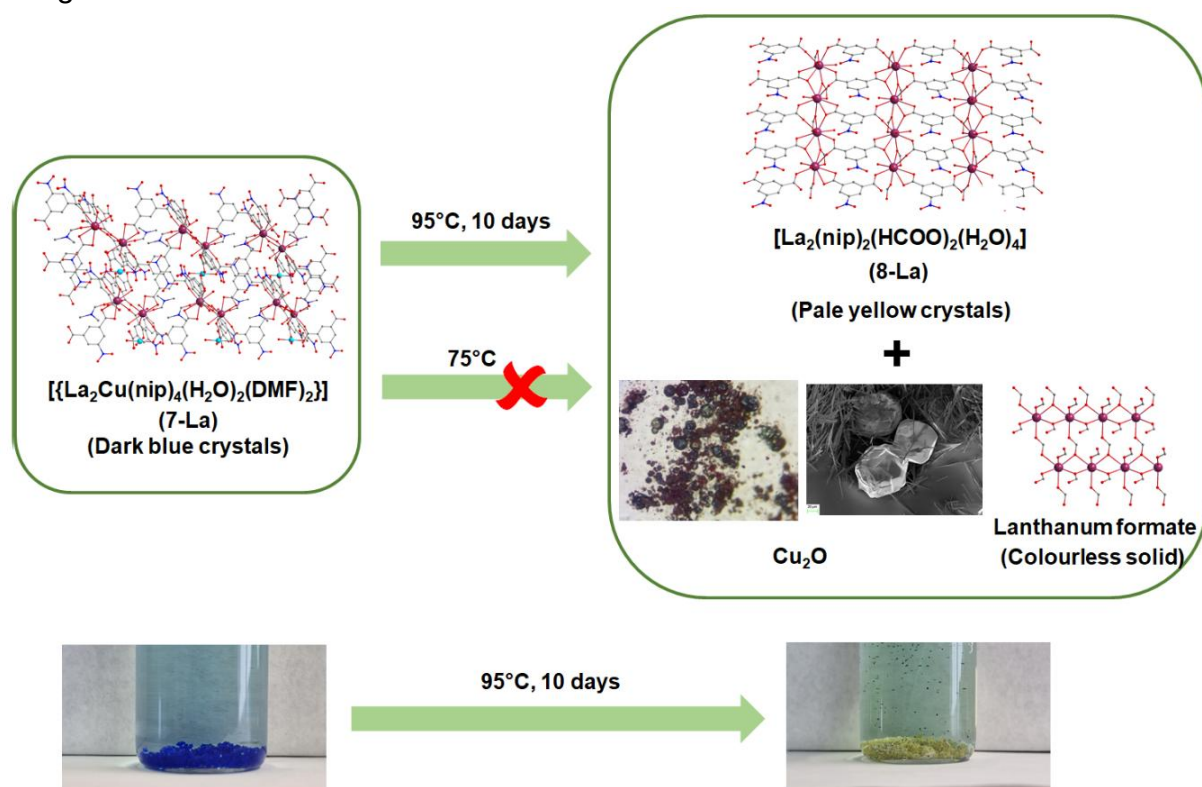


Figure 5.10. Temperature dependence of crystal transformation of **7-La** into **8-La**.

It is important to note that this structural transformation process is not observed when the reaction is performed at 75°C (Figure 5.10). The dark blue crystals and the pale blue mother liquor stays remained stable for about a month.

5.2.4.2. At Room Temperature

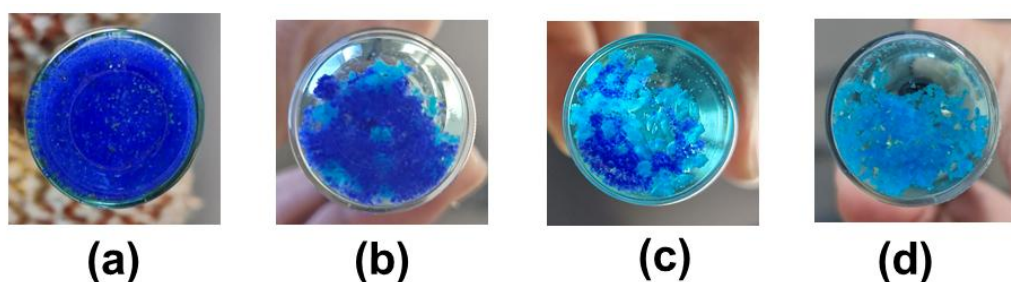


Figure 5.11. Crystal transformation from **7-La** into **9-La-A** over 2 months.

For the dark blue crystals of **7-La** obtained over 48 hours of heating, another transformation is visible when they are stored with the mother liquor at room temperature for about two months (Figure 5.11). These crystals slowly dissolve into the solution and a new crystalline phase form. The SCXRD of the new crystals revealed the structure to be $[\text{La}_4\text{Cu}_{2.35}(\text{nip})_{6.7}(\text{Hnip})_{1.3}(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_6(\text{H}_2\text{O})_{16.7}]^+ \cdot 8.3\text{H}_2\text{O}$ (**9-La-A**).

5.3. Investigation of Temperature-Induced, Solvent-Mediated Structural Transformation at 95 °C

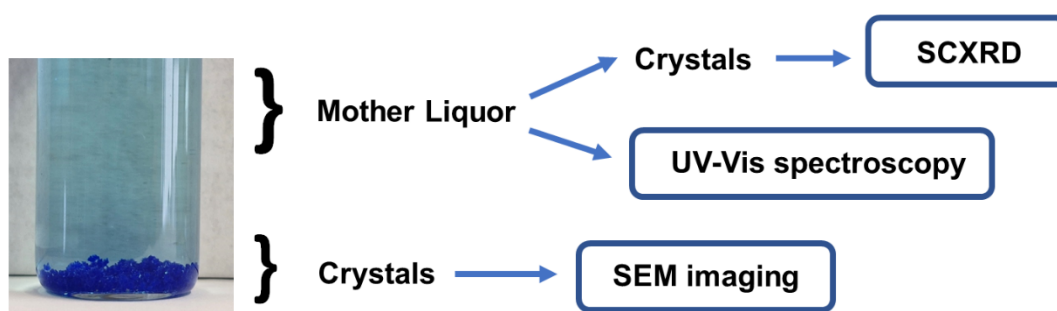


Figure 5.12. Phases analyzed during crystal transformation of **7-La** into **8-La**.

In this section the structural transformation of the heterometallic MOF **7-La** leading to homometallic MOF **8-La** at 95 °C is investigated. As a first step, the synthesis of **7-La** was performed at 95 °C in a preheated oven to avoid the formation of the side product **6-La**. The pure crystalline phase of **7-La** was obtained within 12 hours from the start of heating. The transformation process was investigated from the structural characterisations on the dark blue crystals of **7-La** and UV-Vis spectroscopy on the pale blue mother liquor. To analyse the morphological changes, solid samples (crystals) were collected at different stages and examined via SEM imaging (Figure 5.12). Additionally, the mother liquor was sampled at various time points (1 day and 3 days from the start of reaction), and crystals obtained from it through evaporation were analysed by SCXRD to identify potential intermediate compounds present during the transformation. Furthermore, UV-Vis spectra on the mother liquor were recorded before and after the complete transformation to gain insight into the changes occurring in the solution phase (Figure 5.12).

5.3.1. Investigation Using SEM Imaging

The structural transformation of **7-La** at 95 °C was monitored using SEM imaging of the crystals and solid materials obtained during the process.

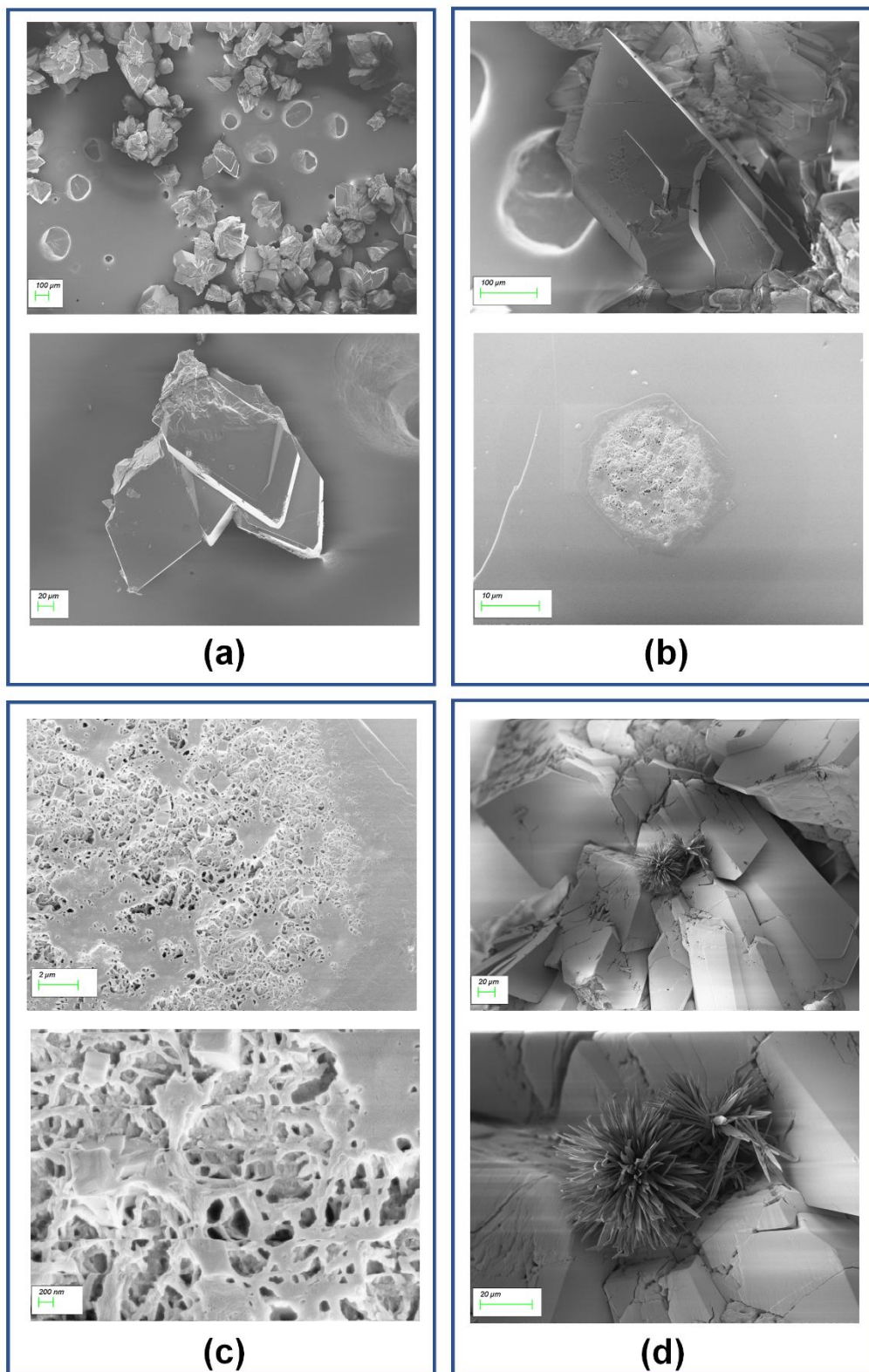


Figure 5.13. SEM images of crystals of **7-La** (bottom image is the enlarged version of top image): (a) Crystals isolated after 24 hours since the start of reaction; (b), (c) Porous surface on crystals indicating onset of transformation; (d) Crystals after 72 hours since the start of reaction indicating the formation of a new crystalline phase.

The freshly synthesized crystals of **7-La** had smooth surfaces (Figure 5.13a). After about 72 hours (3 days), the crystals surfaces began to become porous which indicate the dissolution of crystals (Figure 5.13b, c). In addition, the formation of new phases of hedgehog-like crystalline materials are also visible (Figure 5.13d).

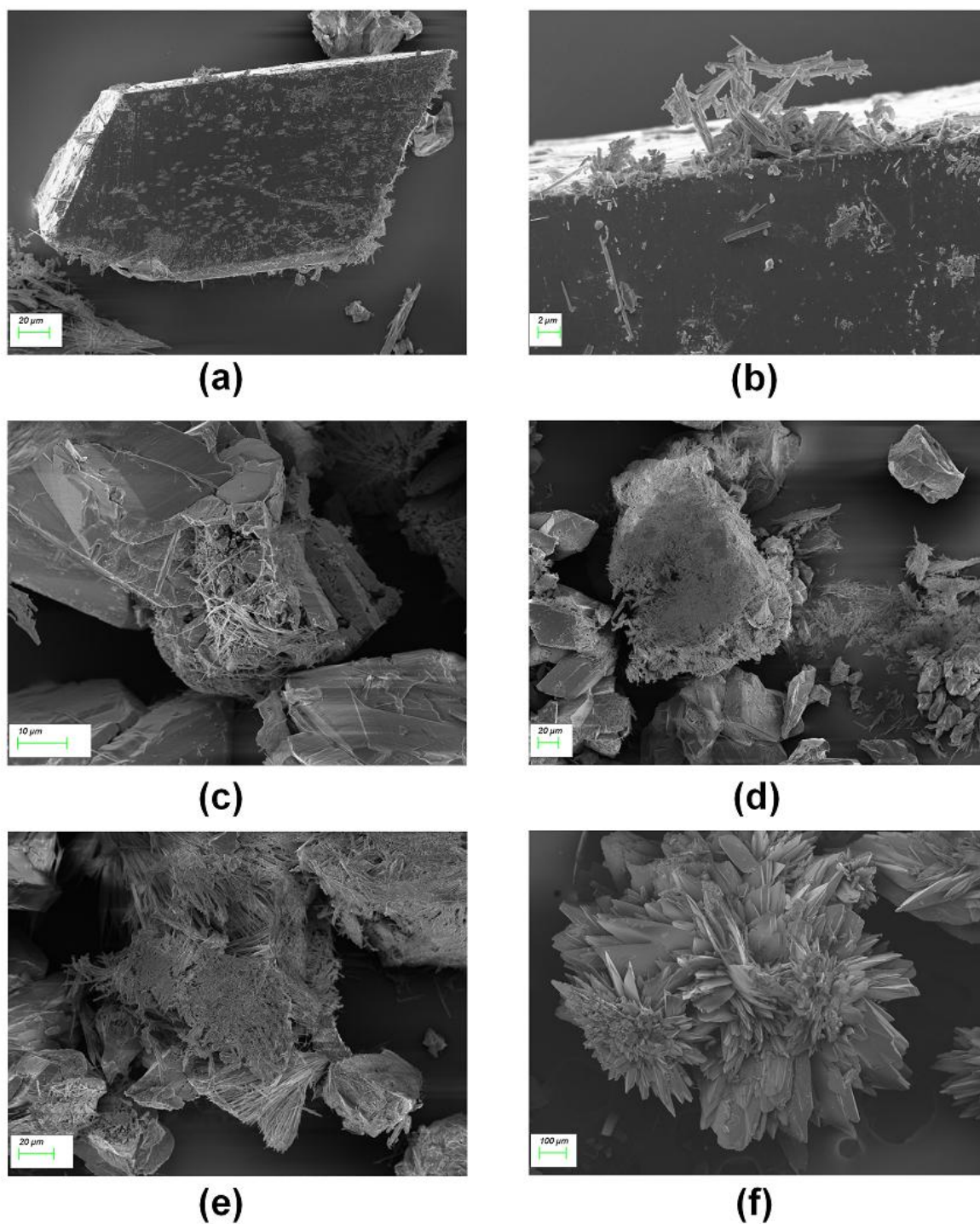


Figure 5.14. SEM images of (a), (b) Onset of transformation of crystals of **7-La**; (c) Fully transformed crystals along with transforming crystals; (d) Fully transformed crystals of **8-La**.

By the fifth day, the amount of dark blue crystals of **7-La** had decreased and a few pale-yellow crystals of **8-La** and white fibrous material had started to form on the crystal surface. The SEM images of the individual crystals clearly depict the surface dissolution of crystals leaving behind the fibrous lanthanum formate ($\text{La}(\text{HCOO})_3$) (Figure 5.14a-e). These materials and the newly formed crystals of **8-La** (Figure 5.14f) have completely different morphology from that of crystals of **7-La** (Figure 5.13a).

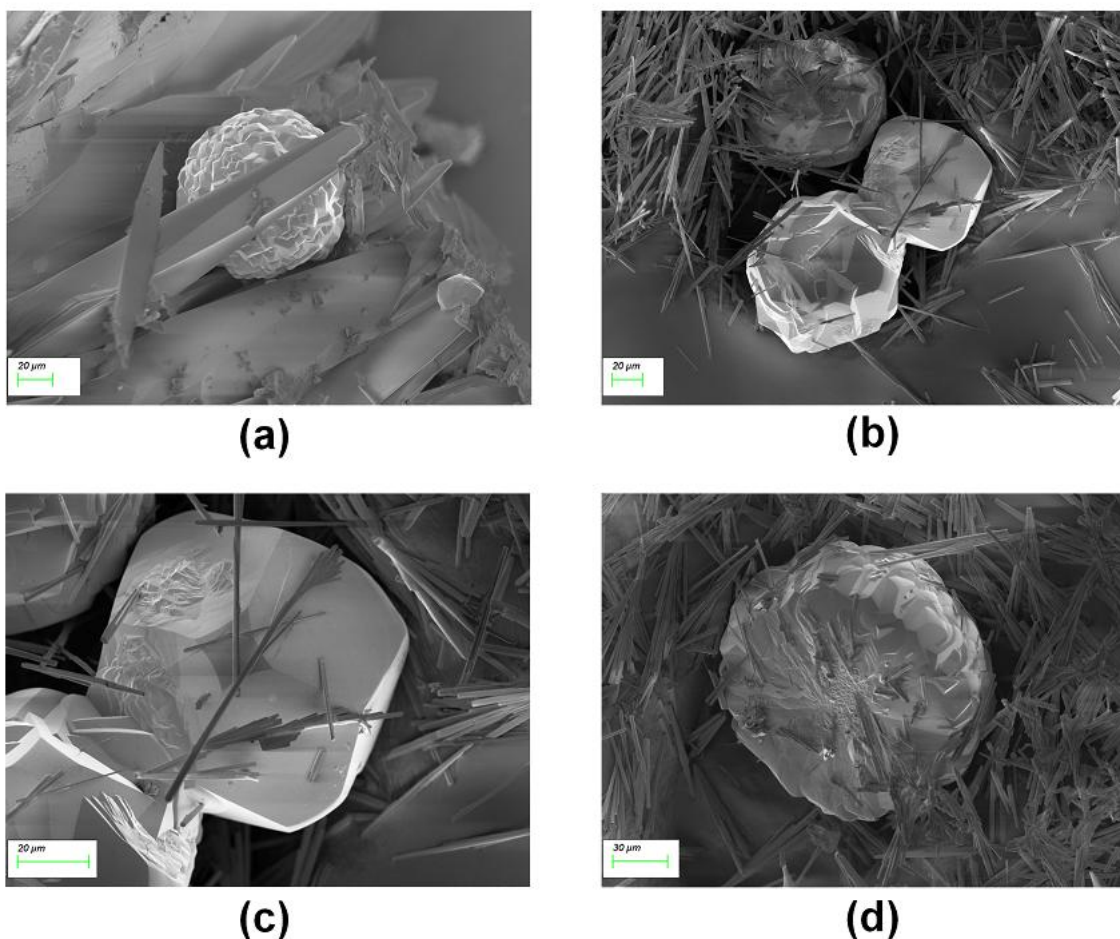


Figure 5.15. SEM images of Cu_2O particles (large globules) along with transformation products of **7-La**, lanthanum formate (fibre-like materials).

The entire transformation is accompanied by the formation of Cu_2O particles of different morphologies (Figure 5.15).

5.3.2. Investigation of Mother Liquor

From the SEM imaging studies, the fresh crystals of **7-La** obtained following the preheating method at 95 °C, showed no surface dissolution, while those collected after 3 days exhibited slight dissolution. After about 10 days, the transformation of **7-La** was complete with pale-yellow crystals of **8-La** becoming the major product. Given the

solvent-mediated nature of the transformation, it is of interest to investigate the mother liquor, i.e., the solvent in which the transformation of **7-La** happens.

Taking the above observations into account, three reaction batches (vials 1, 2, 3) were kept in a preheated oven at 95 °C. Vial 1 and 2 were removed from the oven after 1 day and 3 days respectively and the mother liquors were collected by filtration. Vial 3 remained under continuous heating for 10 days. The mother liquors isolated after filtration were kept for evaporation to observe if any crystalline materials formed (Figure 5.16).

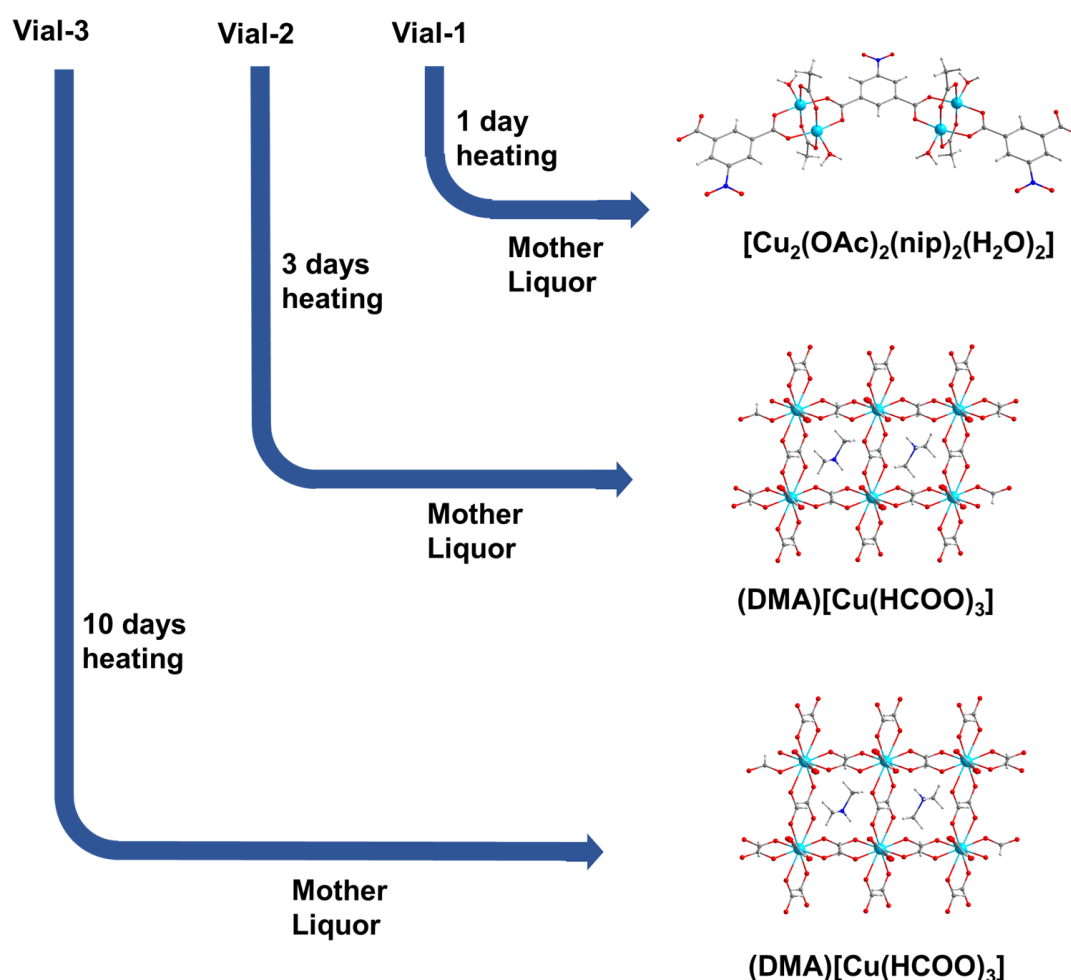


Figure 5.16. Representation of the crystal structures obtained from mother liquor after 1, 3 and 10 days of heating in oven.

The mother liquor collected after 1 day (Vial 1) was pale-blue coloured. The UV-Vis spectrum of this solution shows a strong absorption band at 770 nm, which is likely due to the Cu^{2+} ions in the solution (Figure 5.18a). Upon evaporation for several days, greenish-blue crystals of a coordination polymer $[\text{Cu}_2(\text{OAc})_2(\text{nip})_2(\text{H}_2\text{O})_2]$ were obtained.

The mother liquor collected after 3 days (Vial 2) yielded crystals of $(\text{DMA})[\text{Cu}(\text{HCOO})_3]$ ($\text{DMA}^+ = \text{dimethylammonium cation}$) (which is a different polymorph of previously known dimethylammonium copper (II) formate).^[134] This is explained by the fact that this DMA^+ and formate are well-known hydrolysis products of DMF (Figure 5.17) in the solution.^[135]

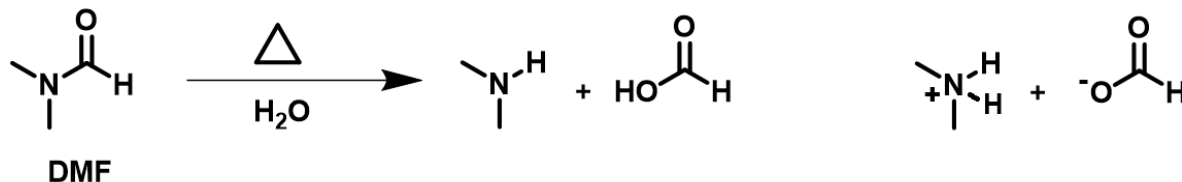
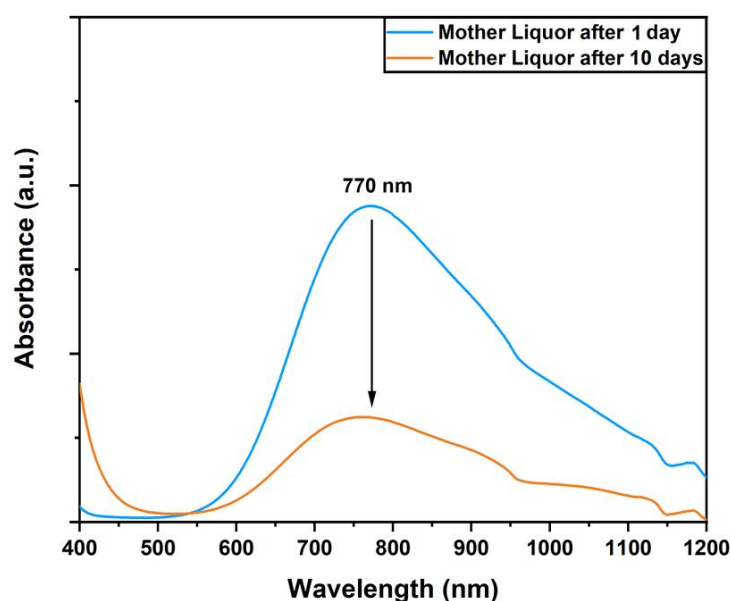
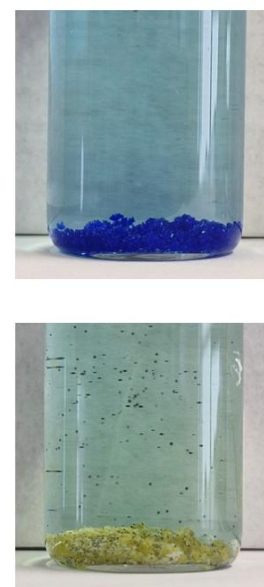


Figure 5.17. Hydrolysis of DMF.

In vial 3, it was visible that the amount of dark blue crystals of **7-La** has decreased with the increase in formation of pale-yellow crystalline phase of **8-La** after about 5 days. After about 10 days, the entire transformation from **7-La** to **8-La** is complete. These observations suggest that the hydrolysis of DMF likely drives the structural transformation from **7-La** to **8-La**. It is noted that **8-La** contains formate anions and is likely to be a thermodynamic sink.



(a)



(b)

Figure 5.18. (a) UV-Vis spectra of mother liquor collected within 1 day and 10 days since the start of reaction indicating the reduction of Cu^{2+} in solution; (b) Vials showing the crystals of **7-La** (top) and **8-La** along with Cu_2O particles on walls of the vial (bottom).

The UV-Vis spectrum of the mother liquor in vial 3 at this point indicated a decrease in Cu^{2+} concentration compared to that in vial 1, which correlated with the pale colour of the solution (Figure 5.18a). In addition, dark brown particles of Cu_2O formed as the reduction product of Cu^{2+} ions in the solution (Figure 5.18b).

5.3.3. Cu_2O Formation from the Mother Liquor

The reduction of Cu^{2+} species to Cu_2O particles during the crystal transformation of **7-La** is of interest. As mentioned earlier, Cu_2O particles were observed forming on the walls of the vial during the dissolution of **7-La** into the solution on heating. This suggests that Cu^{2+} ions in the mother liquor were being reduced to Cu_2O rather than directly from the crystal. During this process, the **7-La** crystals dissolved and Cu^{2+} ions from these were released into the solution. Formation of colourless fibre-like lanthanum formate happens in parallel.

As the amount of dark blue crystals of **7-La** decreases, the amount of pale-yellow crystals of **8-La** and Cu_2O particles increases. The UV-Vis spectra (Figure 5.18a) show a decrease in Cu^{2+} concentration, indicating that most of the Cu^{2+} ions in the solution were reduced to Cu_2O . When the solution becomes low in Cu^{2+} ion concentration, the remaining La^{3+} ions bond with the nip^{2-} and formate anions to form **8-La**. For possible explanations on how the Cu_2O particles form in solution, the redox chemistry of copper species gives some interpretation.

Copper redox chemistry has been widely studied, especially in the areas of catalysis and semiconductors. The synthetic approaches to metallic copper, various copper oxides (CuO , Cu_2O), and nanoparticles has become important because of the influence of methodology on the properties and potential application of these materials.^[136] Investigations in order to understand the redox chemistry of Cu^{2+} ions through varying several parameters like solvent, sources of Cu^{2+} ions, coordinating ligands temperature etc have been carried out. The important results of these are discussed in the following section.

The primary process that is involved during the formation of cuprous oxide (Cu_2O) is the reduction of Cu^{2+} ions, which usually involves using reducing agents. Formic acid (HCOOH) is a known reducing agent, and has been reported as a reductant in the hydrothermal synthesis of Cu_2O . This was done by the reduction of copper nitrate solution in solvent systems like DMF,^[137] $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ ^[138] etc. There are also reports

using different Cu^{2+} salts, such as copper sulphate and copper acetate, as sources of Cu^{2+} ions which produce Cu_2O under various.^[139-140] These studies demonstrate the ease of obtaining Cu_2O starting from copper (II) salts.

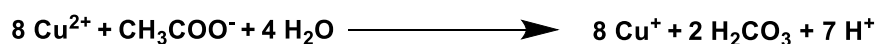
In other studies, the reduction of Cu^{2+} ions were systematically studied by varying factors such as ligand field coordination geometry. It was observed that amino compounds such as ethylenediamine (en, $\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2$) coordinated to Cu^{2+} ions, favours its reduction to $\text{Cu}(0)$ under solvothermal conditions. This process was shown to be driven by a ligand to metal charge transfer (LMCT) through the chelating en ligand.^[141] Considering the chelate effect of ligands, another hydrothermal approach using N, O-type organic chelates has shown the reduction of Cu^{2+} ions to produce $\text{Cu}_2\text{O}/\text{CuO}$ nanoparticles.^[142]

Based on the above examples, the chemistry of Cu_2O formation during the solvent-mediated structural transformation at 95 °C in the Cu- H_2nip -La system in water-DMF solvent system can be explained. In general, the formation of cuprous oxide (Cu_2O) involves the reduction of Cu^{2+} ions to Cu^+ ions in a reducing environment.

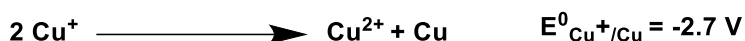
As previously described, during the initial phases of reaction (1-2 days since heating started) greenish-blue crystals of $[\text{Cu}_2(\text{OAc})_2(\text{nip})_2(\text{H}_2\text{O})_2]$ could be isolated from the mother liquor, and after about four days, blue crystals of $(\text{DMA})[\text{Cu}(\text{HCOO})_3]$ were obtained. This indicate the hydrolysis of DMF forming dimethylamine and formic acid and this is also when the dissolution of **7-La** and formation of lanthanum formate and reddish-brown particles of Cu_2O are observed.

The Cu^{2+} ions in the solution interact with acetic acid or acetate ions (AcO^- ions), dimethylamine and formic acid (HCOOH). The pH of the mother liquor at this point was around 6. The reduction of Cu^{2+} into Cu^+ can take place in two pathways:

(a) Reduction of Cu^{2+} by acetate ions



Once the Cu^{2+} ions are reduced to Cu^+ ions by the AcO^- ions, several redox reactions are possible in solution. The Cu^+ ions can form $\text{Cu}(\text{OH})$, which decomposes to Cu_2O , or further reduces to metallic copper (Cu). Alternatively, a disproportionation reaction could occur, where Cu^+ ions are simultaneously oxidized to Cu^{2+} and reduced to metallic Cu .^[140]

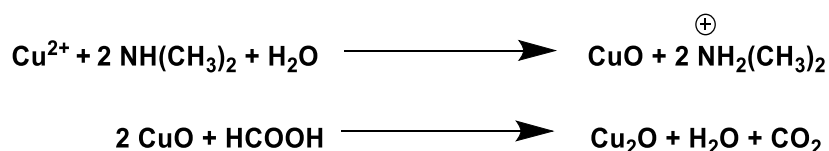


According to the reference^[140], a mixture of Cu and Cu₂O will be obtained under either highly acidic or highly basic conditions whereas pure Cu₂O forms at approximately neutral pH.

In the reaction mixture studied here, the presence of dimethylammonium cations in solution is likely helping to maintain the pH and prevent reduction and disproportionation of Cu⁺ ions in the solution.

(b) Reduction of Cu²⁺ by formate ions

As mentioned in the reference^[137], dimethylamine (NH(CH₃)₂) and formic acid (HCOOH) formed from the hydrolysis of DMF may be responsible for the reduction of Cu²⁺ ions to Cu⁺ ions.



The PXRD pattern of the brown particles showed reflections corresponding only to Cu₂O with no trace of metallic Cu or CuO particles. This confirms that the reduction of Cu²⁺ ions by acetate or formate ions in solution results in the formation of Cu₂O. The formation of Cu₂O in the Cu-H₂nip-La system in water-DMF mixture is observed at 95 °C whereas this typically requires elevated temperatures (around 150 °C or more) for the formation of copper oxides.

For the entire crystal transformation process, the hydrolysis of DMF at 95 °C serves as the driving force. Prolonged heating of DMF-water mixture leads to the formation of dimethylamine and formic acid which participate in the chemical reactions responsible for the dissolution of **7-La** and formation of **8-La**. This also explains why this process is slower at 75 °C, where the rate of hydrolysis of DMF is lower.

5.4. Effect of Addition of Extra Ligand

The reaction in the Cu-H₂nip-La in H₂O/DMF solvent system discussed here followed a reagent ratio of Cu(OAc)₂·H₂O : H₂nip : La(NO₃)₃ = 1 : 1: 1.5, i.e, 1.5 equivalents of La(NO₃)₃ were added to the Cu-H₂nip metallogel (1:1) before the addition of DMF.

As explained in the previous Chapter 4, the stoichiometry of the reagents can affect the structure of the products in a reaction. For example, with the case of Cu-H₂nip-La in H₂O system, after the addition of La(NO₃)₃, for various equivalents of extra H₂nip ligand, heterometallic MOFs based on Cu²⁺ and La³⁺ with different topologies were obtained. A similar procedure was considered here also with the extra addition of H₂nip to this system (1, 2 eq. H₂nip). However, adding extra amounts of H₂nip made no difference to the nature of the end product.

Table 5.2. Stoichiometries of the starting materials including the extra added H₂nip ligand.

Trial	Equivalent of Cu(OAc) ₂ ·H ₂ O	Equivalent of H ₂ nip	Equivalent of La(NO ₃) ₃	Equivalent of H ₂ nip	Observation
1	1	1	1.5	0	Dark blue crystals of 7-La
2	1	1	1.5	1	Dark blue crystals of 7-La
3	1	1	1.5	2	Dark blue crystals of 7-La

As shown in Table 5.2, the addition of further equivalents of H₂nip also yielded dark blue crystals of [La₂Cu(nip)₄(DMF)₂(H₂O)₂] (**7-La**), as was the case without the addition, however, the yield of the crystals got better. Another interesting observation is that the stability of the crystals of **7-La** in the reaction mixture improved and the dark blue crystals remained with no formation of Cu₂O or other phases being observed during heating. This is probably due to consumption of unreacted Cu²⁺ ions (and La³⁺ ions) in the solution with the H₂nip added in excess. In particular, for the case where 2 equivalents of H₂nip were added (Trial 3 in the Table 5.2), the crystals remained without decomposition for more than 3 weeks.

Similarly, the reaction performed at 75 °C with this molar ratio of Cu(OAc)₂·H₂O : H₂nip : La(NO₃)₃ : H₂nip = 1 : 1: 1.5 : 2 showed that the crystals remained stable over a period of one month under the heating condition. Hence this molar ratio was also used for future comparative studies with other lanthanide ions.

The dark blue crystals of **7-La** obtained with the new molar ratio $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{La}(\text{NO}_3)_3 : \text{H}_2\text{nip} = 1 : 1 : 1.5 : 2$ were stored with the mother liquor at room temperature for about two months. These crystals undergo a transformation into dichroic greenish-blue crystals, instead of the blue crystals as for the older ratio $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{La}(\text{NO}_3)_3 = 1 : 1 : 1.5$ (section 5.2.4.2). The SCXRD of the new crystals (**9-La-B**) revealed that these were isostructural with **9-La-A** despite the colour difference.

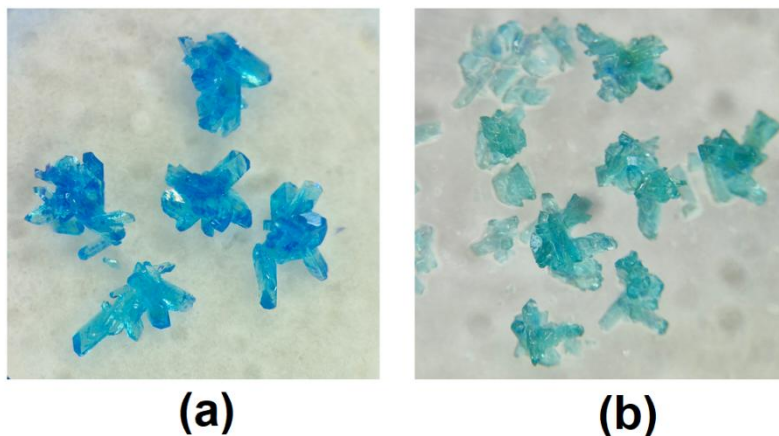


Figure 5.19. (a) Blue crystals of **9-La-A** and (b) greenish blue crystals of **9-La-B**.

5.5. Cu-H₂nip-Ln in H₂O/DMF Solvent System

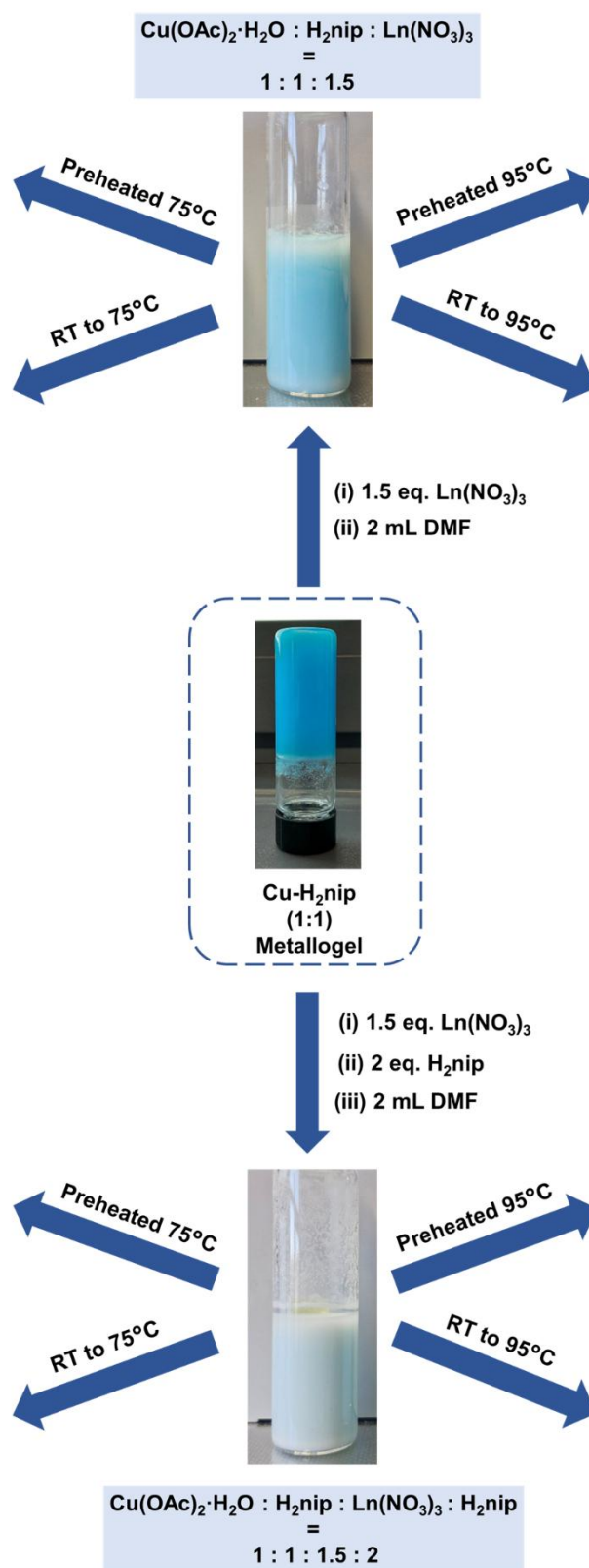


Figure 5.20. Metalloligand approach using Cu-H₂nip metallogel to incorporate Ln³⁺ ions in H₂O/DMF solvent system.

In the previous sections, the synthesis of HMOF $[\text{La}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$ (**7-La**) and its structural transformation to homometallic MOF $[\text{La}(\text{nip})(\text{HCOO})(\text{H}_2\text{O})]$ (**8-La**) was investigated. Similar studies were carried out for different lanthanide (Ln^{3+}) ions. Reagent ratios of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3 = 1 : 1 : 1.5$ and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3 : \text{H}_2\text{nip} = 1 : 1 : 1.5 : 2$ were followed here. Experiments were conducted at 95 °C and 75 °C either with heating starting from room temperature to 95 °C (or 75 °C) or directly heating at 95 °C (or 75 °C) in a preheated oven over 10-14 days (Figure 5.20). The reactions are registered as complete when the blue precipitate (and or any solid materials) is used up and the crystallisation of dark blue crystals via Ostwald ripening has happened (Figure 5.21).

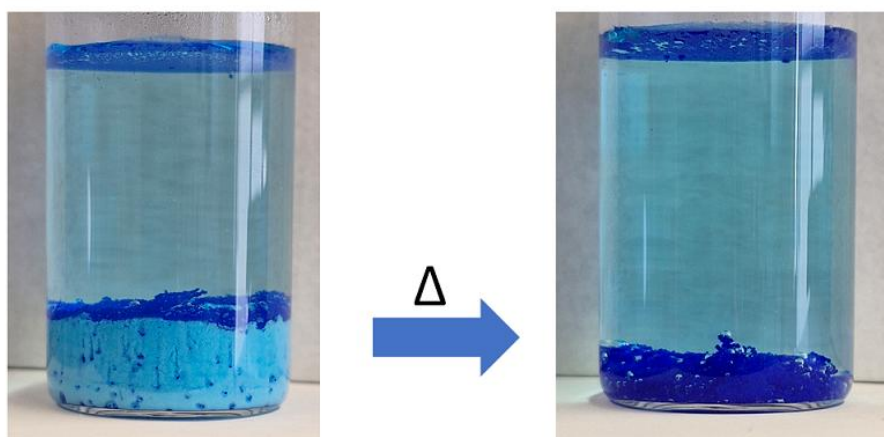


Figure 5.21. Crystallisation of dark blue crystals from blue precipitate.

5.5.1. Structural Transformation at 95 °C and 75 °C

5.5.1.1. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3$ ratio of 1 : 1 : 1.5

- **Reactions at 95 °C**

Similar to the La^{3+} -analogue, the reactions which were first performed in a preheated oven at 95 °C by following the reagent ratio $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3$ of 1 : 1 : 1.5. Dark blue crystals of $[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$ (**7-Ln**), for $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$ and Y^{3+} were obtained here. The crystallisation from blue precipitate took from 1 to 4 days to complete. The remaining lanthanides did not yield any crystals (Figure 5.22).

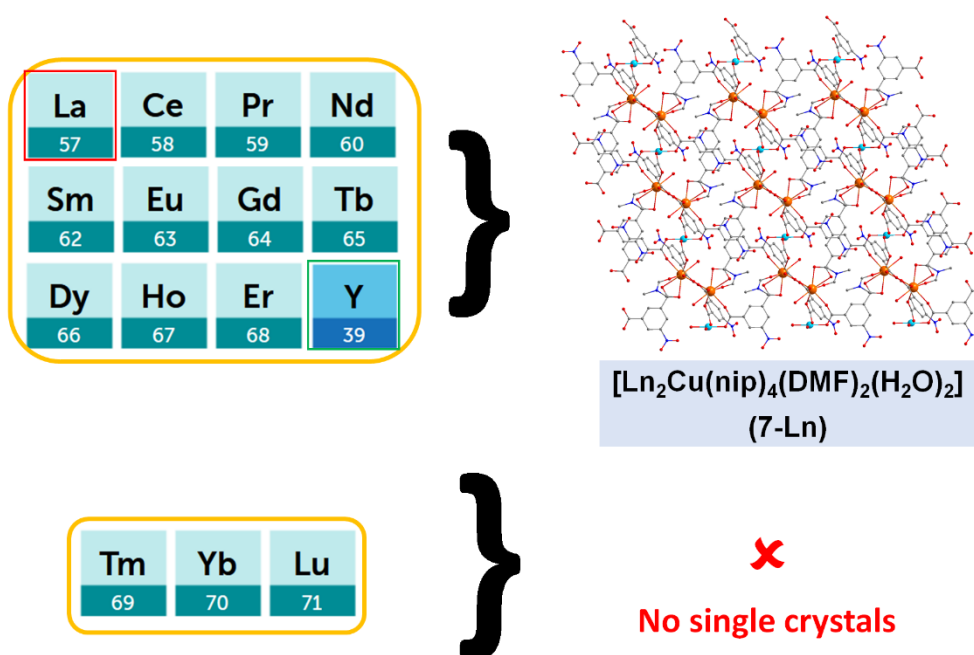


Figure 5.22. Representation of crystals structure obtained for Cu-H₂nip-Ln system in H₂O/DMF solvent for various Ln³⁺ ions.

After the formation of crystals of **7-Ln** was complete, the reaction mixture was continued to heat at 95 °C further for about two weeks. A solvent-mediated structural transformation was observed in **7-Ln** for Ln³⁺ = Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺ and Gd³⁺. The dark blue crystals of **7-Ln** dissolved and colourless crystals of [Ln₂(OAc)₂(nip)₂(H₂O)₂] $\cdot$ xH₂O (**3-Ln**) started to form simultaneously within a week. The formation of reddish brown Cu₂O was also observed here. The hydrolysis of DMF could be a driving force for the structural transformation in **7-Ln**, as explained for **7-La**. However, the final products after the transformation [Ln₂(OAc)₂(nip)₂(H₂O)₂] $\cdot$ xH₂O (**3-Ln**) and [La(nip)(HCOO)(H₂O)] (**8-La**) differ in the structure, in particular with the absence or presence of the formate ions (a hydrolysis product of DMF) in the crystal structure.

For a similar duration of heating, the dark blue crystals of **7-Ln**, for Ln³⁺ = Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Y³⁺ remained stable without dissolving and the formation of any colourless crystals was not observed (Figure 5.23). Here, some globular amorphous material was formed after about 4 weeks.

When the reactions were repeated by heating from room temperature to 95 °C, a similar crystallisation process was observed. However, the initial crystallisation of **7-Ln** from the precipitate took longer time for heavier lanthanides.

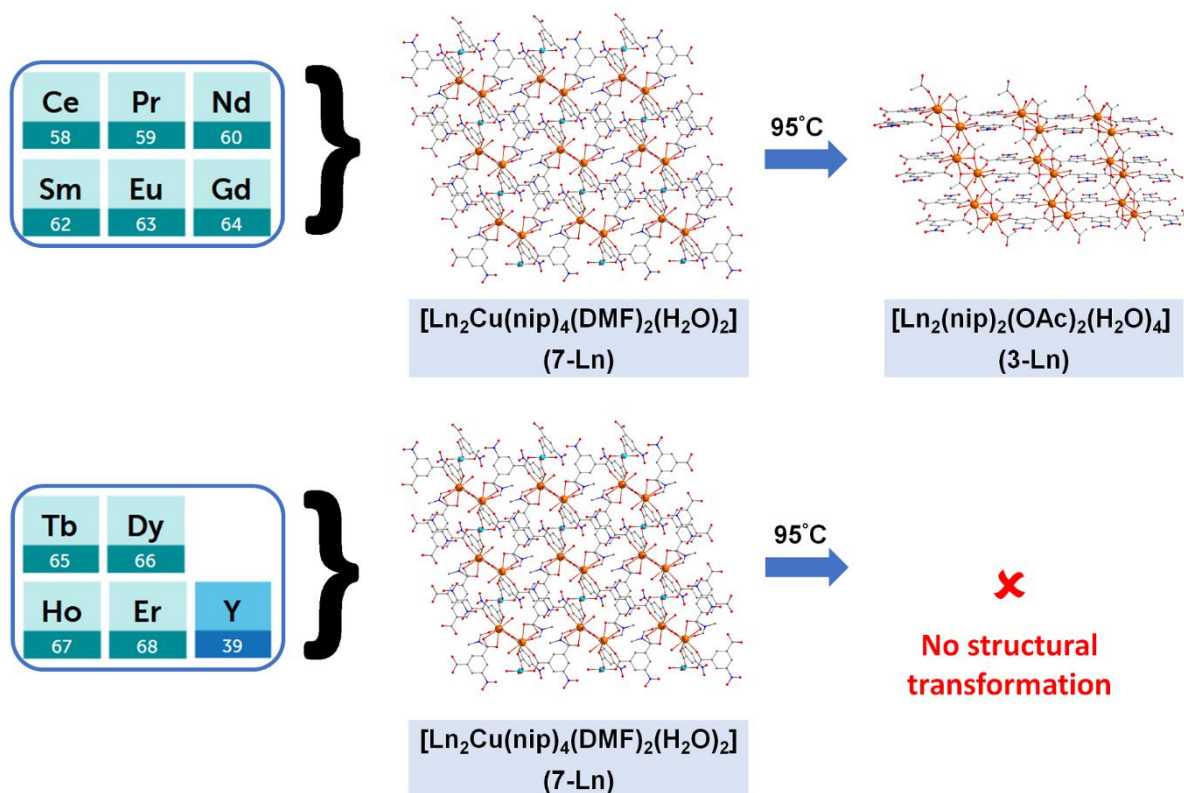


Figure 5.23. Representation of crystals structure obtained by the structural transformation of 7-Ln into 3-Ln at 95 °C.

- **Reactions at 75 °C**

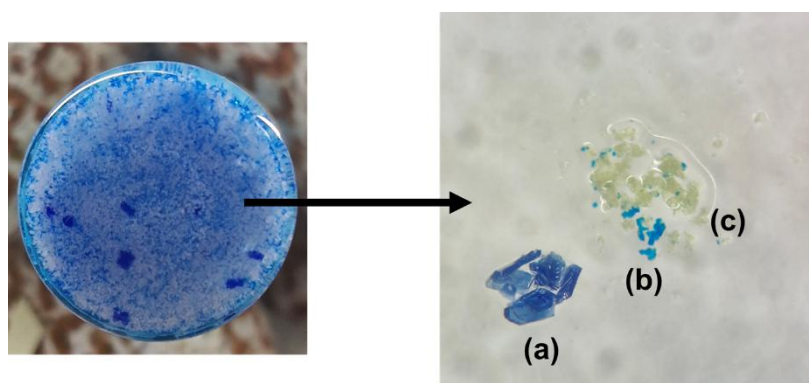


Figure 5.24. Reaction vial and the crystalline mixture obtained during the synthesis of 7-Er. The crystals are identified as (a) 7-Er (dark blue); (b) 11-Er (blue); (c) 10-Er (colourless) viewed under optical microscope.

When the reaction mixtures were heated in a preheated 75 °C oven, dark blue crystals of 7-Ln were obtained within 24 hours for $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$ and Gd^{3+} . A mixture of dark blue crystals of 7-Ln, blue crystals and colourless crystals were obtained for $\text{Ln}^{3+} = \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$. In particular for $\text{Ln}^{3+} = \text{Er}^{3+}$, the blue crystals

that were isolated here were found to be a three-dimensional porous MOF, $[\text{Cu}_4\text{Er}_3(\text{nip})_8(\text{DMF})_4(\text{H}_2\text{O})_8] \cdot 11\text{DMF}$ (**11-Er**) and the colourless crystals were found to be $[\text{Er}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ (**10-Er**) (Figure 5.24).

When the reaction mixtures were heated from room temperature to 75 °C, it was observed that for heavier lanthanides ($\text{Ln}^{3+} = \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$), the yields of blue crystals (**11-Ln**) and colourless crystals (**10-Ln**) were higher. Nevertheless, in each case these products eventually dissolved over the period of two weeks. At the same time, the quantity of crystals of **7-Ln** became more and later was the only product in the reaction vial.

The prolonged heating of **7-Ln** at 75 °C did not result in the formation of any colourless crystals of **3-Ln** until about 3 weeks. However, after about a month of heating, decomposition of the dark blue crystals of **7-Ln** were observed.

5.5.1.2. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3$ of 1 : 1 : 1.5 : 2

- **Reaction at 95 °C**

For both pre-heated and room temperature to 95 °C heating conditions, the dark blue crystals of **7-Ln** were predominantly obtained. For $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$, the dark blue crystals were obtained within 24-48 hours, while for the rest, it took about 72-96 hours for completion of crystallisation from precipitate.

- **Reaction at 75 °C**

When the reactions were performed at 75 °C, the dark blue crystals of **7-Ln** were obtained within 2 days for $\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$. A mixture of dark blue crystals of **7-Ln**, blue crystals and colourless crystals (Figure 5.25) were obtained within 2 days for heavier lanthanides like $\text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$. When $\text{Ln}^{3+} = \text{Er}^{3+}$, two different blue crystals **11-Er** and **12-Er** were identified along with the dark blue crystals **7-Er** and colourless crystals **10-Er**. Both blue crystals that were isolated here were found to be three-dimensional porous MOFs with different topologies.

As in the case of **12-Er**, isomorphous crystals of compounds **12-Dy** and **12-Ho** were also obtained for corresponding reactions.

During the prolonged heating of **7-Ln** prepared both at 95 °C and 75 °C, the crystals remained stable for about 2-3 weeks.

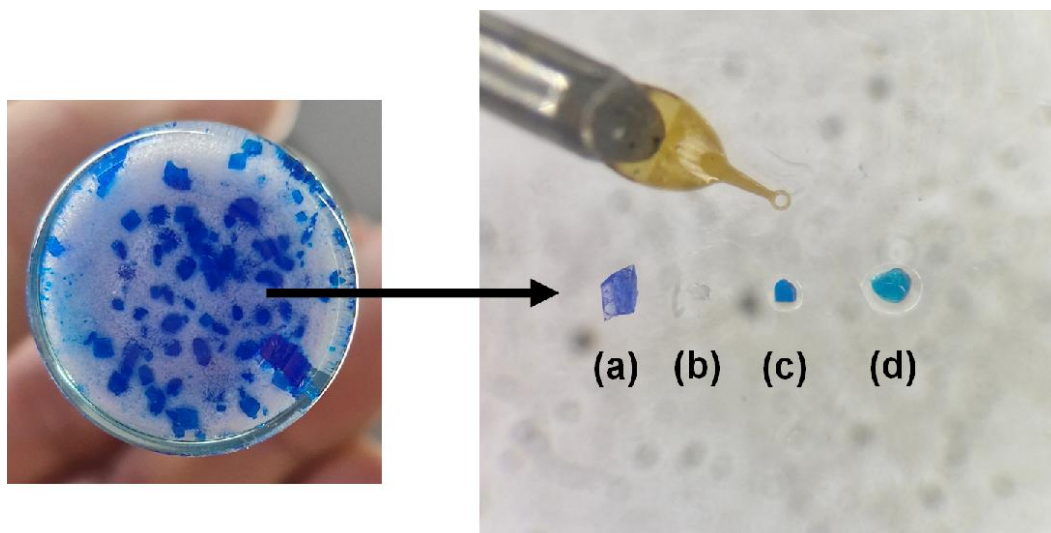


Figure 5.25. Reaction vial showing a crystalline mixture during the synthesis of **7-Er** (left). The crystals identified as (a) **7-Er** (dark blue); (b) **10-Er** (colourless); (c) **11-Er**; (d) **12-Er** viewed under optical microscope (right). Crystal mount and microloop of aperture size 100 μm also shown for size comparison.

5.5.2. Structural Transformation at Room Temperature

Unlike the transformation observed for **7-La** into **9-La** at room temperature, no similar transformation was observed for other lanthanide analogues (**7-Ln**).

5.6. Characterizations of New MOFs

5.6.1. Crystallography

Crystal Structure Description of $[\text{La}_4\text{Cu}_6(\text{nip})_{12}(\text{DMF})_2(\text{H}_2\text{O})_{10}] \cdot 2\text{DMF} \cdot 6\text{H}_2\text{O}$ (6-La)

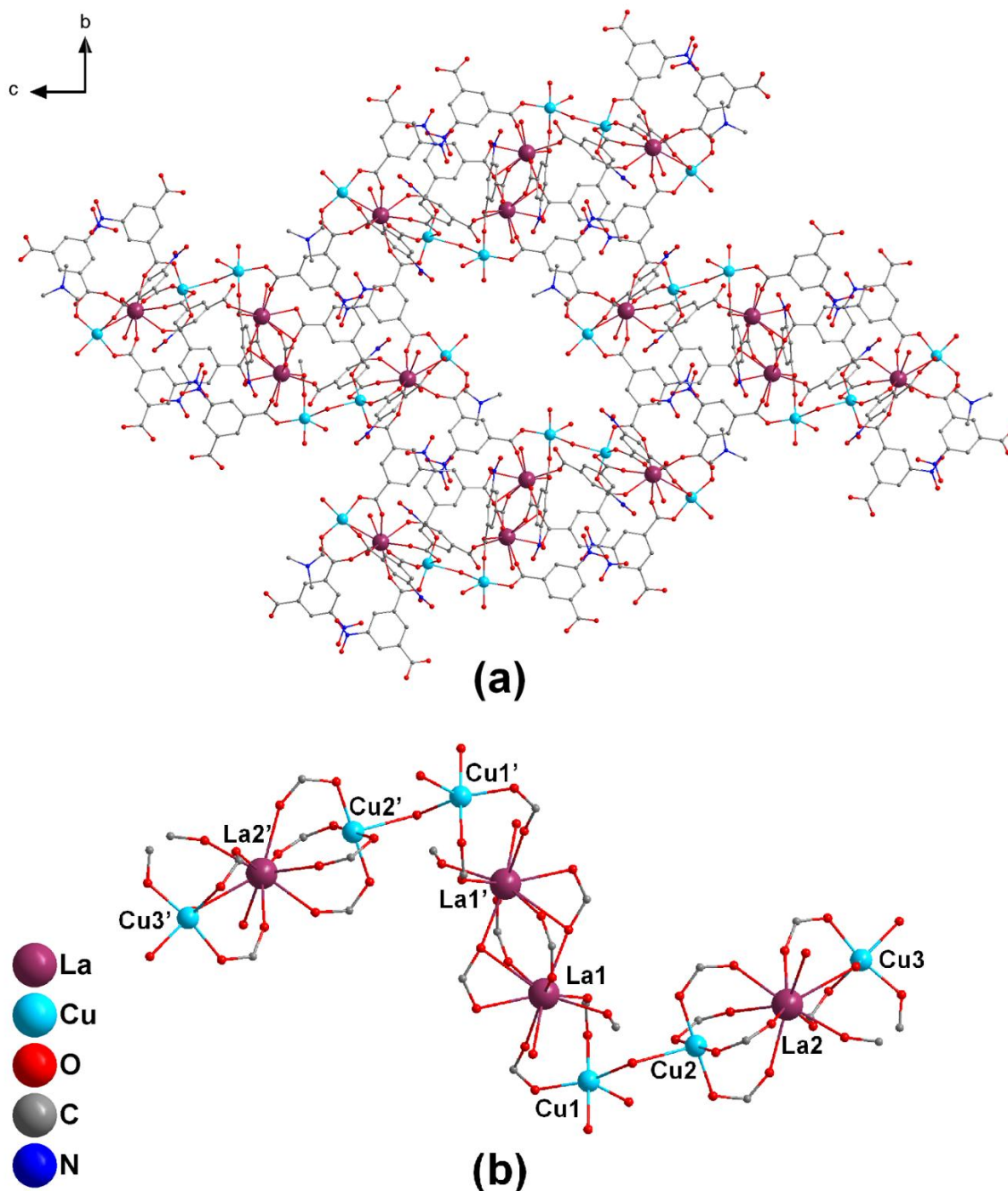


Figure 5.26. (a) Single-crystal X-ray structure of **6-La** indicating the La_4Cu_6 core along with nip^{2-} ligands, coordinated DMF and water ligands; (b) Simplified view of the La_4Cu_6 core (disordered atoms with lower occupancy has been removed for clarity).

The SCXRD analysis revealed that **6-La** crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains two La^{3+} ions (La1, La2), three crystallographically independent Cu^{2+} ions (Cu1, Cu2 and Cu3), six nip^{2-} ligands, two DMF (one coordinated to Cu3 and other as lattice solvent). In addition, twelve coordinated water molecules, out of which eight are ordered (two on Cu1, one on La1, one between Cu1 and Cu2, one on Cu3) and two are disordered (one on each of the La2 and Cu3 as shown in Figure 5.27).

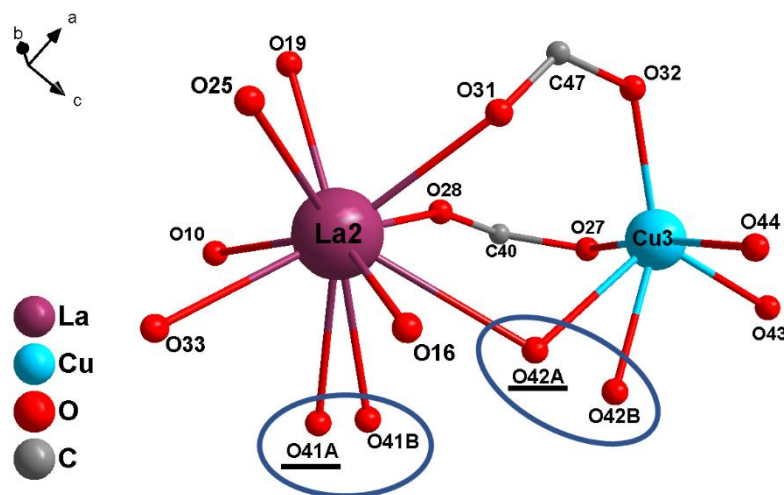


Figure 5.27. Disordered oxygen atoms O41A and O41B on La2 and O42A and O42B on Cu3 in **6-La**. Underlined oxygen atoms have major occupancy.

The disordered oxygen on La2, O41A, O41B have occupancies of 0.75 and 0.25 respectively, while the disordered oxygen on Cu3, O42A, O42B have occupancies of 0.75 and 0.25 respectively. Here, the water oxygen O42A bridges La2 and Cu3. Among the disordered oxygen atoms, only those with higher occupancy are considered in the later discussions for clarity.

Table 5.3. Distances between metal atoms and corresponding coordinated disordered oxygen atoms.

Distances				
La2-O41A	La2-O41B	La2-O42A	Cu3-O42A	Cu3-O42B
2.61 Å	2.50 Å	2.86 Å	2.22 Å	2.08 Å

The crystal structure of **6-La** shows a 3D network with two distinct building units, one of which has a central La_2Cu_2 unit which is attached to two Cu_2La units of either side in an anti-anti fashion through the nip^{2-} ligands and water (Figure 5.26a). Thus, the La_4Cu_6 units can be considered as secondary building units (SBUs), consisting of (CuLaCu) -

(CuLaLaCu)-(CuLaCu) units (Figure 5.26b). An inversion centre can be placed at the centre of the line connecting La1 and La1'.

The central La₂Cu₂ unit is made up of two symmetrically equivalent lanthanum ions (La1 and La1') which are 9-coordinated and two symmetric equivalent copper ions (Cu1 and Cu1') which are 5-coordinated. The distances La1-La1', La1-Cu1' and Cu1-Cu1' are 4.26 Å, 4.48 Å and 12.8 Å respectively. The Cu₂La units, (which is *anti* to the central La₂Cu₂ unit) contains a 9-coordinated lanthanum ion La2 and two crystallographically independent copper ions: Cu2 which is 4-coordinated and Cu3 which is 5-coordinated. The Cu3 has a coordinated DMF.

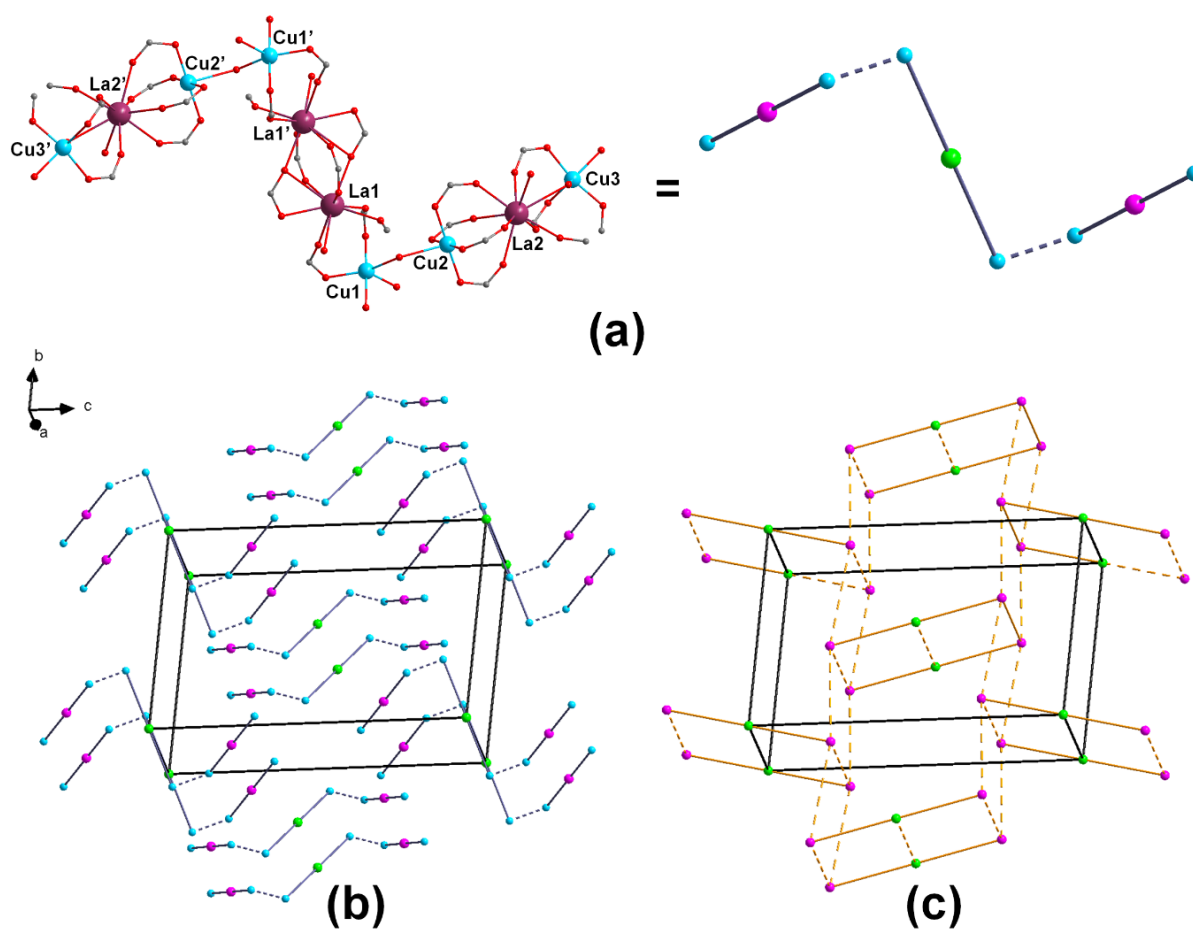


Figure 5.28. (a) Simplified representation of the La₄Cu₆ core unit in **6-La**. The three-dimensional packing of core units in a unit cell is shown (a) with Cu atoms and (b) without Cu atoms. Pink spheres represent the centre of mass of (CuLaCu) unit formed by Cu3, La2, Cu2 atoms and green spheres represent the centre of mass of (CuLaLaCu) unit formed by Cu1 and La1 atoms.

The complex 3D structure of compound **6-La** (Figure 5.28) is associated with a La_4Cu_6 units which are coordinated by six pairs of nip^{2-} ligands in different coordination modes. Considering the central La_2Cu_2 unit, there are two pairs of symmetrically equivalent nip^{2-} ligands that bridge the two La1 (as shown in Figure 5.29a and b).

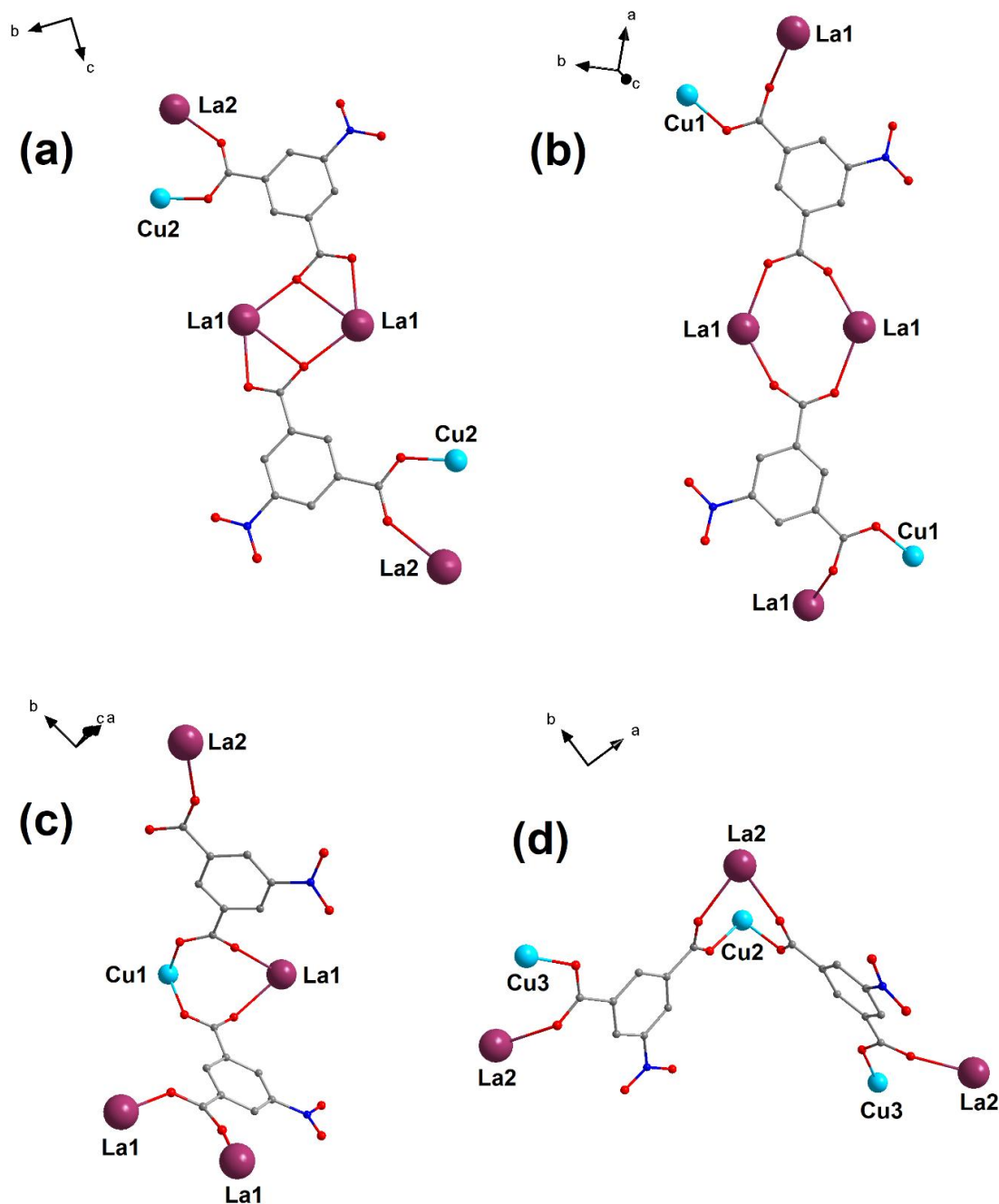


Figure 5.29. Various coordination modes of nip^{2-} ligands associated with a La_4Cu_6 unit in **6-La**.

In the first pair, one of the carboxylate groups bridges the two La1 in a tridentate $\kappa^2\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn, anti*) fashion and the other links to La2 and Cu2 of the two Cu_2La units with bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (*syn, syn*) coordination (Figure 5.29a). For the second pair of the

ligands, a carboxylate group connects the two La1 with bidendate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (syn, syn) coordination and the other carboxylate group connects to La1 and Cu1 of another La₂Cu₂ unit with similar coordination, as shown in Figure 5.29.b. The remaining sets (four) of the nip²⁻ ligands connect the metal ions in such a way that its symmetric equivalent is not bridging the same set of metal ions, in bidendate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (syn, syn) or monodendate $\kappa^1\text{-}\kappa^0\text{-}\mu_1$) fashion, as shown in Figure 5.29c and d.

The geometries of each La³⁺ ions and Cu²⁺ ions in **6-La** (Figure 5.30) were analyzed by continuous shape measures (CShM).^[105-106] Both La1 and La2 exhibit distorted nine-coordinated geometries with capped square antiprism geometry (CSAPR-9, C_{4v}) (CShM = 2.08 for La1, CShM = 0.65 for La2). Cu1 and Cu3 are penta-coordinated with a trigonal bipyramid geometry (TBPY-5). Cu2 is also penta-coordinated and has a geometry closer to vacant octahedron (vOC-5) (Table 5.4).

Table 5.4. Continuous shape measures (CShM) values for Cu1, Cu2 and Cu3 in **6-La**. The lowest value is marked in bold.

Compound	Atom	Shape	Ideal Value	Continuous Shape Measurements (CShM)
6-La	Cu1	vOC-5 Vacant octahedron	0	3.33
		TBPY-5 Trigonal bipyramid	0	2.56
		SPY-5 Spherical square pyramid	0	2.84
	Cu2	vOC-5 Vacant octahedron	0	1.20
		TBPY-5 Trigonal bipyramid	0	6.43
		SPY-5 Spherical square pyramid	0	1.26
	Cu3	vOC-5 Vacant octahedron	0	6.50
		TBPY-5 Trigonal bipyramid	0	0.50
		SPY-5 Spherical square pyramid	0	4.13

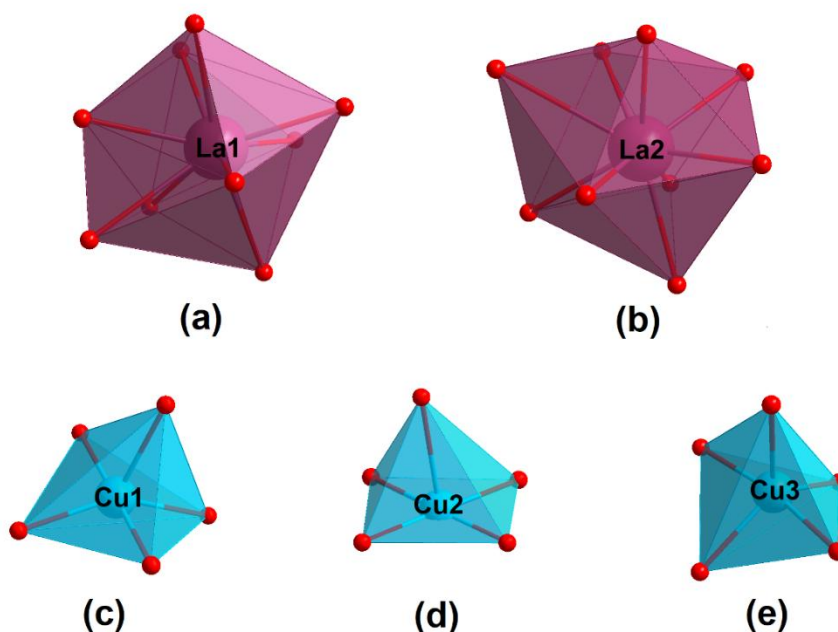


Figure 5.30. Coordination polyhedral representation for La1, La2, Cu1, Cu2 and Cu3 in **6-La**.

Crystal Structure Description of $[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$ (7-Ln**, $\text{Ln}^{3+} = \text{La}^{3+}$, Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Y^{3+})**

The single-crystal X-ray analysis reveals that compound **7-Ln** crystallizes in the triclinic space group $P\bar{1}$. Since all the lanthanide variants are crystallographically same, the general structural features of the La^{3+} - version (**7-La**) is discussed here. The detailed structural characteristics of other analogues will be discussed later.

The asymmetric unit of **7-La** contains $1/2 \text{ Cu}^{2+}$, 1 La^{3+} and 2 nip^{2-} ligands, 1 water and 1 DMF (both attached on La^{3+}). The three-dimensional network structure is formed from 8-coordinated La^{3+} ions and 4-coordinated square planar Cu^{2+} ions which lie on one of the inversion centres (Figure 5.31). Another inversion centre lies at the middle of the line joining two La^{3+} ions. The carboxylate groups of nip^{2-} ligand bridges or chelates the metal ions via bidentate $\kappa^1\text{-}\kappa^1\text{-}\mu_2$ (syn, syn) coordination mode.

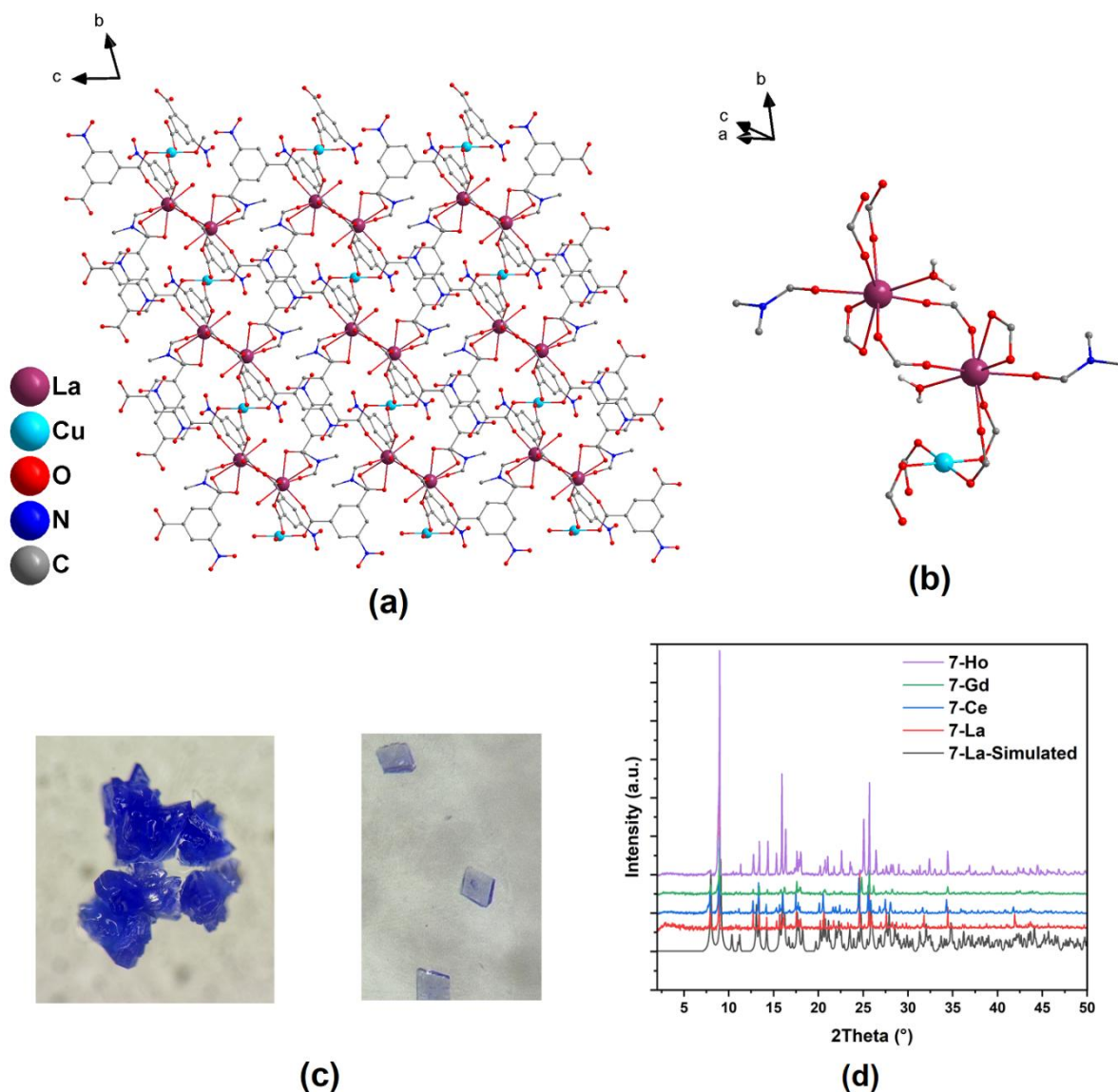


Figure 5.31. (a) Three-dimensional network structure of **7-La** (Hydrogen atoms and lattice solvent omitted for clarity); (b) Simplified view of the La_2Cu core; (c) Dark blue crystals of **7-La**, (d) PXRD of selected examples of **7-Ln** ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Gd}^{3+}$ and Ho^{3+}).

This compound is structurally similar to heterometallic Ln–Cu coordination polymers $[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$, (**4-Ln**) ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}$ and Er^{3+}) as previously described for reference.^[103] In those compounds, there were two water molecules coordinated on each Ln^{3+} ions, whereas in **7-La** (and the remaining **7-Ln**) a DMF and a water molecule are coordinated. Furthermore, analogues for $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}$ were not reported.

The continuous shape measures (CShM)^[105-106] on the 8-coordinated La³⁺ describes it as a biaugmented trigonal prism (BTP, C_{2v} : CShM = 2.70). Coordination number of 8 for early lanthanides is not so common.

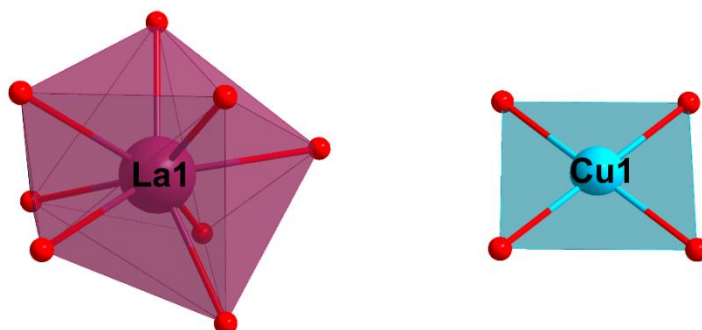


Figure 5.32. Coordination polyhedral representation for La1 and Cu1 in 7-La.

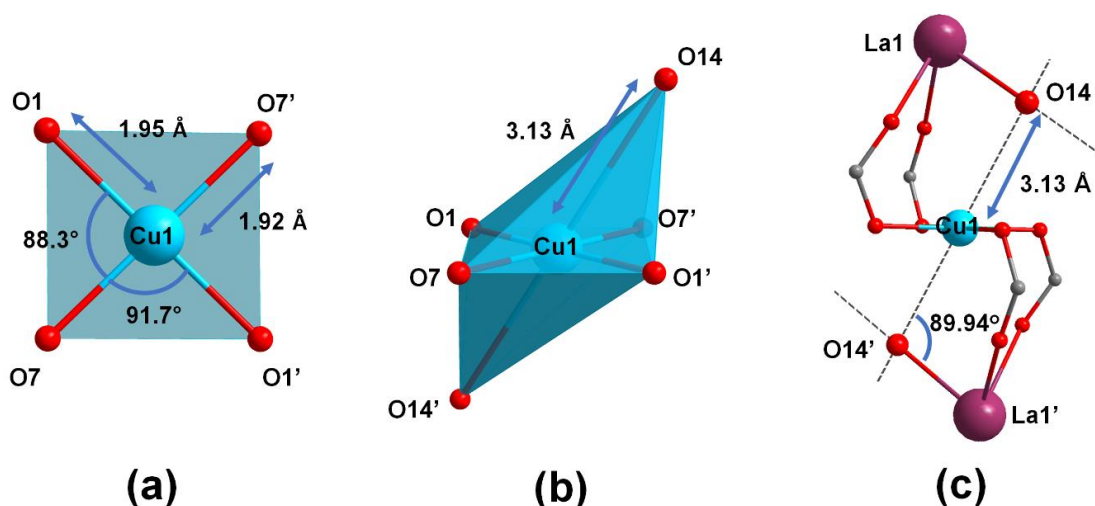


Figure 5.33. (a) The square planar coordination around Cu1; (b) six-coordinated polyhedral of Cu1; (c) La₂Cu core showing the coordination environment around Cu²⁺ ion (Oxygen of water on each of the La³⁺ (O14 and O14') are represented with larger radii compared to carboxylate oxygen).

The Cu²⁺ ion which is located in the centre of inversion of the La₂Cu core unit. The square planar coordination of Cu is satisfied by the oxygen atoms from four nip²⁻ ligands (Cu-O bond length = 1.95 Å and 1.92 Å) and adjacent O-Cu-O angles are around 88.3° and 91.7° (Figure 5.33a). Cu1 has a square planar geometry (SP-4, D_{4h} , CShM = 0.028). There is a molecule of water on each of the two La³⁺ ions about 3.13 Å away from the Cu²⁺ ion. This is too far away to be considered as an interaction with the Cu²⁺ ion (Figure 5.33b). If these two water molecules are considered for a six-coordinated Cu, the corresponding coordination polyhedra shows large deviation from ideal

octahedra according to the SHAPE analysis (CShM = 10.56). The Cu-O(H₂O)-La angle is close to 90° (Figure 5.33c).

Crystal Structure Description of [La(nip)(HCOO)(H₂O)₂] (**8-La**)

The compound **8-La** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit has a La³⁺ ion, a formate ion (HCOO⁻), a nip²⁻ ligand and a water ligand.

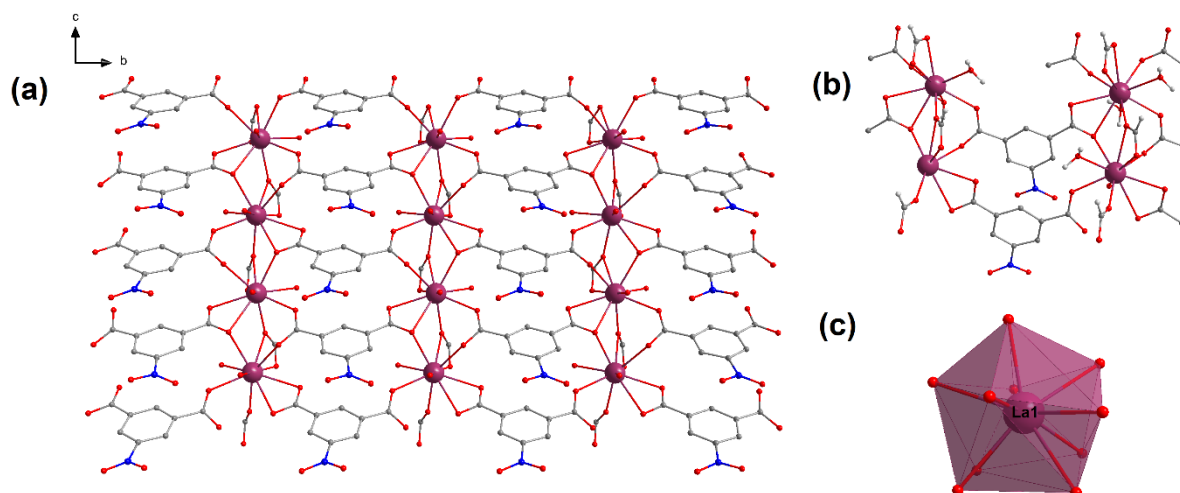


Figure 5.34. (a) Single-crystal X-ray structure showcasing the layer structure of **8-La** core; (b) Coordination modes of carboxylate groups from nip²⁻ and HCOO⁻ around La³⁺; (c) Deca-coordinated La³⁺ in polyhedral representation.

In the two-dimensional sheet structure, each La³⁺ ions are 10-coordinated and are interconnected by nip²⁻ ligand which has two coordination modes on each carboxylate groups. Also, the formate group chelates on each La³⁺ ions. La1 exhibit distorted ten-coordinated geometries with bicapped square antiprism (JBCSAPR-10, D_{4d}) (CShM = 4.59).^[105-106]

Crystal Structure Description of

$[\text{La}_4\text{Cu}_{2.35}(\text{nip})_{6.7}(\text{Hnip})_{1.3}(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_6(\text{H}_2\text{O})_{16.7}]^+ \cdot 8.3\text{H}_2\text{O}$ (9-La)

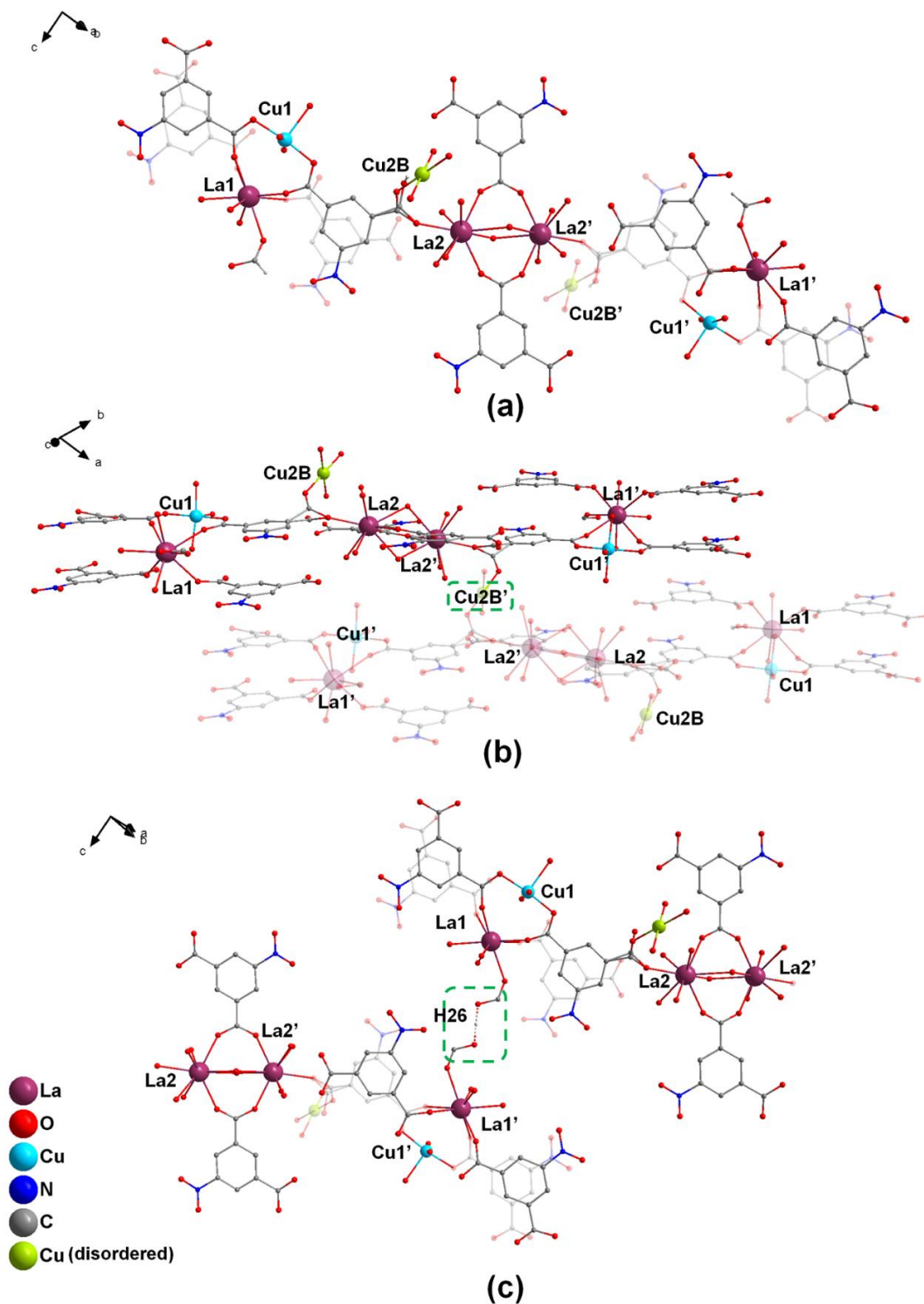


Figure 5.35. The core structure in 9-La-A with different inversion centres (a) at the midpoint of symmetrically equivalent La2 and La2'; (b) on disordered copper Cu2B and (c) on the hydrogen atom that forms hydrogen-bond with formate oxygen atoms. (Lattice solvents, DMF ligands, hydrogen atoms on phenyl rings removed for clarity)

When the dark blue crystals **7-La** obtained for a reagent ratios of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3 = 1 : 1 : 1.5$ and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O} : \text{H}_2\text{nip} : \text{Ln}(\text{NO}_3)_3 : \text{H}_2\text{nip} = 1 : 1 : 1.5 : 2$ were stored at room temperature for about two months, blue crystals of **9-La-A** and greenish blue crystals of **9-La-B** were obtained through a structural transformation (Figure 5.19). However, from the SCXRD data both these compounds are isostructural. The only difference for the compounds was the colour, which was also substantiated using absorption spectroscopy as discussed later. The crystal structure of **9-La-A** is described here.

The compound **9-La-A** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains two La^{3+} (La1, La2), a Cu^{2+} (Cu1, with 100% occupancy) forming the La_4Cu_2 core units. There is a disordered Cu^{2+} (Cu2B with 35% occupancy) and four nip^{2-} ligands (out of which, one is disordered and exist as Hnip^- in 35% of the sites in the crystal), and a formate (HCOO^-) anion. There are coordinated DMF and water ligands as well as lattice water. In the crystal structure, the centrosymmetric La_4Cu_2 core units are extended into a three-dimensional framework structure (Figure 5.35).

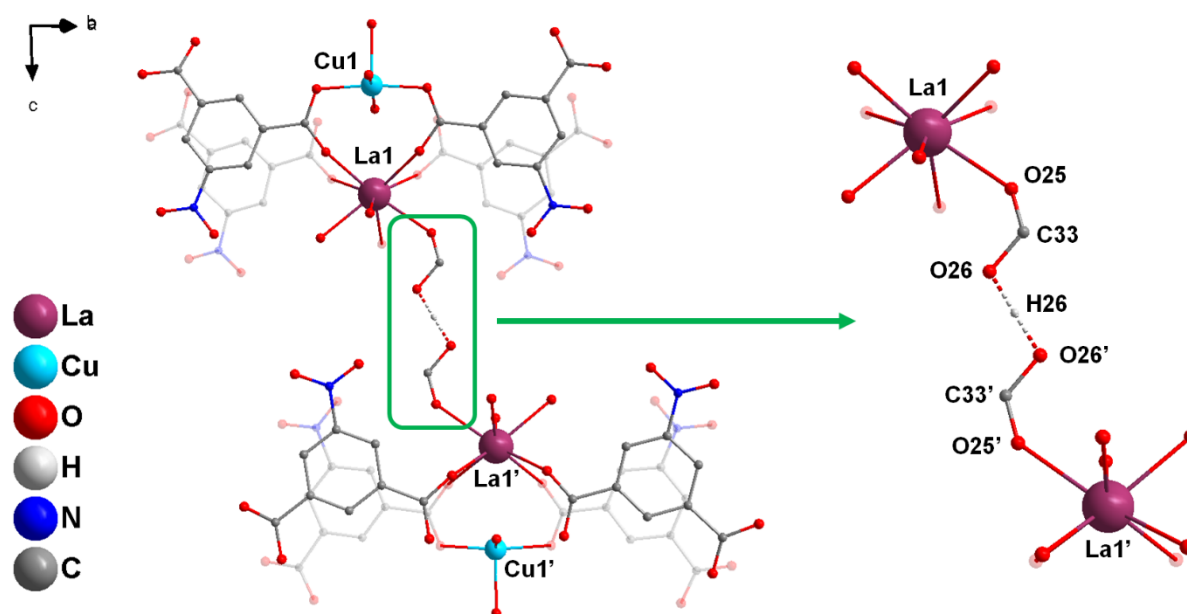


Figure 5.36. Disordered proton (H26) that bridge the formate groups attached on La1.

One must consider here the degree of protonation of the unidentate formate ligands attached to the La1 atoms. The uncoordinated oxygen atoms of two formate groups from two units (O26 and O26') are separated by about 2.74 Å and therefore must be hydrogen bonded and bridged by a proton (H26).^[143] In Figure 5.36, H26 is shown at the midpoint of the hydrogen bond, although it is more likely disordered over two

positions. Therefore, for every asymmetric unit, half of the formate anions are deprotonated.

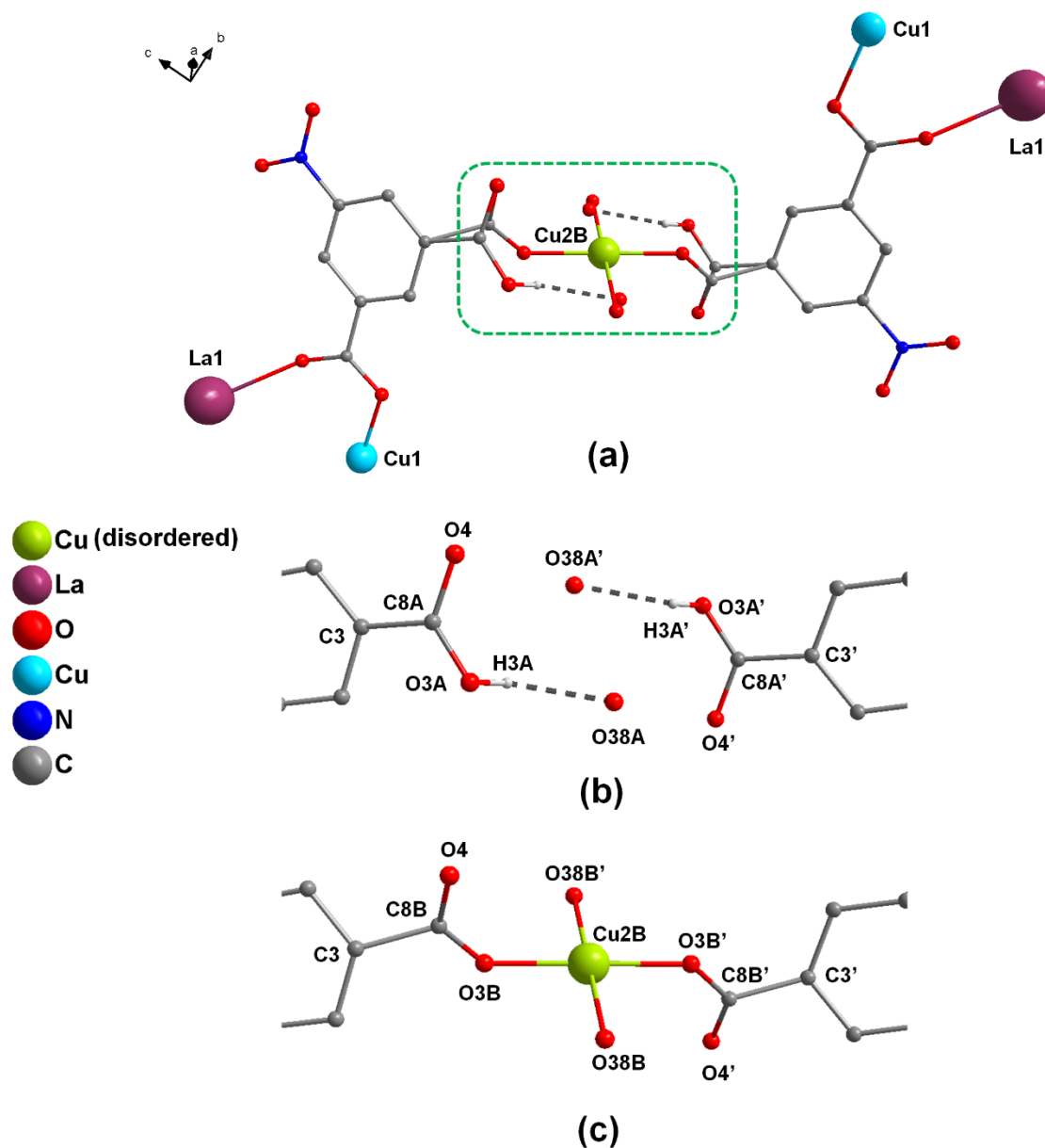


Figure 5.37. (a) Disordered atoms of the carboxylate groups of a pair of inversion-related 5-nitroisophthalic acid ligands and the disordered Cu^{2+} (Cu2B); Enlarged view of the disordered atoms with (b) higher occupancy (65%) with prefix A and (c) lower occupancy (35%) with prefix B.

A more significant disorder in the crystal lies at the degree of protonation of the carboxylate groups of a pair of inversion-related 5-nitroisophthalic acid ligands and the associated absence or presence of a Cu^{2+} (Cu2B) in the lattice (Figure 5.37). This disorder is very similar to that seen in the compound **2-La-meta** in Chapter 4. One of the carboxylate groups of the ligand in **9-La-A** always bridges La1 and Cu1 (Figure

5.37a), but the other group (containing O3 and O4) exists either as -COOH in Hnip^- (65 %) or -COO^- in nip^{2-} (35 %) (Figure 5.37b, c). When this group together with its inversion-related counterpart are protonated (Hnip^- form) they are linked via hydrogen bonds to the lattice waters O38A and O38A'. (Figure 5.37b). The remaining 35% of the carboxylate groups are deprotonated and now coordinate to a Cu^{2+} ion (Cu2B) with 35% occupancy which lies on the inversion centre (Figure 5.37c). The two lattice water molecules (O38B and O38B') are now also coordinated to the copper ion as aqua ligands. The disorder is therefore between a Cu^{2+} cation and a pair of protons, and so does not affect the overall charge. When present, the disordered copper acts as a linker between two La_4Cu_2 core units in two planes (Figure 5.38).

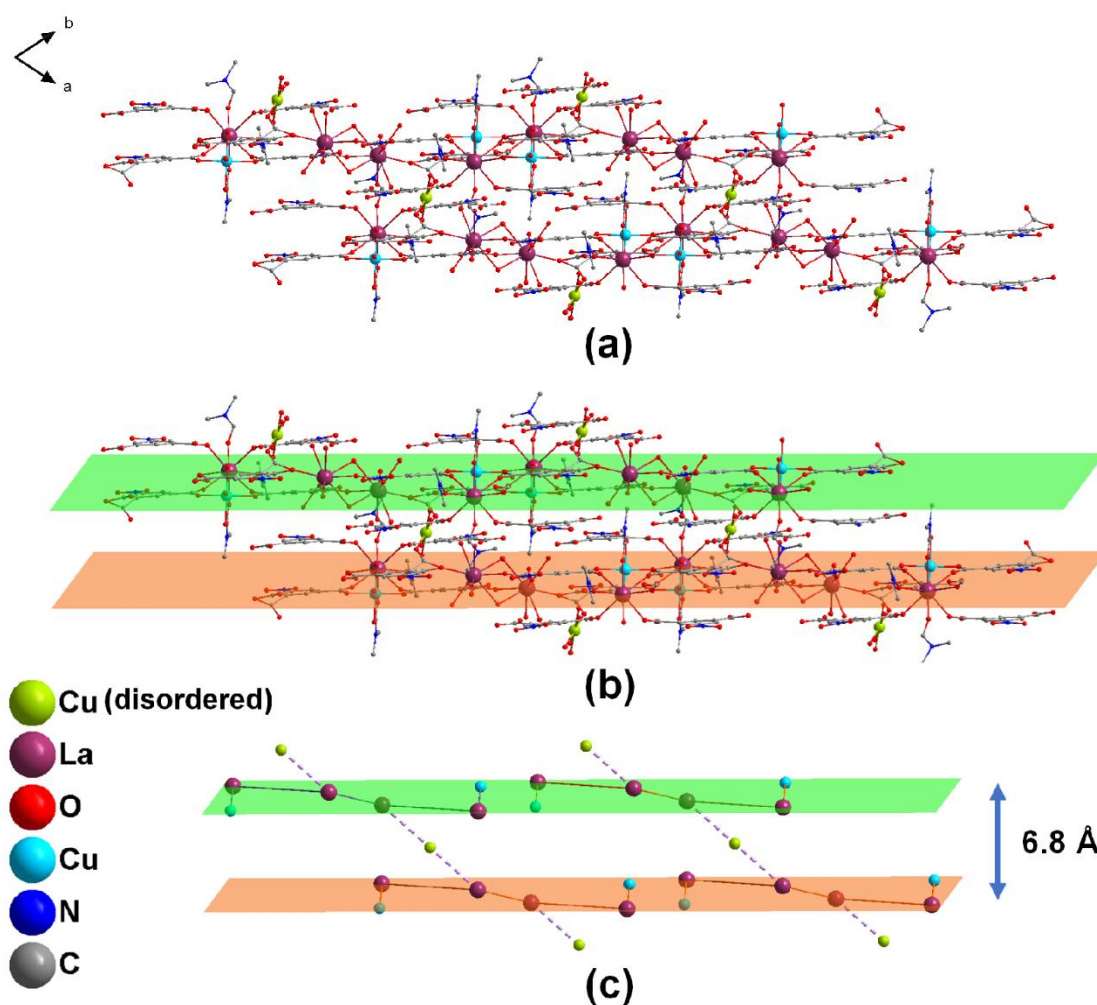


Figure 5.38. (a) and (b) The three-dimensional arrangement of La_4Cu_2 core units as planar layers in **9-La-A**; (c) Arrangement of the La_4Cu_2 core are in coplanar sheets, interconnected by disordered Cu atoms.

Combining the disordered atoms and the La_4Cu_2 core units, the three-dimensional structure in **9-La-A** can be simplified as shown in Figure 5.38. The La_4Cu_2 core units which are related by an inversion centre on hydrogen atom (H26) of the formate groups are arranged in a sheet (Figure 5.38a and b). Each of these sheets are about 6.8 Å apart and the disordered Cu atoms (when present) act as the linking unit of these as shown in Figure 5.38c.

The phenyl rings of the 5-nitroisophthalic acid ligands in **9-La-A** are arranged coparallel resulting in a π - π stacking arrangement with distances of 3.5 Å and 3.72 Å (Figure 5.39).

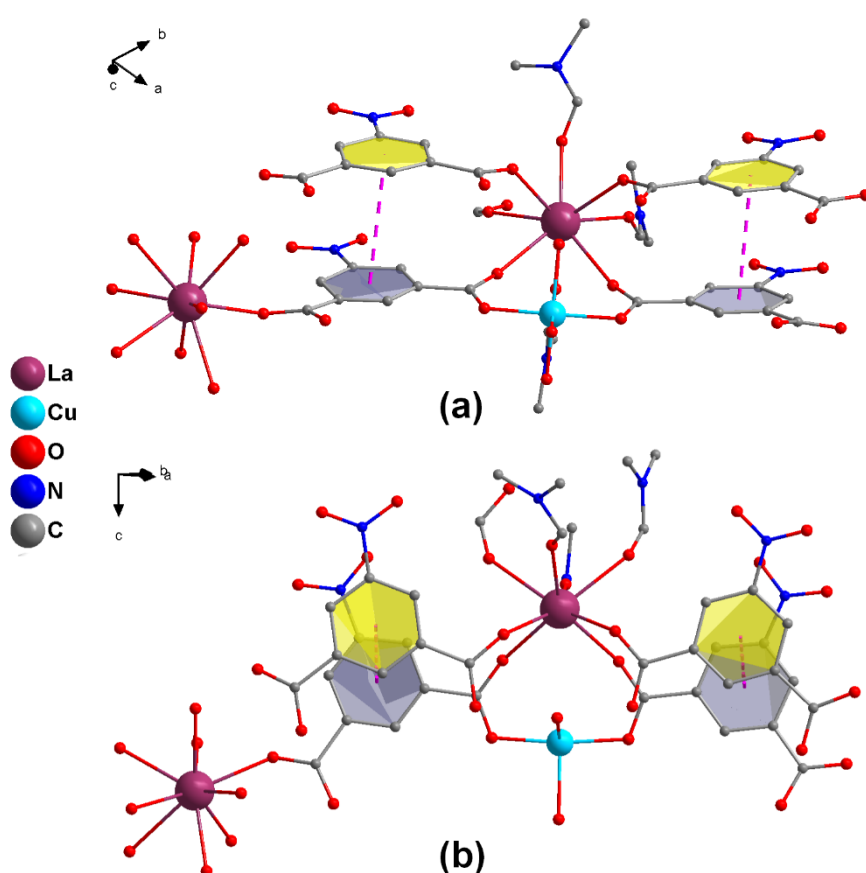
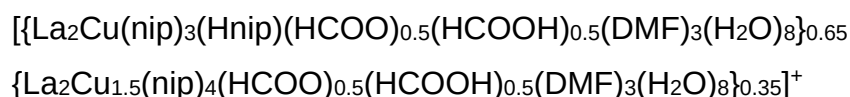


Figure 5.39. π - π stack arrangement of the 5-nitroisophthalic acid ligands of the asymmetric unit of **9-La-A**.

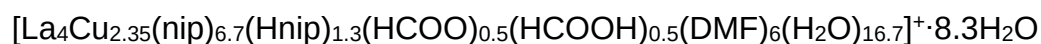
Considering first all the ordered atoms in the lattice, the La_2Cu metal core and the three nip^{2-} ligands in the asymmetric unit contribute charges of +8 and -6 respectively. If the disordered Cu^{2+} (Cu2B) atoms were absent in the structure, then the fourth set of 5-nitroisophthalic acid ligands would have been existing as Hnip^- , and the ideal formula for the asymmetric unit (excluding the solvent molecules) would be $[\text{La}_2\text{Cu}(\text{nip})_3(\text{Hnip})]^+$. On the other hand, if Cu2B was ordered and fully occupied in the crystal structure, then

the corresponding 5-nitroisophthalic acid ligands would now be nip^{2-} . In addition, the Cu2B is on an inversion centre and hence is shared between two asymmetric units and the ideal formula in this case would then be $[\text{La}_2\text{Cu}_{1.5}(\text{nip})_4]^+$. Furthermore, there is a negative charge shared between two asymmetric units from the formate group (-0.5 charge per unit). Hence the entire asymmetric unit would be either $[\text{La}_2\text{Cu}(\text{nip})_3(\text{Hnip})(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_3(\text{H}_2\text{O})_8]^{+0.5}$ or $[\text{La}_2\text{Cu}_{1.5}(\text{nip})_4(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_3(\text{H}_2\text{O})_8]^{+0.5}$. What balances the partial charge is unclear.

The total molecular formula of the network in **9-La-A** can be calculated as the weighted average of the two disordered components:



Finally, the lattice waters need to be considered. Noting that two waters in the structure can be either lattice waters or aqua ligands, depending on the Cu2B disorder, it is possible to arrive at the complete formulation:



No obvious difference between the crystal structures to explain the different colours of **9-La-A** and **9-La-B** could be found. The amount of disordered Cu^{2+} (Cu2B) in both compounds did not differ significantly between the two structures. One possible explanation might be explained by the Jahn-Teller distortion of the disordered Cu^{2+} .

Table 5.5. SHAPE analysis for Cu2B in 6 and 4- coordinated environment in **9-La-A** and **9-La-B**.

Compound	Atom	Coordination number	Shape	Ideal Value	Continuous Shape Measurements (CShM)
9-La-A	Cu2B	4	SP-4 Square plane	0	0.03
		6	OC-6 Octahedron	0	2.04
9-La-B	Cu2B	4	SP-4 Square plane	0	0.20
		6	OC-6 Octahedron	0	1.70

The SHAPE analysis^[105-106] of Cu2B in **9-La-A** and **9-La-B** for 4-coordination and 6-coordination were compared (Table 5.5). Pairs of Cu2B-O3B (O3B is carboxylate oxygen) and Cu2B-O38B (O38B is aqua ligand) bonds constitute the 4-coordination around Cu2B (Figure 5.40). The Cu-O bond distances were slightly different and this is reflected in the deviation of coordination polyhedra from ideal geometries as evident in the continuous shape measurements (CShM) values. When symmetrically equivalent O36 atoms (coordinated to La2) are considered as the 5th and 6th coordination sites for Cu2B, the resultant coordination shape is octahedra (Figure 5.40). The Cu2B-O36 bond distances are 2.48 Å and 2.49 Å in **9-La-A** and **9-La-B** respectively and thus the Jahn-Teller distortion is visible here.

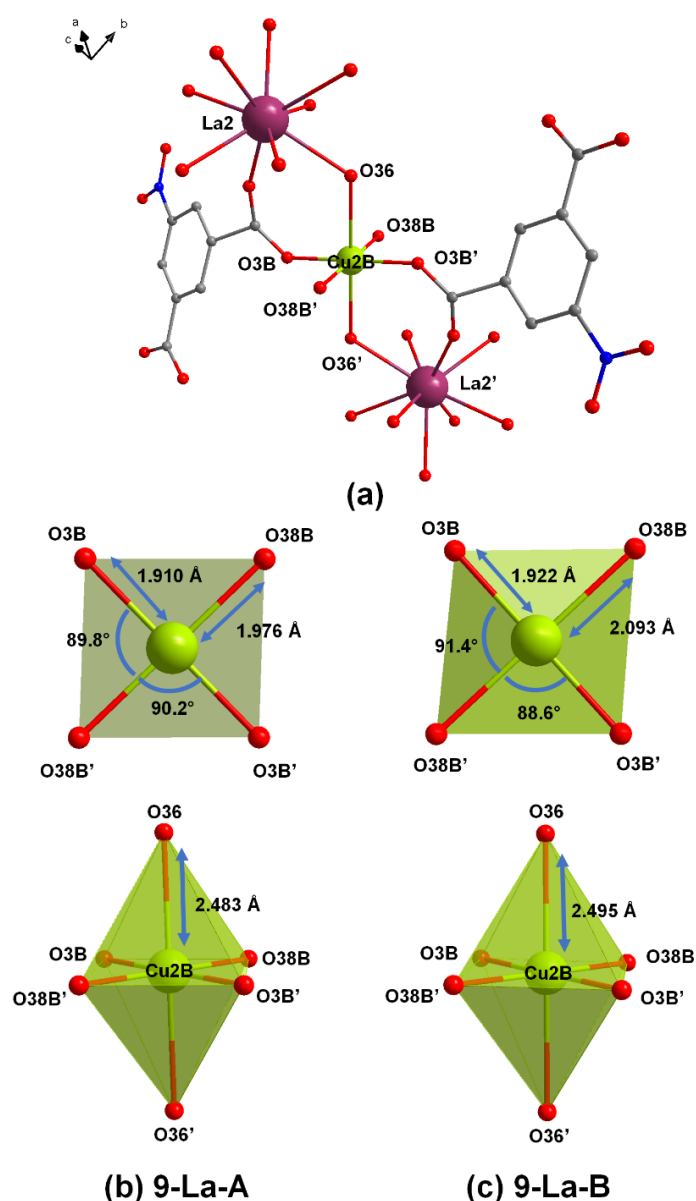


Figure 5.40. (a) Coordination environment of Cu2B in **9-La-A**; 4-coordinated (top) and 6-coordinated (bottom) Cu2B in (b) **9-La-A**; (c) **9-La-B**.

Crystal Structure Description of $[\text{Ln}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4]\cdot 6\text{H}_2\text{O}$ (10-Ln**, $\text{Ln}^{3+} = \text{Ho}^{3+}$, Er^{3+})**

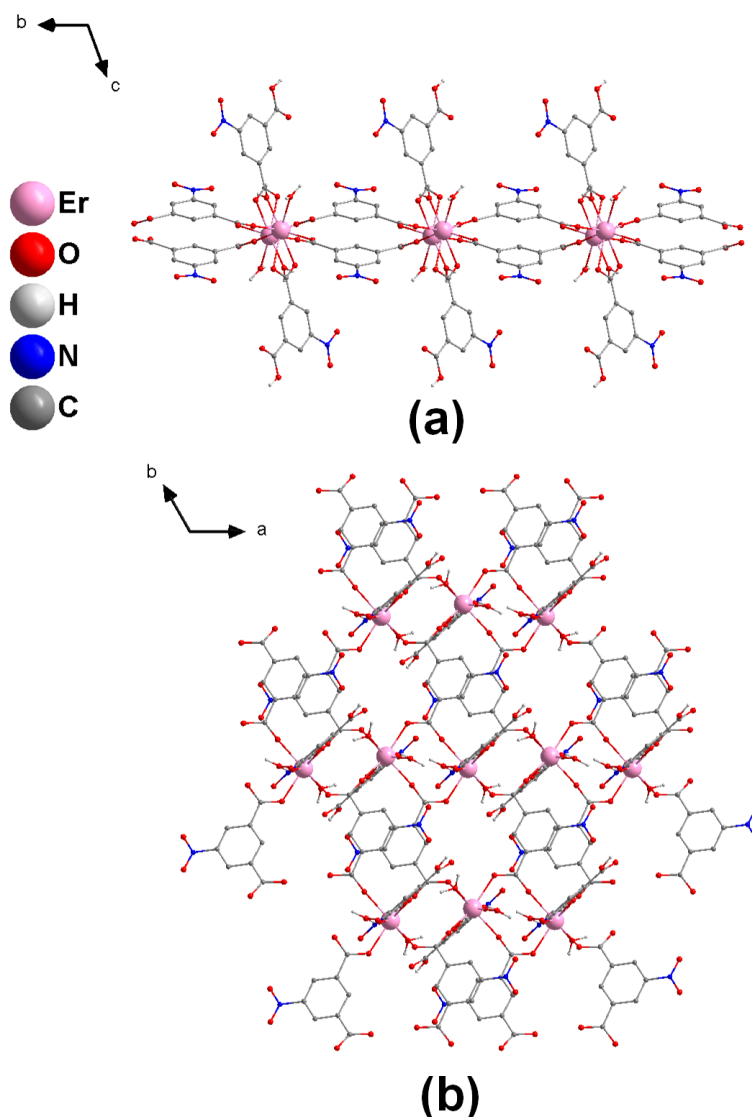


Figure 5.41. Crystal structure of **10-Er** viewed along (a) *a*-axis; (b) *c*-axis.

Single crystal X-ray diffraction analyses reveal that **10-Ln** (where $\text{Ln}^{3+} = \text{Ho}^{3+}$, Er^{3+}) crystallizes in $P\bar{1}$ of triclinic space group. Since both are isomorphous compounds, only the Er- analogue is discussed here. The nip^{2-} and Hnip^- ligands interconnect the Er_2 -units by their carboxylate groups forming a one-dimensional chain. Each of the one-dimensional chains are interconnected via the nip^{2-} ligands, forming two-dimensional sheet-like structure (Figure 5.41).

Interestingly, the network structure in **10-Ln** is very similar to that in **5-Ln**. The only difference arises in the orientation of ligands in the crystal packing. The unit cells are rather similar, with only slight differences in angles (Table 5.6). One has the cell with all obtuse angles in the conventional right-handed setting (**10-Er**) and the other cell with all acute angles (**5-Ln**). Relative to the $\text{Ln}_2(\text{carboxylate})_2$ planar unit, the chelating carboxylate of the Hnip^- ligand has rotated by about 90 degrees in the **5-Gd** compared to the **10-Er** (Figure 5.42).

Table 5.6. Comparison of unit cell parameters of (a) **10-Er** and (b) **5-Gd**. Note the difference in angles

<u>Compound</u>	10-Er	5-Gd
Space Group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6949(5)	9.6203(3)
b (Å)	10.5867(5)	10.4685(3)
c (Å)	13.2937(7)	13.4671(4)
α (°)	104.381(4)	68.181(2)
β (°)	97.732(4)	70.411(2)
γ (°)	116.207(3)	65.262(2)
V (Å³)	1138.03(11)	1117.28(6)
Z	1	1

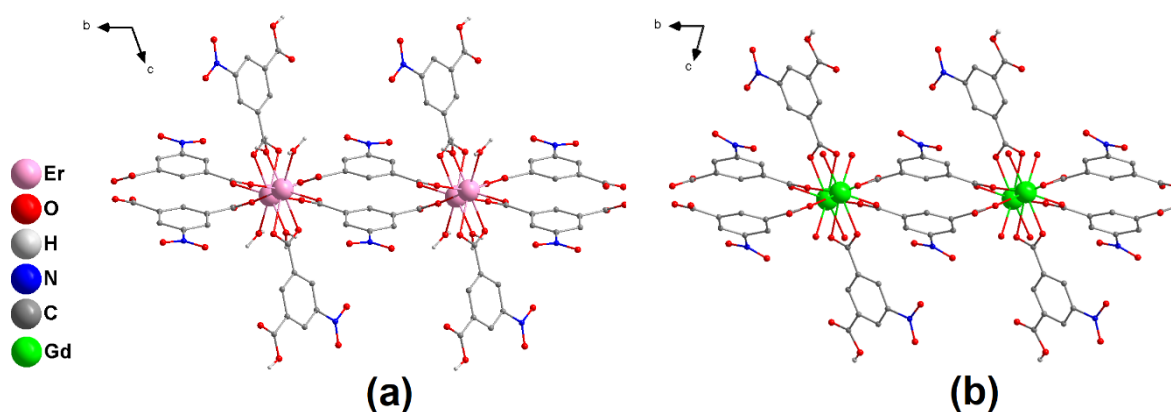


Figure 5.42. Crystal structures viewed along a-axis for (a) **10-Er** and (b) **5-Gd**. Note the difference in angles in the coordinate system.

Crystal Structure Description of $[\text{Er}_3\text{Cu}_4(\text{nip})_8(\text{DMF})_4(\text{H}_2\text{O})_8]^+ \cdot 11\text{DMF}$ (**11-Er**)

The compound **11-Er** crystallises in the tetragonal space group $P\bar{4}n2$ with a cell volume 14190.8(5) Å³ and $Z = 4$. The formula unit has two asymmetric units and consists of a trinuclear ErCu_2 unit and two dinuclear ErCu units (Figure 5.43).

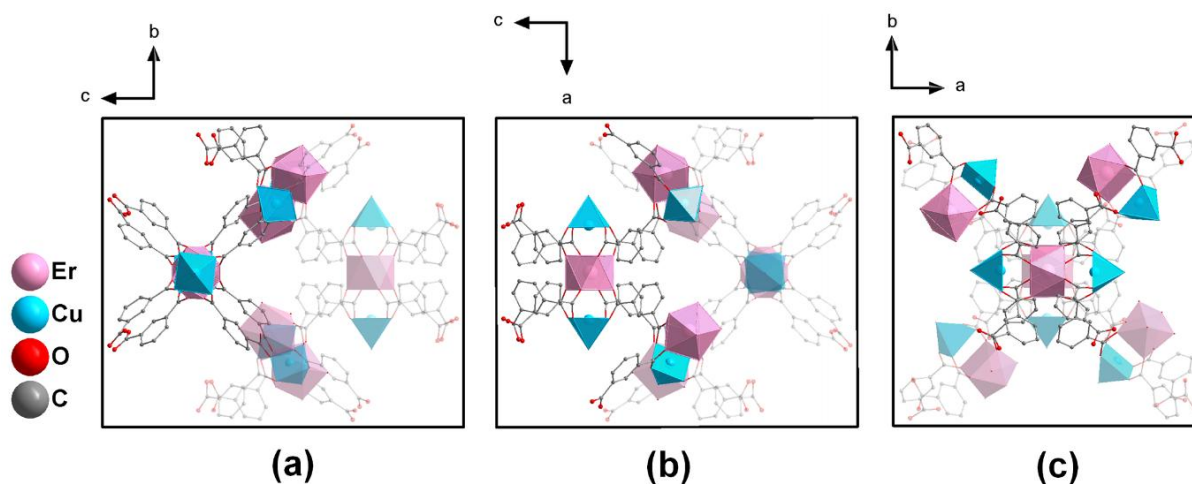


Figure 5.43. Unit cell and atoms of **11-Er** viewed along (a) a-axis; (b) b-axis and (c) c-axis. Metal atoms are represented as coordination polyhedra. Nitro groups and hydrogen atoms omitted for clarity.

The centrosymmetric ErCu_2 unit is made up from two inversion-related Cu^{2+} ions (Cu1 , $\text{Cu1}'$) which are 5-coordinated, and a central Er^{3+} (Er1) ion which is 8-coordinated, forming a double-paddlewheel structure (Figure 5.44a). This unit is linear ($\text{Cu1-Er1-Cu1}'$ angle = 180°). The ErCu unit is a single paddle-wheel structure comprising a Cu^{2+} (Cu3A) ion and an Er^{3+} (Er2A) ion which are again 5-coordinated and 8-coordinated respectively (Figure 5.44b). The coordination polyhedra around the Cu^{2+} are square pyramidal, with the carboxylate oxygen atoms of nip^{2-} ligands defining the square base of the pyramid and a water ligand at the apical position. The eight vertices of the square antiprism around the Er^{3+} in the trinuclear unit (Er1) is formed from carboxylate oxygen atoms. In the ErCu unit, one square base of the polyhedra around the Er^{3+} (Er2A) are formed from carboxylate oxygen atoms, whereas the other is formed by a pair of DMF and water ligands

The SHAPE analyses for metal ions are summarised in Table 5.7.^[105-106]

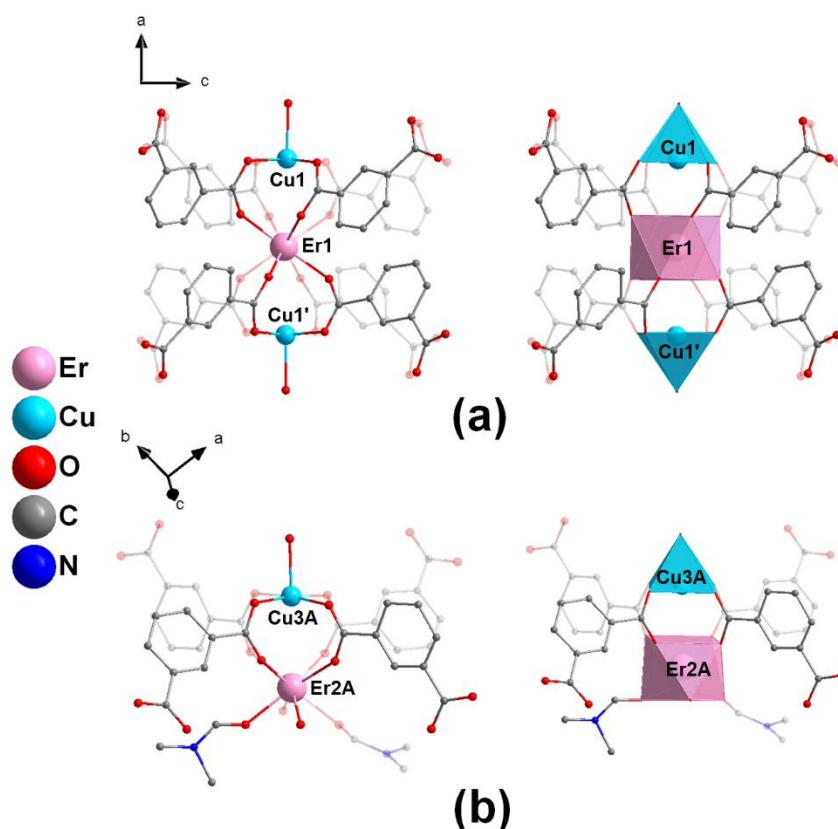


Figure 5.44. Ball and stick (left) and polyhedral (right) representation of (a) ErCu_2 units and (b) ErCu unit. Hydrogen atoms and nitro groups and on the ligands omitted for clarity.

Table 5.7. SHAPE Analysis of metal ions is **11-Er**.

Unit	Atom	Shape	Ideal Value	Continuous Shape Measurements (CSHM)
ErCu_2	Cu1	Square pyramid (SPY-5)	0	0.62
	Er1	Square antiprism (SAPR-8)	0	0.82
ErCu	Cu3A	Square pyramid (SPY-5)	0	0.75
	Er2A	Square antiprism (SAPR-8)	0	0.42

The ErCu units exhibit an unusual disorder of the metal sites. A plane can be drawn through the carbon atoms of the four bridging carboxylate groups, and the Cu and Er centres can be exchanged by being reflected in this plane (Figure 5.45a). This disorder is, however, minor, with relative occupancies of 95:5 for each of the metals. Although it was possible to locate the water ligand on the minor Cu component (Cu2B) it was not

possible to locate the DMF ligand atoms coordinated to Er3B. For simplicity, only the atoms of the major (95%) disorder component are shown for the ErCu unit (Figure 5.45b).

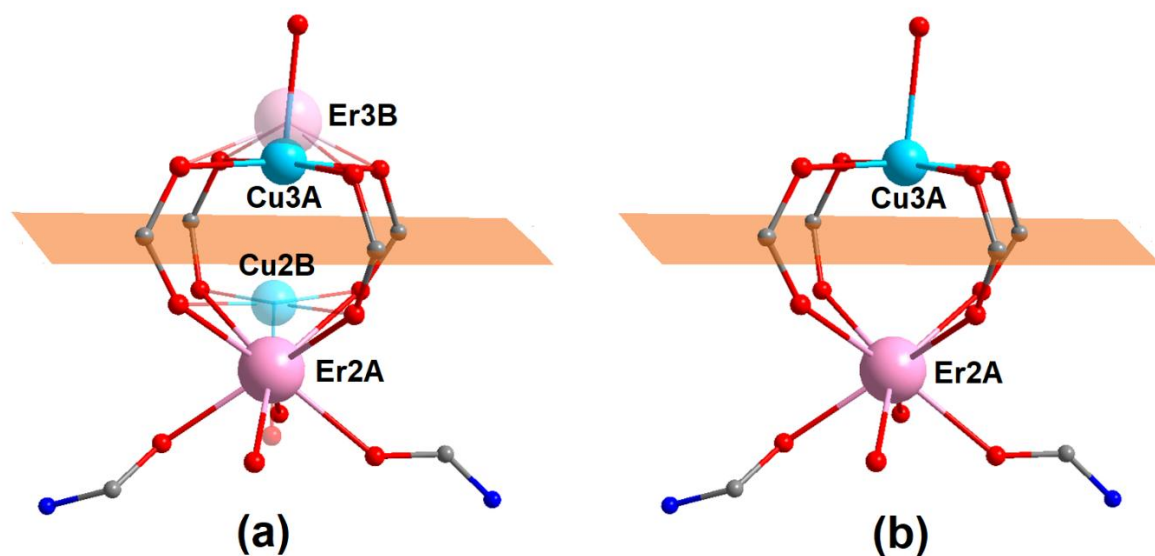


Figure 5.45. (a). Disordered ErCu unit with pseudo mirror plane. Atoms with minor occupancy (5%) are shown as transparent; (b) ErCu unit with atoms of major occupancy (95%).

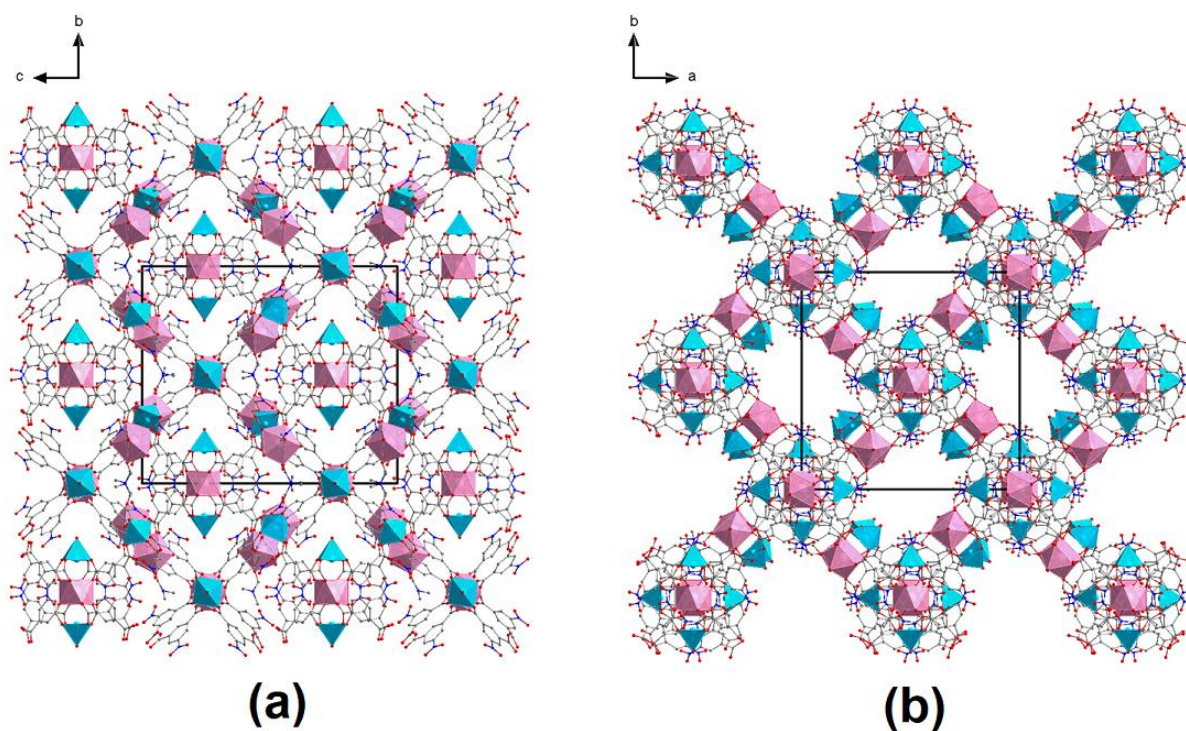


Figure 5.46. The three-dimensional framework structure in **11-Er** viewed along (a) a-axis; (b) c-axis, showcasing the porous structure.

In the crystal lattice, the ErCu_2 and ErCu units are interconnected over three dimensions forming a porous MOF structure. In this tetragonal lattice, the pores are along the c-axis (Figure 5.46). The solvent accessible volume was calculated using the SQUEEZE function within PLATON^[144] in Olex2 software^[145] and amounts to 39.3% of the total unit cell volume, which is occupied by the 11 lattice DMF molecules.

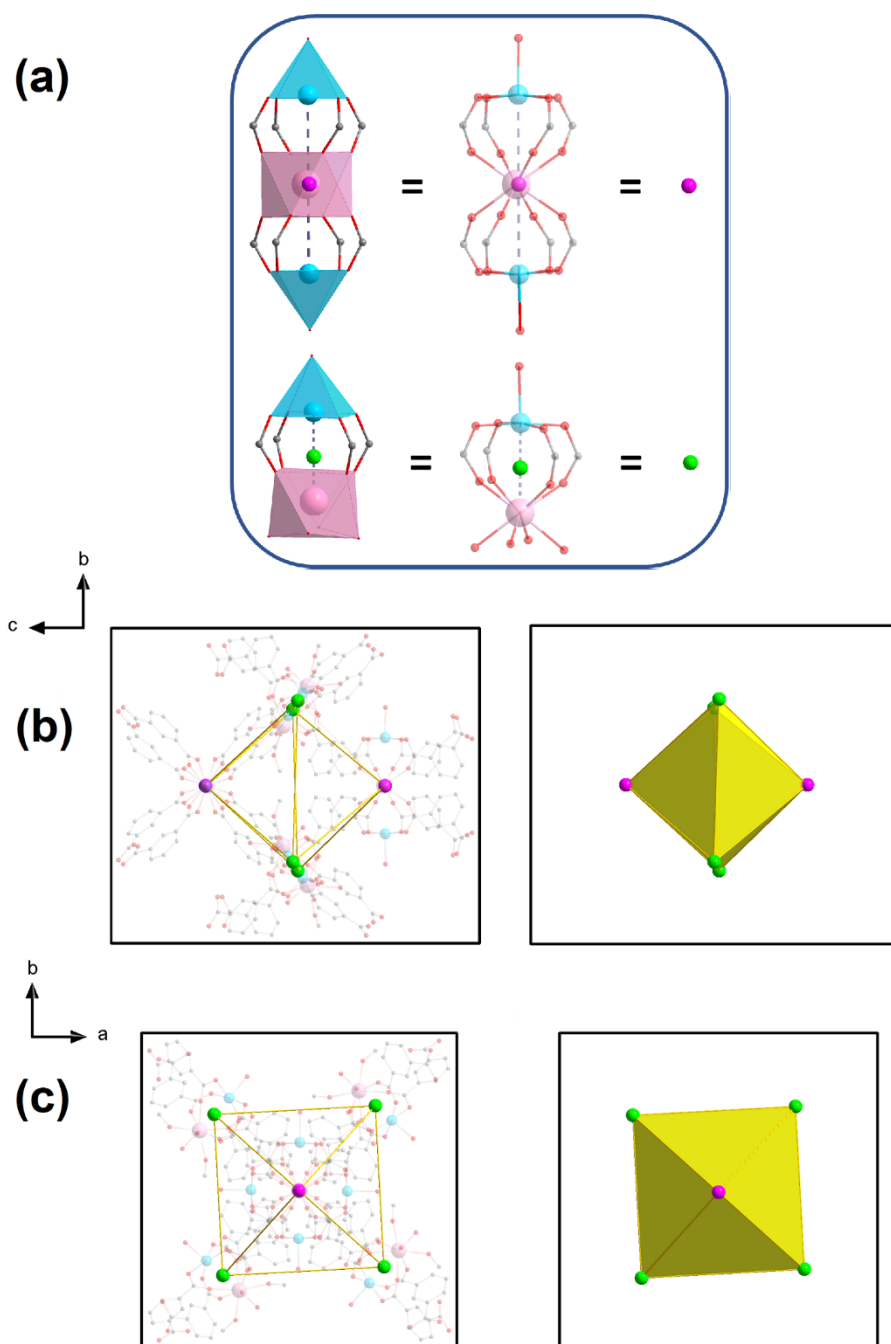


Figure 5.47. (a) Simplified representation of ErCu_2 and ErCu units in **11-Er** using dummy atoms; (b) and (c) Octahedra formed by joining the dummy atoms (viewed along a and c axes). Other atoms are shown in transparent.

The formula unit of **11-Er** is given by $[\{\text{ErCu}_2(\text{H}_2\text{O})_2\} \{\text{ErCu}(\text{DMF})_2(\text{H}_2\text{O})_3\}_2 (\text{nip})_8]^+$ and the molecular formula is given by $[\text{Er}_3\text{Cu}_4(\text{nip})_8(\text{DMF})_4(\text{H}_2\text{O})_8]^+ \cdot 11\text{DMF}$. The counter anion to balance the positive charge of the framework structure could not be accounted from the SCXRD data. This could be present in the pores along with the lattice solvents and cannot be identified and refined.

For the topological understanding of the structure of **11-Er**, a simplified representation using dummy atoms is introduced now. The Cu_2Er unit is represented by a pink sphere centred on Er1, while the ErCu unit is represented by a green sphere at the mid-point of the Cu-Er vector (Figure 5.47a). If one now considers the linkages of these Cu_2Er and ErCu units via the nip^{2-} ligands, the topology of the structure can be seen to be composed of vertex-sharing octahedra, where in each octahedron the Cu_2Er units occupy these vertices Figure 5.47b, c). The three-dimensional network of **11-Er** can thus be visualised as shown in Figure 5.48.

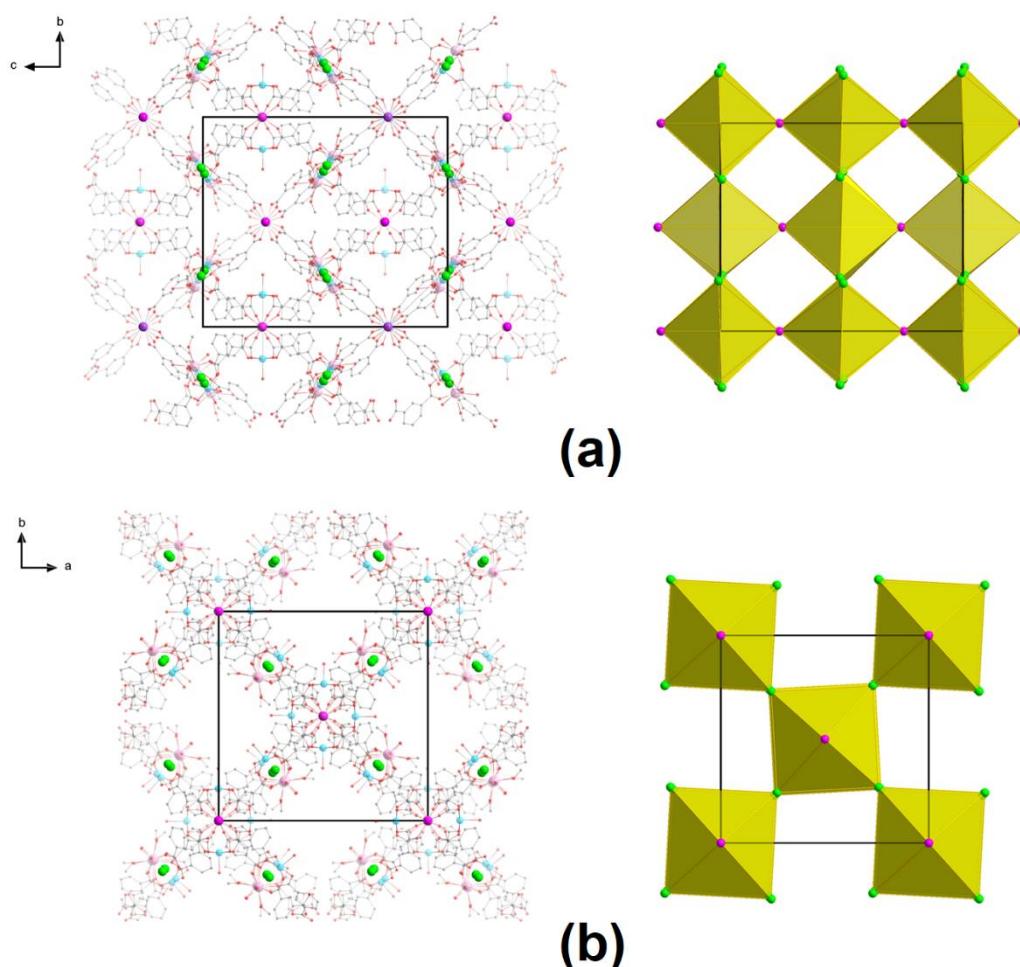


Figure 5.48. Simplified topological representation of **11-Er** viewed along (a) *a* axis and (b) *c* axis.

Crystal Structure Description of $[\text{Ho}_{3.75}\text{Cu}_{6.25}(\text{nip})_{12}(\text{H}_2\text{O})_{13.25}]^{(0.25)-} \cdot 9\text{DMF}$ (**12-Ho**)

As described in section 5.5.2., blue crystals of **12-Ln** were obtained for $\text{Ln}^{3+} = \text{Dy}^{3+}$, Ho^{3+} and Er^{3+} . In addition to the porous structure with many lattice solvents inside and metal disorders (*vide infra*), the solving of these MOF structures were very difficult. Twinning of crystals made this even worse for Dy and Er analogues. **12-Ho** had a better data set and this is described below.

Table 5.8. Unit cell parameters of **12-Dy**, **12-Ho** and **12-Er**.

<u>Compound</u>	<u>12-Dy</u>	<u>12-Ho</u>	<u>12-Er</u>
a (Å)	39.8206(3)	39.7218 (4)	39.6509(3)
b (Å)	39.8206(3)	39.7218 (4)	39.7218 (4)
c (Å)	22.9328(2)	22.8785(2)	22.8656(2)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å ³)	36364.1(5)	36098.2(6)	35949.2(5)
Z	8	8	8

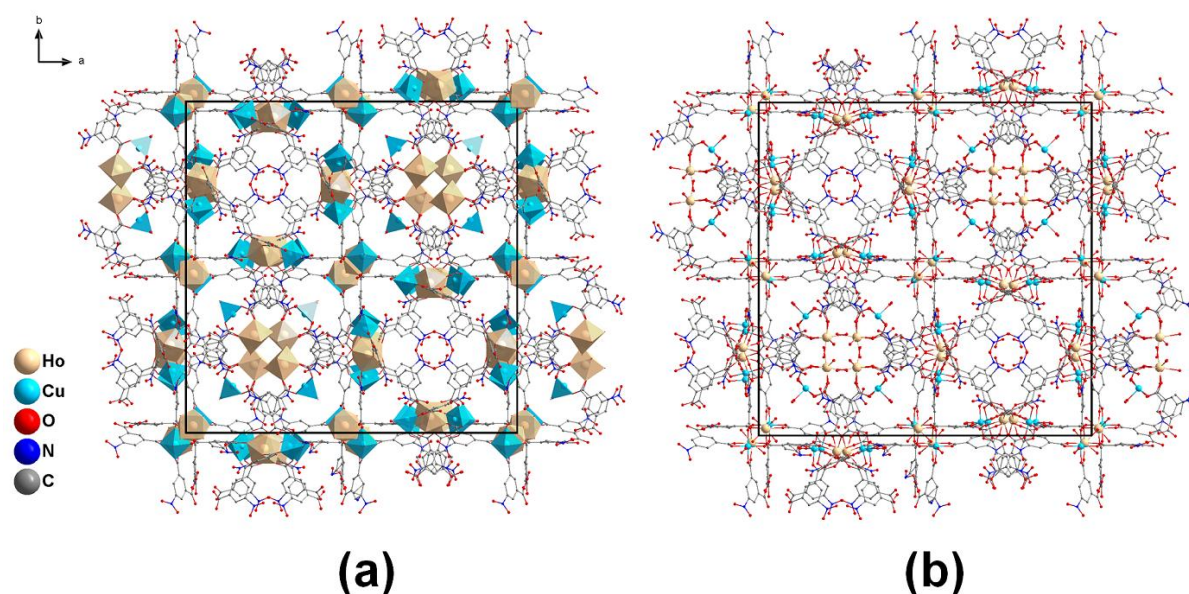


Figure 5.49. The three-dimensional structure and unit cell in **12-Ho** when viewed along c-axis. Metal coordination environment in (a) polyhedral and (b) ball and stick representation.

The compound **12-Ho** crystallises in tetragonal centrosymmetric space group $P4_2/ncm$ with a cell volume 36098.2(6) Å³ and Z = 8 (Figure 5.49). The asymmetric unit consists

of a trinuclear HoCu_2 moiety on a general position and two half dinuclear HoCu moieties which each lie on a mirror plane, and 6 nip^{2-} ligands. Overall, within the formula unit, there are equal numbers of trinuclear and dinuclear moieties.

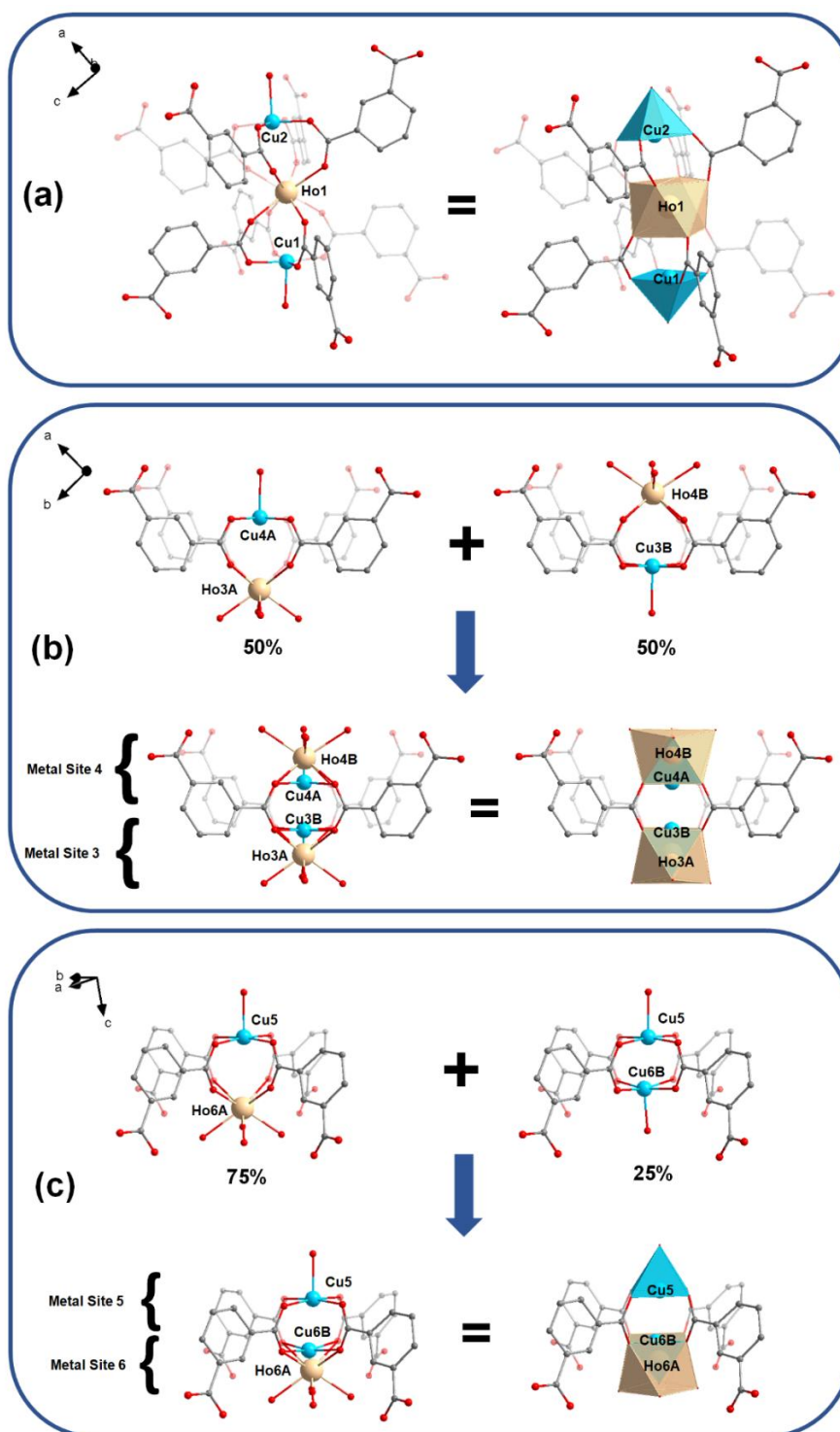


Figure 5.50. Multimetallic moieties in **12-Ho**. (a) Trinuclear HoCu_2 moiety; (b) metal disorder in dinuclear HoCu moiety at two sites 3 and 4 with 50%-50% occupancy; (c) metal disorder in dinuclear HoCu moiety at site 6 with occupancy of 75% Ho and 25%. Hydrogen atoms and nitro groups and on the ligands omitted for clarity.

The trinuclear double-paddlewheel HoCu_2 unit in **12-Ho** (Figure 5.50a) is isostructural to the ErCu_2 unit in **11-Er**, although here the unit is acentric and non-linear (Cu1-Ho1-Cu2 angle = 165.45°). The two distinct dinuclear HoCu units each show metal disorder similar to that seen in **11-Er**. In one of them, a single paddle-wheel structure is formed at sites 3 and 4 by metal ions forming a HoCu unit. Unlike **11-Er**, the metal disorder here is not minor, rather 50%-50% occupancy (Figure 5.50b). In the other HoCu unit, the Cu (site 5) is ordered, whereas the other metal site (6) has an occupancy of 75% Ho and 25% Cu (Figure 5.50c). The metal content in this site is thus non-stoichiometric. The Ho^{3+} ions are 8-coordinated with square antiprism and the Cu^{2+} ions are 5-coordinated with square pyramidal geometries.

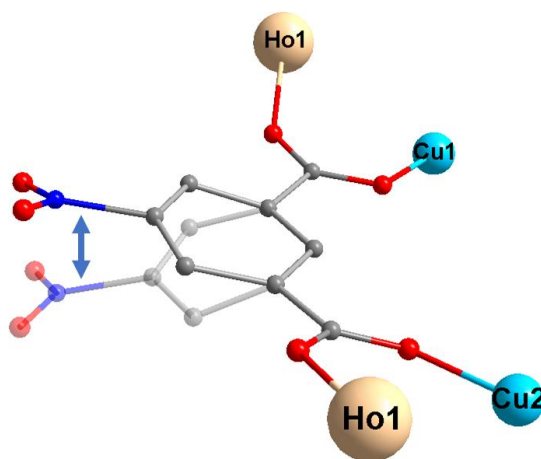
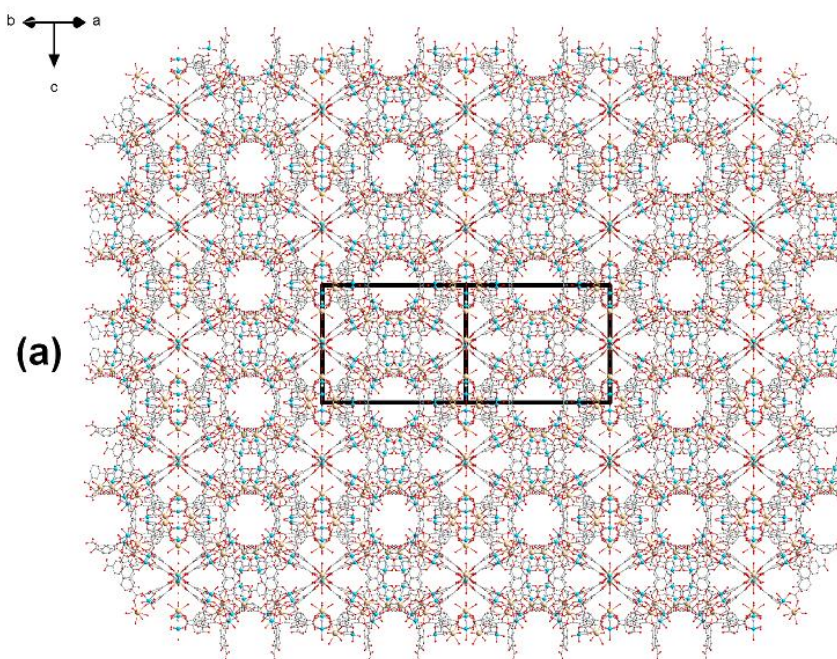


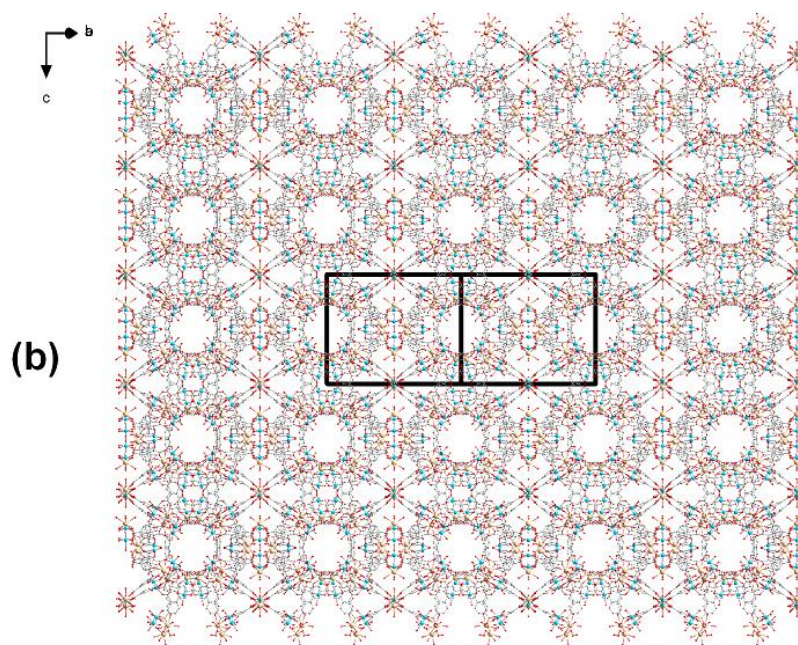
Figure 5.51. Ring flapping-disorder in 5-nitroisophthalic acid ligand in **12-Ho**.

In addition to the disorders at the metal sites, most of the 5-nitroisophthalic acid ligands in **12-Ho** are also disordered. While both carboxylate groups of the ligands are coordinated to the metal ions, three carbon atoms in the phenyl ring and the nitro group undergo a ring flapping (Figure 5.51).

The three-dimensional tetragonal lattice of **12-Ho** has a porous MOF structure. Here, the pores can be viewed along two channels which are along the normal to the (110) or $(\bar{1}10)$ planes (Figure 5.52). In the case of **11-Er**, the porous channels were along the c -axis. The solvent accessible volume was calculated using the SQUEEZE function within PLATON^[144] in Olex2 software^[145] and amounts to $12046 \text{ \AA}^3$ which corresponds to 33.4% of the total unit cell volume. This is occupied by the ca. 9 DMF molecules.



Viewed along normal to 110 plane



Viewed along normal to $\bar{1}10$ plane

Figure 5.52. The three-dimensional framework structure in **12-Ho** viewed along the direction of normal to (a) 110 plane and (b) $\bar{1}10$ plane, showcasing the porous channels.

Without the disorder, the formula unit in **12-Ho** would have been $[\{\text{HoCu}_2(\text{H}_2\text{O})_2\}_2 \{\text{HoCu}(\text{H}_2\text{O})_5\}_2 (\text{nip})_{12}]$ or simply $[\{\text{HoCu}_2\}_2 \{\text{HoCu}\}_2 (\text{nip})_{12} (\text{H}_2\text{O})_{14}]$. However, for every Ho^{3+} ions missing (x) in one of the $\{\text{HoCu}(\text{H}_2\text{O})_5\}$ units, there are 'x' Cu^{2+} ions present at that site, which is accompanied by the loss of 4x water ligands and a gain of 1x water

ligand (Figure 5.50c). In effect, there is a loss of 3x water ligands due to the metal disorder. Therefore, the formula unit with disorder is $[\{\text{HoCu}_2(\text{H}_2\text{O})_2\}_2 \{\text{HoCu}(\text{H}_2\text{O})_5\} \{\text{Ho}_{1-x}\text{Cu}_{1+x}(\text{H}_2\text{O})_{1+(4-3x)}\}]$, or simply $[\{\text{HoCu}_2\}_2 \{\text{HoCu}\} \{\text{Ho}_{1-x}\text{Cu}_{1+x}\} (\text{nip})_{12} (\text{H}_2\text{O})_{14-3x}]^x$ where $x = 0.25$.

The molecular formula for **12-Ho** is given by $[\text{Ho}_{3.75}\text{Cu}_{6.25}(\text{nip})_{12} (\text{H}_2\text{O})_{13.25}]^{(0.25)-} \cdot 9\text{DMF}$. A quarter of a positive charge could not be accounted from the SCXRD data. Due to the complexity of the structure with disorder and large pores with lattice solvents, it is reasonable to assume that the missing cation is somewhere in the crystal lattice.

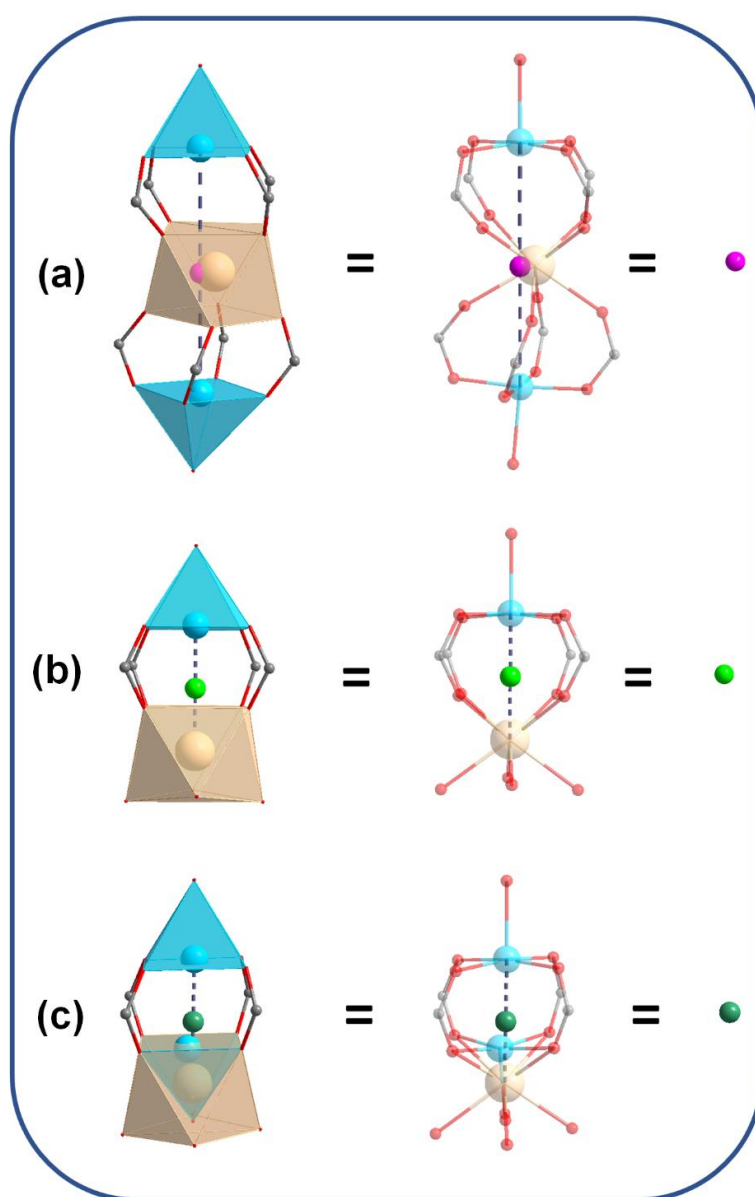


Figure 5.53. Simplified representation of HoCu_2 and disordered HoCu units in **12-Ho** using dummy atoms.

For the topological understanding of the structure of **12-Ho**, a simplified representation using dummy atoms as in **11-Er** is introduced here. The {HoCu₂} unit is represented by a pink sphere centred on the vector joining two Cu atoms and is slightly off from the position of Er (Figure 5.53a). The disordered {HoCu} unit with 50%-50% occupancy is represented by a green sphere at the mid-point of the Ho-Cu vector (Figure 5.53b). Finally, the highly disordered {Ho_{0.75}Cu_{1.25}} unit is represented by a dark green sphere at the mid-point of the Ho-Cu vector (Figure 5.53c).

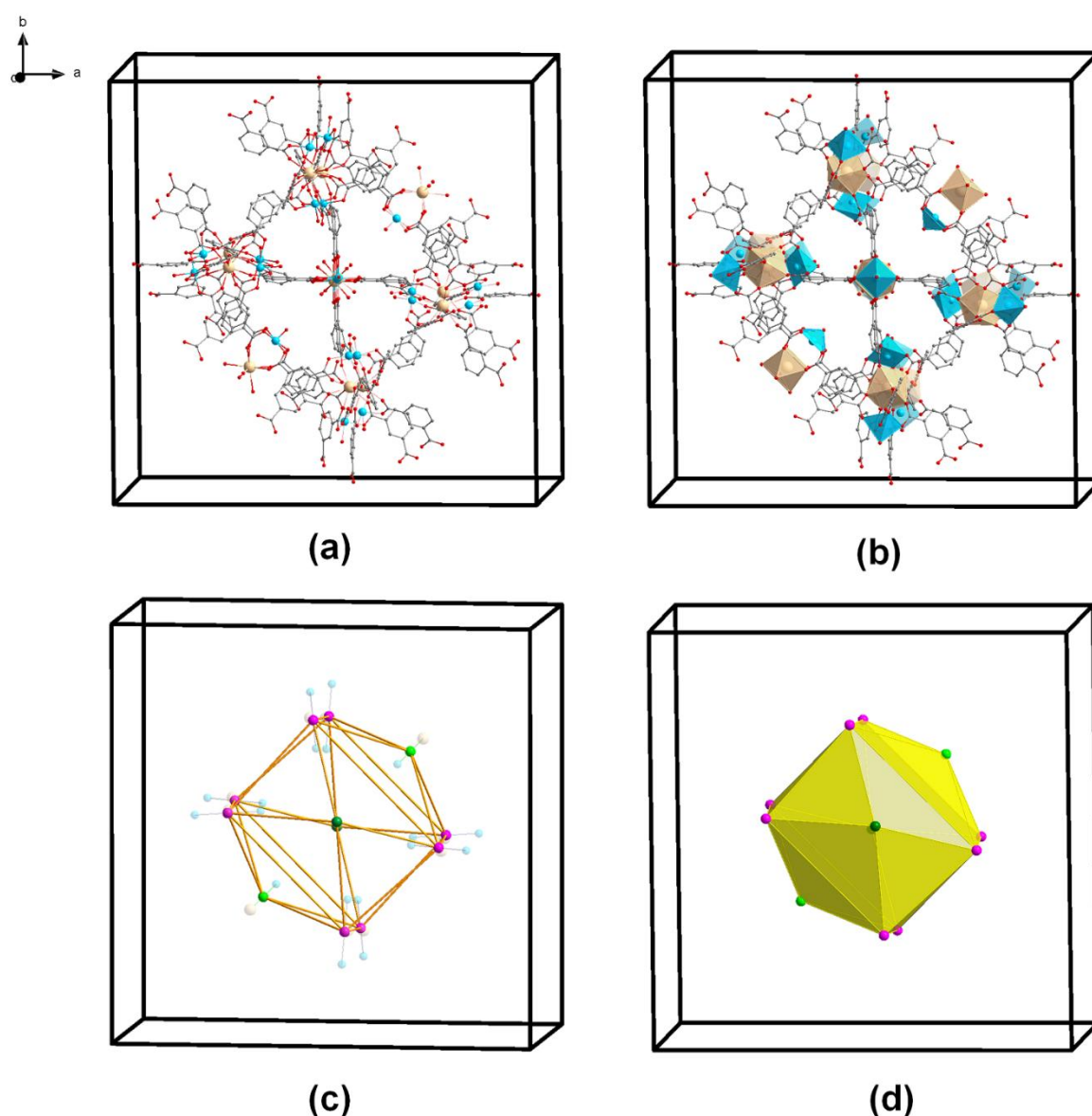


Figure 5.54. (a) Ball and stick representation and (b) polyhedral representation of metal cores unit in the unit cell of **12-Ho**; (c) and (d) Polyhedra (square prism) formed by joining the dummy atoms. Hydrogen atoms and nitro groups and on the ligands omitted for clarity.

The pink spheres (HoCu_2 units) form 8 vertices of the square prism (slightly elongated cube) which has a pair of square faces and two pairs of rectangular faces. Each pair of green spheres (HoCu units) and dark green spheres ($\text{Ho}_{0.75}\text{Cu}_{1.25}$ units) occupy the centres of opposite pairs of rectangular faces of the prism. The pair of square faces are not capped. The topology of the structure obtained from these dummy atoms can be pictured as an approximate tetracapped square prism. (Figure 5.54c and d). The topology of **12-Ho** is defined by of these vertex-sharing polygons, where the HoCu_2 units occupy these vertices (Figure 5.55).

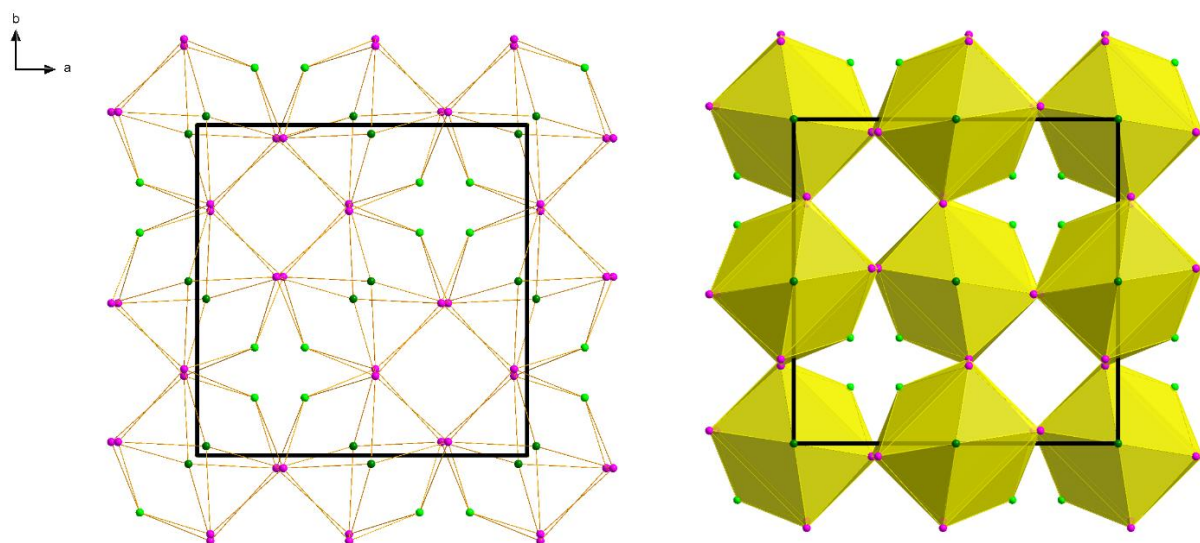


Figure 5.55. Simplified topological representation of **12-Ho** viewed along c-axis.

5.6.2. Solid-State UV-Vis Spectroscopy

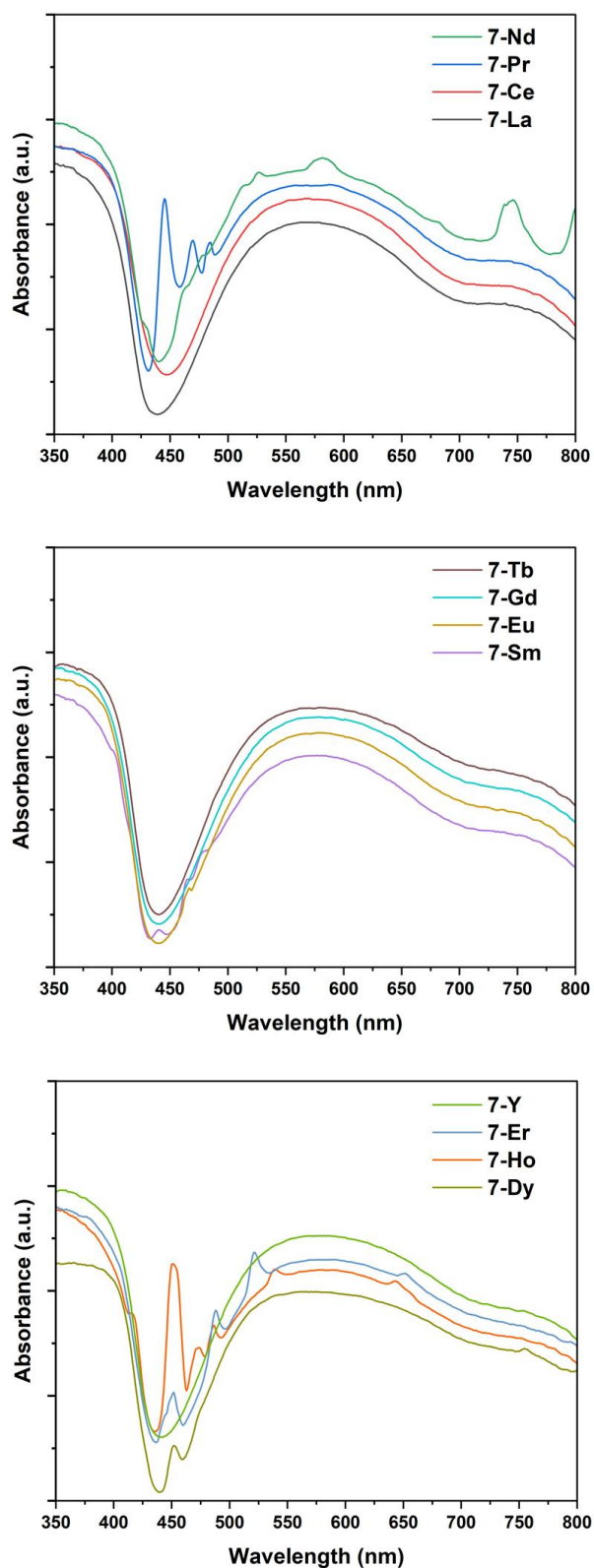


Figure 5.56. Solid state UV-Vis absorption spectra in the range of 350 to 800 nm for 7-Ln ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$ and Y^{3+})

The solid-state UV-Vis absorption spectroscopy of compounds **7-Ln** ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$ and Y^{3+}) were performed using crushed crystals (Figure 5.56). The dark blue colour in **7-Ln** is due to the absorption by Cu^{2+} ions which is visible as the broad peak from 500 to 800 nm. The absorption peaks corresponding to the f-f transitions (in the visible region) is also additionally visible for $\text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}$ and Er^{3+} analogues. The other analogues like, **7-La**, **7-Ce** and **7-Gd** does not show these transitions in visible region, the spectra for these are similar and only accounts for the absorption by Cu^{2+} ions.

As discussed in one of the previous sections, the crystals of isostructural La^{3+} compounds **9-La-A** and **9-La-B** appeared in two different colours. The blue and greenish-blue colours for the respective colours indicate their difference in absorption in the visible-light spectrum. The solid-state UV-Vis absorption spectra of these compounds were found to be exactly same as for the band from 550-800 nm, from the absorption by Cu^{2+} ions. The exception was that the compound **9-La-B** had an extra absorption band at 420-500 nm (Figure 5.57). However, the reason behind this absorption band and the colour difference for this compound compared to **9-La-A** is unclear.

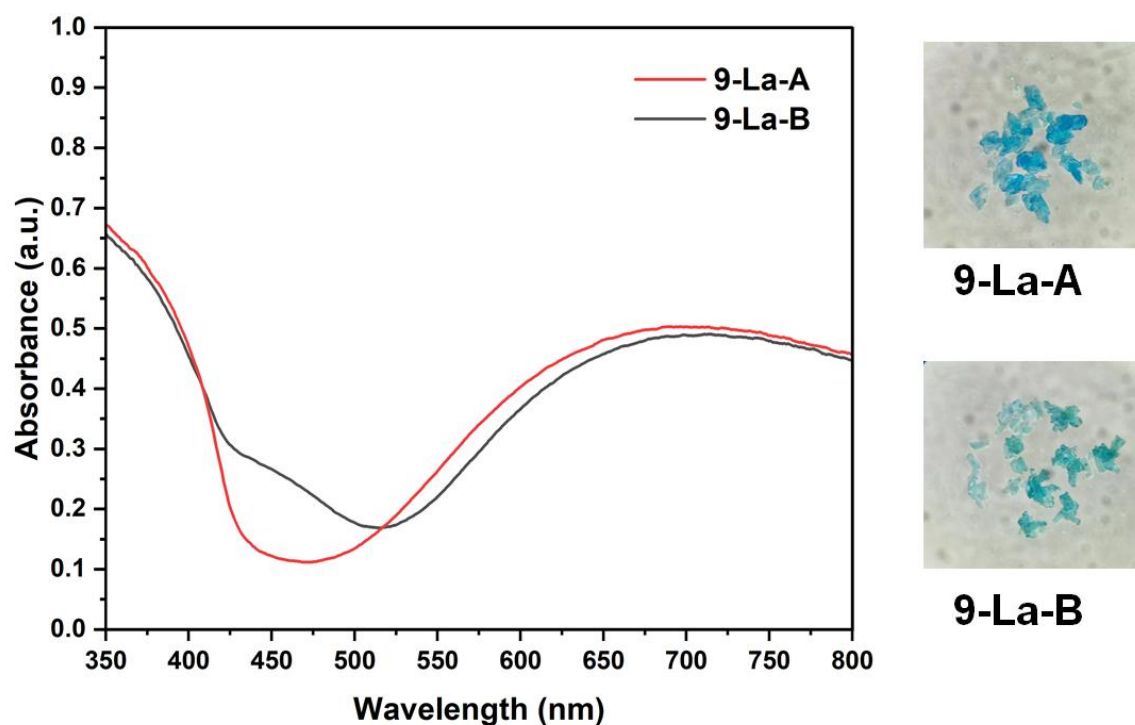


Figure 5.57. Solid-state UV-Vis absorption spectra in the range of 350 to 800 nm for **9-La-A** (blue crystals) and **9-La-B** (greenish blue).

5.6.3. Solid-State Photoluminescence Spectroscopy

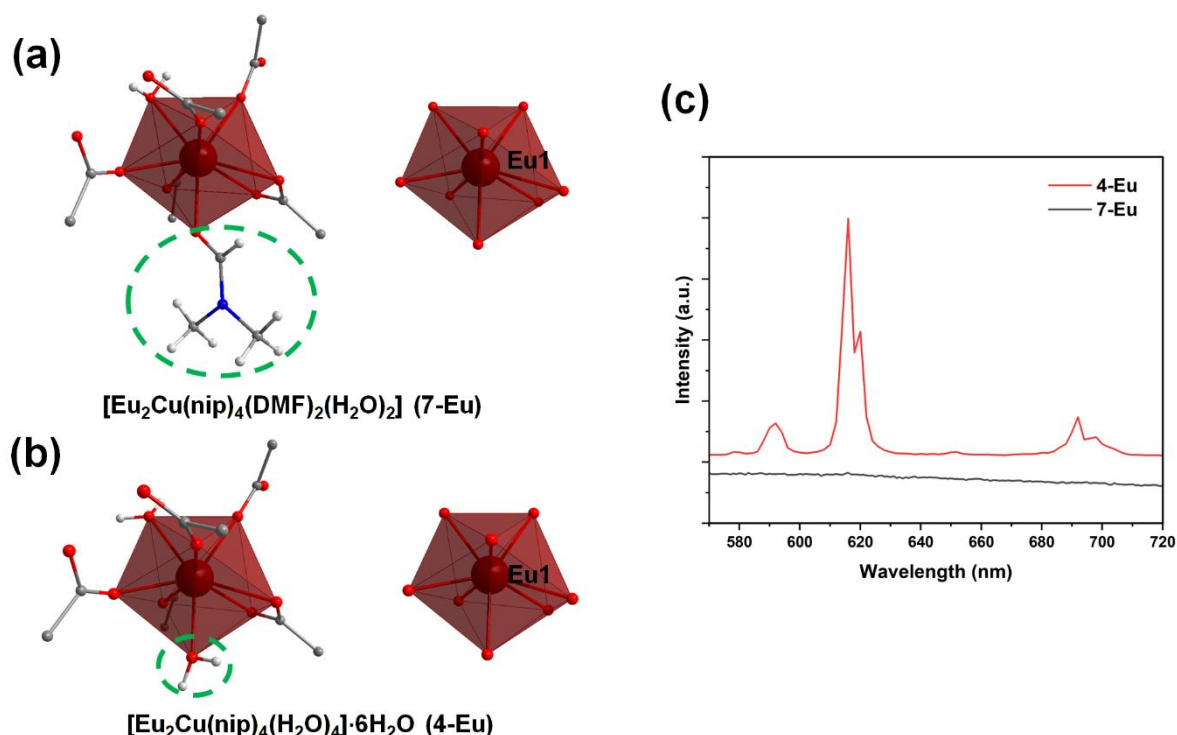


Figure 5.58. Coordination polyhedra of Eu^{3+} showcasing ligands in (a) **7-Eu** and (b) **4-Eu**; (c) Photoluminescence spectra of **7-Eu** and **4-Eu**.

For the compound **7-Eu**, the solid-state photoluminescence (PL) spectra were measured to investigate its emission properties.^[116] Similar procedure as for the compound **2-Eu** (Chapter 4, section 4.10.5) were considered here. However, when an emission spectrum was measured by exciting the sample with an arbitrary wavelength of 375 nm, no emission was observed (Figure 5.58c). This was also the case, when the sample were excited at characteristic absorption wavelengths of Eu^{3+} ions (394 nm and 465 nm).

For comparison, the PL measurements were repeated for **4-Eu** which is structurally same as **7-Eu**, except that the former compound has two water ligands, while the latter one has a water and a DMF ligand (Figure 5.58a, b). The compound **4-Eu** was emissive, although the intensity was low (Figure 5.58c).

The quenching of photoluminescence in **7-Eu** can be explained by the non-radiative decay via vibronic relaxations. The DMF ligand coordinated to Eu^{3+} has C-H and C-N oscillators which can act as non-radiative relaxation channels (Figure 5.58a). Albeit the

two water ligands in **4-Eu** offer non-radiative relaxation channels, this is still minor compared to DMF. This is why **4-Eu** is still emissive with weak PL intensity.

5.6.4 Thermogravimetric Analysis (TGA)

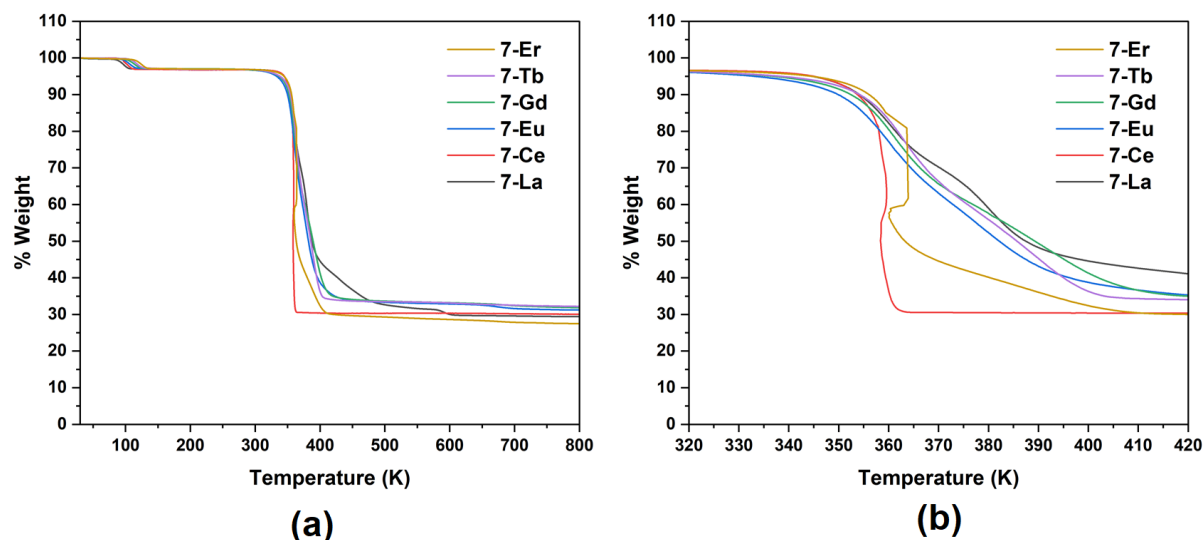


Figure 5.59. (a) TGA of **7-Ln** ($\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$ and (b) region between 320 °C and 420 °C shown as enlarged.

The thermal stability of HMOF compounds was investigated by TG analysis under air in the range of temperature 30 °C –700 °C.

For the compounds **7-Ln**, the derivatives for $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$ and Er^{3+} were chosen (Figure 5.59.a). In all compounds, a weight loss of about 4% is observed from 85 °C up to around 140 °C which correspond to loss of water molecule and DMF. The H_2nip ligand decomposition start at about 340 °C and after about 410 °C. The final phase obtained is probably the mixture of oxides of copper and various lanthanides. In each case, the thermal decomposition of the ligand follows a slightly different pattern. A drop in temperature was observed for some compounds between 345 °C and 385 °C as the heating continued (Figure 5.59b). Similar behaviour has been seen in some MOF compounds, but has not been conclusively explained.^[113-114]

The TGA analysis of the blue crystals of **9-La-A** and green crystals of **9-La-B**, show almost same thermal decomposition (Figure 5.60a), suggesting that these compounds are isostructural as seen from the SCXRD data. About 10% weight loss is observed up to 90 °C indicating loss of lattice solvents. Further loss in weight above 100 °C may be

due to the loss of coordinated water and DMF. The H₂nip ligand decomposition starts around 300 °C.

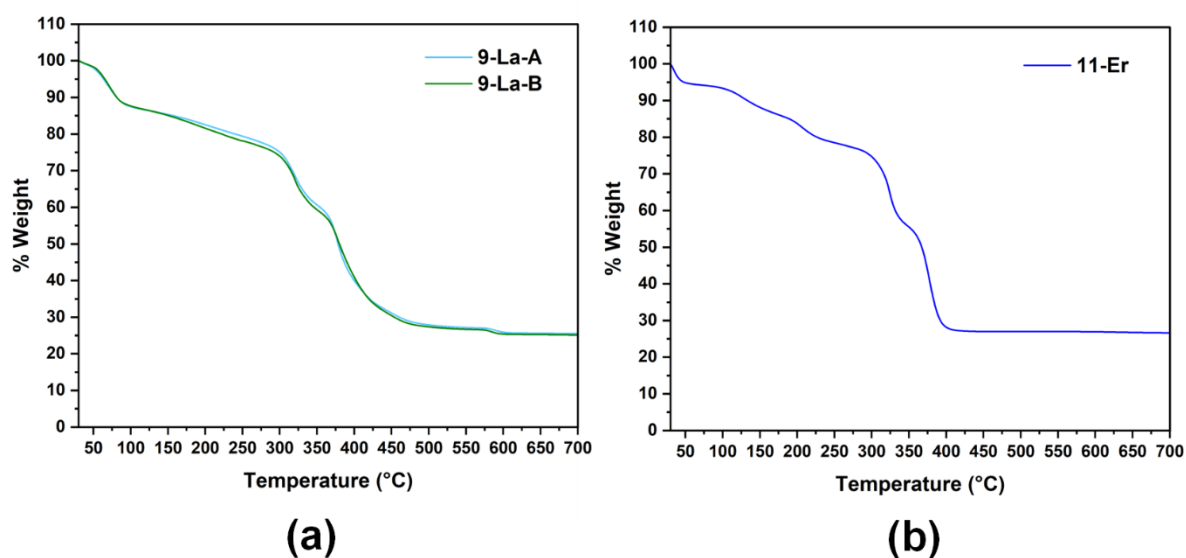


Figure 5.60. TGA of (a) **9-La-A** and **9-La-B**; (b) **11-Er**.

The three-dimensional HMOF **11-Er** shows low thermal stability compared to other MOFs (Figure 5.60b). A weight loss of about 5% was seen below 50 °C is probably because of the loss of solvent molecules in the voids as temperature goes higher. This in turn destabilises the structural integrity of the compound and undergo gradual decomposition below 300 °C. Beyond this point, the decomposition of the H₂nip ligand is visible.

5.7. Solvent-Mediated Structural Transformations in Ln-HMOFs

As discussed in this chapter, the reaction mixture obtained by the addition of lanthanide nitrate in Cu-H₂nip gel in water-DMF solvent system resulted in dark blue crystals of [Ln₂Cu(nip)₄(H₂O)₂(DMF)₂] (**7-Ln**), for Ln³⁺ = Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Y³⁺, when heated at 95 °C. Even though these were the thermodynamic products, these crystals underwent structural transformation because of the chemical modification of the solvent system due to prolonged heating in the oven. In short, the thermal hydrolysis of DMF was the driving force behind the structural transformation in Ln-HMOFs.

However, for different set of lanthanides in **7-Ln**, the transformation at 95 °C gave different outcome. For instance, **7-La** gave a mixture of [La(nip)(HCOO)(H₂O)] (**8-La**) and lanthanum formate, while the crystals of **7-Ln** for Ln³⁺ = Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺ dissolved and crystallised as [Ln₂(OAc)₂(nip)₂(H₂O)₂] $\cdot$ xH₂O (**3-Ln**). In both cases,

the formation of Cu_2O was also observed. For **7-Tb**, **7-Dy**, **7-Ho** and **7-Er**, such solvent-mediated structural transformation into crystalline products was not observed. This could be attributed to more stability of these crystals compared to the other analogues in the reaction medium.

In general, larger (lighter) trivalent lanthanide ions prefer higher coordination numbers (e.g., 9 or 10) and smaller (heavier) ones prefer smaller coordination numbers (e.g., 8). In the case of Cu^{2+} ions, coordination numbers of 6 and 5 are the most common ones. In a 6-coordinated Cu^{2+} systems, the two axial ligands will usually be further away from the metal centre compared to the remaining four in-plane ligands, due to Jahn-Teller distortion. At some point, these axial ligands are too far away from the Cu^{2+} ion and the interaction cannot be considered as a coordination bond, resulting in a square planar coordination.

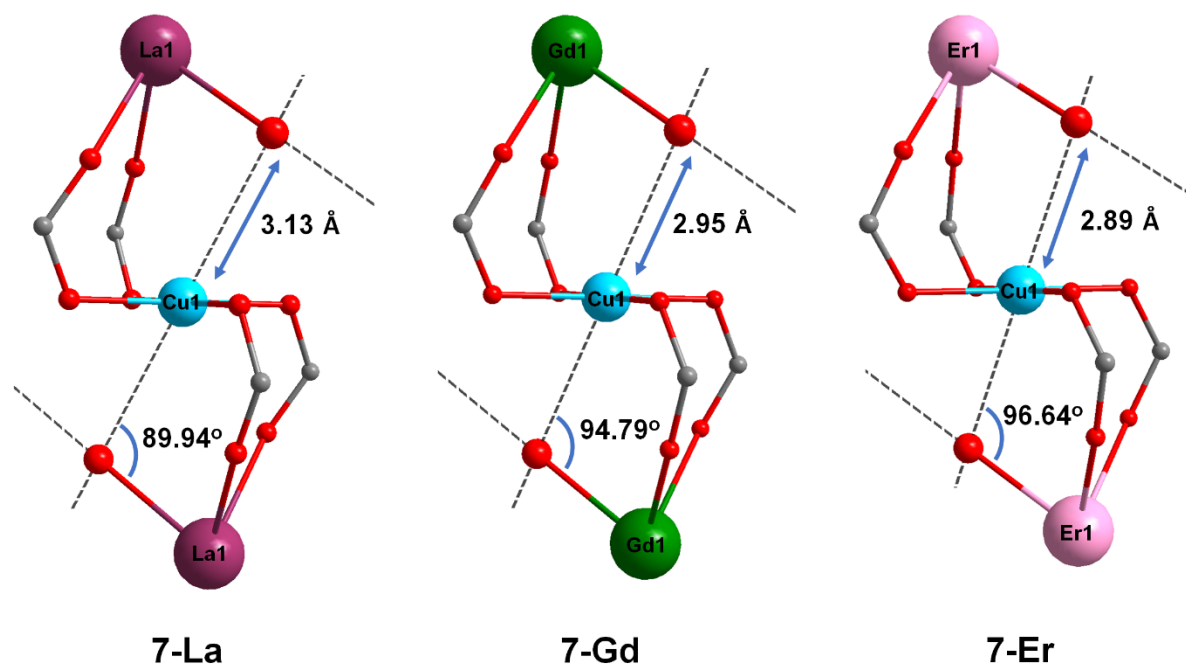


Figure 5.61. Comparison of coordination environment of Cu^{2+} ion in **7-La**, **7-Gd** and **7-Er**.

In **7-Ln**, these two factors can be used to explain the solvent-mediated structural transformation. As representative examples, **7-La**, **7-Gd** and **7-Er** are considered here (Figure 5.61). Over a period of 10 days of heating reaction (at 95 °C in oven), the dark blue crystals of **7-La** transformed into pale yellow crystals of **8-La** (with side product lanthanum formate). At the same time, only a fraction of crystals of **7-Gd** transformed into **3-Gd** and **7-Er** remained almost intact. Clearly, the rate of transformation process reduces from **7-La** to **7-Er**.

The Ln_2Cu core unit here consist of two 8-coordinated Ln^{3+} ions and a four coordinated Cu^{2+} ion (Cu1), which are interconnected by four carboxylate groups from nip^{2-} ligands. Cu1 has a square planar geometry and is on the centre of inversion of the Ln_2Cu core unit in all the cases. There is a molecule of water on each of the two Ln^{3+} ions away from the Cu^{2+} ion. This is too far away to be considered as an interaction with the Cu^{2+} ion (Figure 5.61). When these two water molecules are considered for a six-coordinated Cu, the corresponding coordination polyhedra shows large deviation from ideal octahedra. This deviation in octahedral coordination around the Cu^{2+} ions decreases as we move from **7-La**, **7-Gd** and **7-Er** as indicated by the corresponding CShM values from SHAPE analysis (Figure 5.62). This is further visible from the angle at which the Cu-H₂O bond is deviated from the 4-fold axis formed by the square planar Cu1 . The Cu-H₂O bond distance is also decreasing with lesser distortion in the structure.

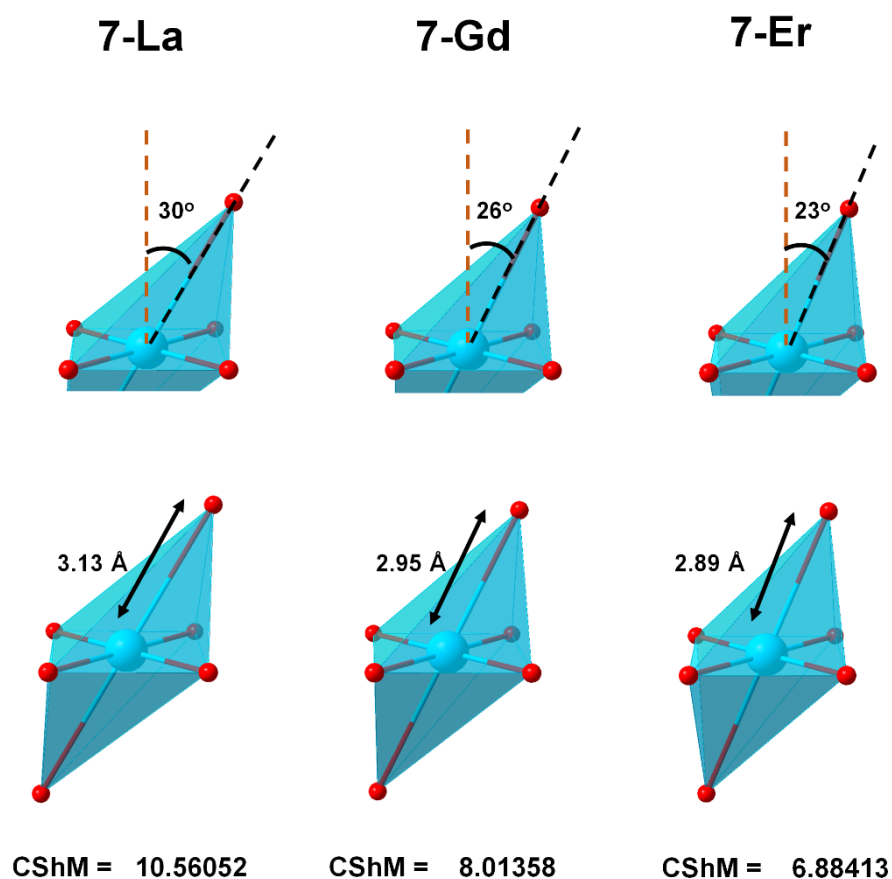


Figure 5.62. Comparison of 6-coordinated Cu^{2+} ion in **7-La**, **7-Gd** and **7-Er**.

As the lanthanide ion gets smaller from La^{3+} to Er^{3+} , this distortion of 6-coordinated geometry around Cu^{2+} also gets smaller (Figure 5.62). Furthermore, the coordination number for lanthanide ions here in **7-Ln** is 8, which is favoured by the smaller lanthanide ions. This is probably why the larger lanthanide-analogues of **7-Ln** undergo faster

dissolution and form the homometallic MOFs which has Ln^{3+} ions with coordination number 9 or 10. The stability of the compounds **7-Ln** in the reaction mixture increases for smaller lanthanide analogues and the rate of dissolution is lower. Here, the lanthanide ions are already in a favourable 8-coordinated environment.

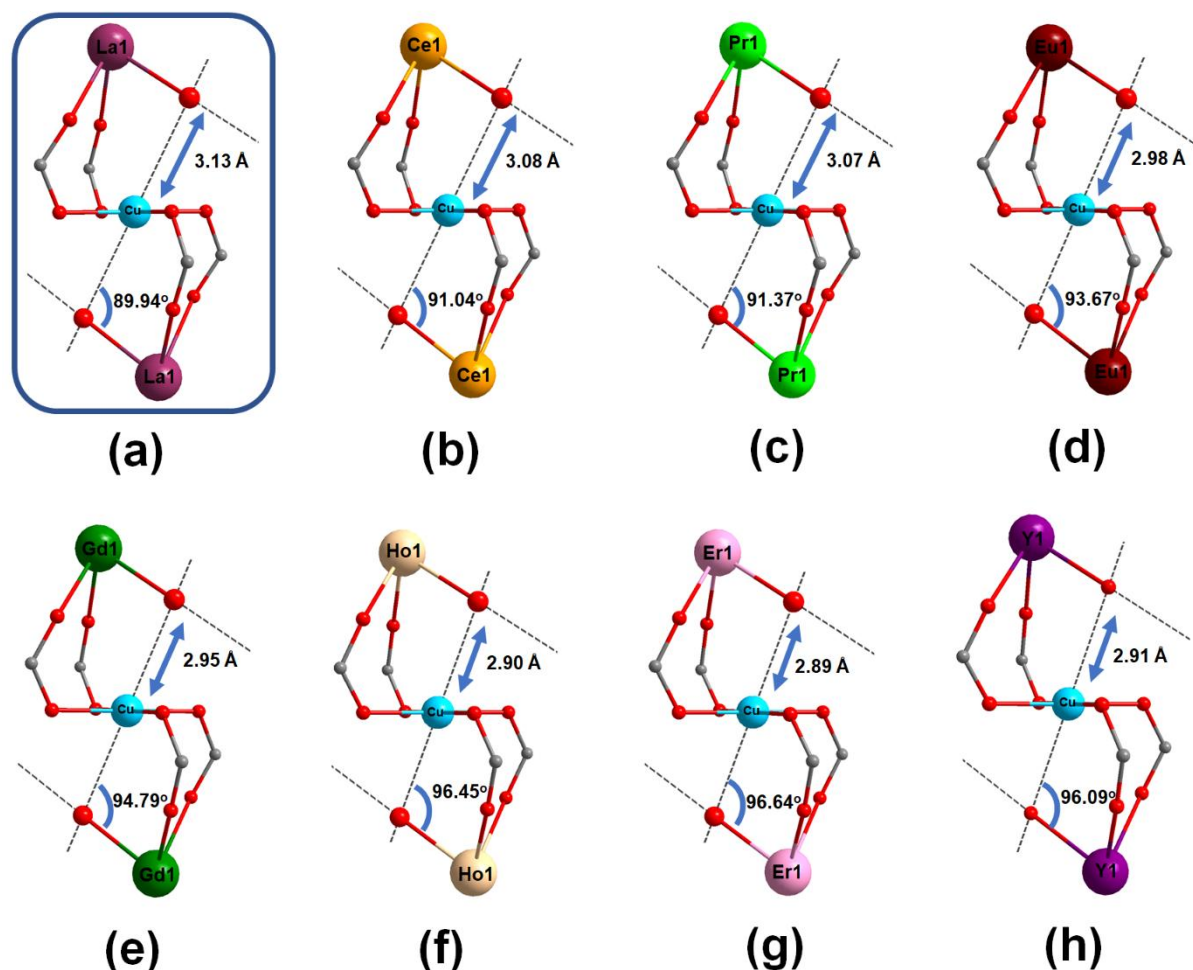


Figure 5.63. Comparison of coordination environment of Cu^{2+} ion in **7-Ln**.

An overview of the coordination environment of Cu^{2+} ion in selected lanthanide analogues of **7-Ln** is shown in Figure 5.63.

5.8. Conclusion and Outlook

In this chapter, a series of Cu-Ln heterometallic MOFs were synthesized in a water-DMF solvent mixture, with a focus on understanding solvent-mediated structural transformations. Initially, La^{3+} -based HMOFs, designated as **6-La** and **7-La**, were obtained under solvothermal conditions via Ostwald ripening. Among these, compound **7-La** underwent a structural transformation into the homometallic framework **8-La** upon prolonged heating. This transformation was attributed to the thermal hydrolysis of DMF,

and the concurrent formation of Cu₂O particles provided evidence for the reaction dynamics involved.

To explore the effect of reagent stoichiometry on structural stability, several trial reactions with varying molar ratios were performed. Despite these changes, including the addition of excess H₂nip, **7-La** remained the predominant product, suggesting its thermodynamic stability. The excess added H₂nip in the reaction led to an increase in the yield of La₂Cu crystals and suppression of Cu₂O formation. This is probably attributed to consumption of unreacted Cu²⁺ ions (and La³⁺ ions) in the solution with the H₂nip added in excess. Interestingly, long-term storage of **7-La** crystals at room temperature led to a transformation into a new phase, **9-La**, which retained the same crystal structure but exhibited differences in colour and Cu²⁺ site occupancy disorder.

The synthetic approach was extended to other lanthanide ions, resulting in analogous **7-Ln** compounds for Ln³⁺ = Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Y³⁺. For heavier lanthanides such as Dy³⁺, Ho³⁺ and Er³⁺, porous HMOFs with very large unit cells and channel structures were initially formed as kinetic products. These subsequently dissolved and recrystallized into the thermodynamically stable **7-Ln** phase, also through Ostwald ripening. Several of these structures displayed significant disorder, opening up new possibilities for advanced crystal engineering.

Cu-Ln HMOFs show diverse structures that change with solvent conditions and lanthanide type. Better control and understanding of these factors will help design materials with targeted functions. Achieving phase-pure porous MOFs remains a major synthetic challenge; thus, future work will focus on optimizing synthesis and conducting detailed characterizations, including gas adsorption studies. Additionally, investigating their photoluminescence, magnetic behaviour and catalytic performance will be important to explore their potential in sensing, magnetism and catalysis applications.

6. Polyoxometalate-based Hybrids as Metalloligands for Polyoxometalate-based Coordination Polymers

6.1. Introduction

Cluster-based frameworks, have been of interest because of the unique structure topologies and applications.^[63, 146] Assembly of transition-metal (TM) clusters with organic linkers into metal-organic frameworks (MOFs) has been a widely considered approach for that. Such molecules have found applications in the fields of magnetism,^[19] catalysis,^[17, 147] luminescence,^[21, 148] etc. Use of lacunary versions of polyoxometalate (POM) clusters like Keggin and Wells – Dawson also has been done to incorporate metal ions creating cluster compounds. Anderson-Evans polyanions has a characteristic planar structure, and can have a wide range of heteroatoms in the centre. These particular POMs have been widely studied to incorporate tripodal tris(hydroxymethyl) methane derivatives (tris-R) ligand, giving rise to tris- functionalized Anderson-Evans (AE) hybrids.^[56-57] The R- group on the alkoxyl ligands opens up diversity and tunability of the POM-hybrids thus formed.^[36, 61] The post-functionalization can be done at R-group, based on amide, imine, coupling reactions etc. and this opens up lot of opportunities in new hybrid molecules. One of the first Anderson-Evans POM hybrids, (*n*Bu₄N)₃[Mn^{III}Mo₆O₁₈{(OCH₂)₃C-NH₂}₂] (**MnMo₆(TRIS)₂**) has been used widely to functionalize and use it for various applications.^[52]

The AE POM hybrids with the functionalised organic ligands grafted onto the inorganic cluster can be used to chelate metal ions to make extended structures as in conventional MOFs. Polyoxometalate-based Metal-Organic Frameworks (POMOFs) and Polyoxometalate-based Coordination Polymers (POMCPs) have been synthesized from functionalized Anderson-Evans POM-hybrid linkers with transition metal ions and lanthanide ions as nodes.^[65, 67-68, 149-151]

In this chapter, several hydroxy-functionalized Anderson–Evans POM hybrids were synthesized by the post-functionalization of **MnMo₆(TRIS)₂**. Some of the hybrid linkers were used to synthesize POMCPs by the reaction with La³⁺ ions.

6.2. Post-functionalization by Schiff Base Reactions

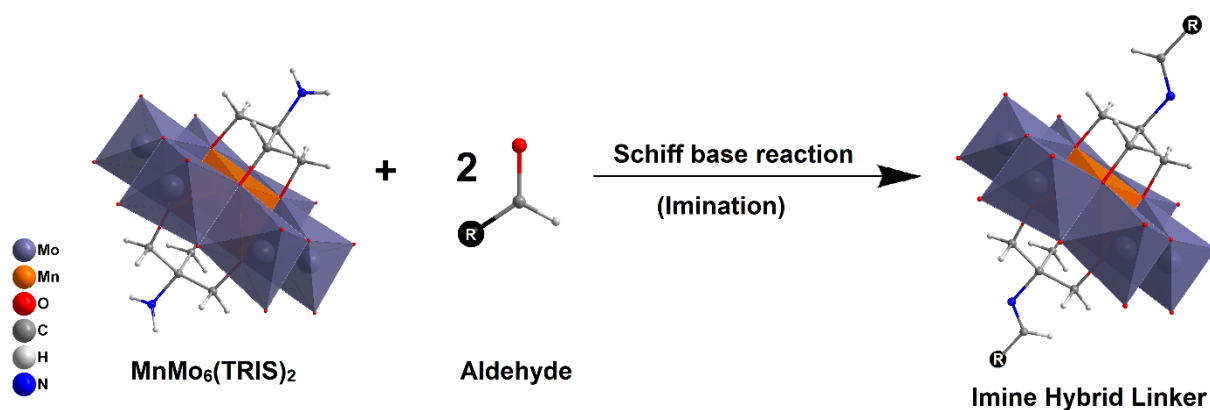


Figure 6.1. Schiff base reaction to functionalize $\text{MnMo}_6(\text{TRIS})_2$ POM hybrid with aldehyde (black sphere R = substituted aromatic group).

The double-decorated Anderson Evans hybrid with tris(hydroxymethyl)aminomethane (TRIS) ligand, $(^n\text{Bu}_4\text{N})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{C-NH}_2\}_2]$ ($\text{MnMo}_6(\text{TRIS})_2$)^[57] was chosen in order to make new hybrid linkers. This hybrid has free amino ($-\text{NH}_2$) groups on either side that can be functionalized by the organic reactions such as amidation, polymerization, nucleophilic substitution, Schiff base reactions etc.^[152] In this work, the functionalization was carried out by Schiff base reaction with aldehydes (Figure 6.1).

The synthesis of six imine hybrid linkers (**HL-1** to **HL-6**) via Schiff base reaction were planned. Six hydroxy-functionalized aromatic aldehydes were considered for that (Figure 6.2) out of which some were multifunctional with additional alkoxy groups on the aromatic ring. For the synthesis, orange crystals of $\text{MnMo}_6(\text{TRIS})_2$ were dissolved in DMF and then the aldehydes were added and stirred with heating for 30 minutes. The clear reaction mixtures thus obtained were transferred to small vials and placed in a diethyl ether atmosphere and after a few days, orange crystals of hybrid linkers were obtained. These were collected and dried in air.

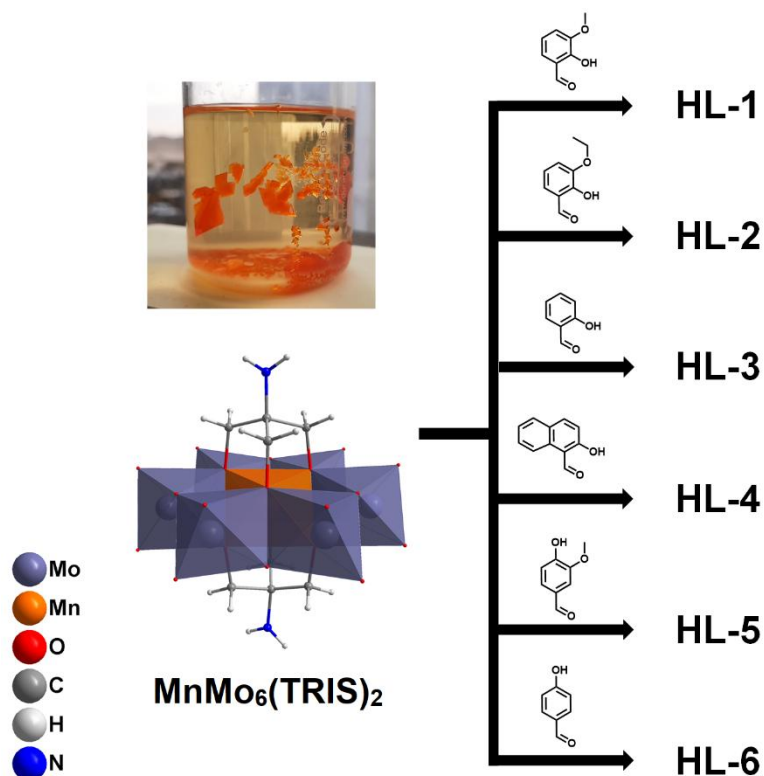


Figure 6.2. Aldehydes considered for Schiff base reaction with $\text{MnMo}_6(\text{TRIS})_2$ POM hybrid to synthesize the hybrid linkers.

6.3. Hydroxy-Functionalized Imine Hybrid Linkers

As shown in the Figure 6.2, six different imine hybrid linkers (**HL-1** to **HL-6**) were aimed by the reaction of six hydroxy (-OH)-substituted aromatic aldehydes with $\text{MnMo}_6(\text{TRIS})_2$. In some of them, there were additional alkoxy (-OMe, -OEt) functional groups as well. The first hybrid linker **HL-1** is based on *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde). This was chosen as the reference while choosing other functionalised aldehydes with similar functional groups to prepare other hybrid linkers (Figure 6.3). The six hybrid linkers are given as follows:

- **HL-1:** Derived from *o*-vanillin (2-hydroxy-3-methoxybenzaldehyde).
- **HL-2:** Derived from 3-ethoxysalicylaldehyde (3-ethoxy-2-hydroxybenzaldehyde).
- **HL-3:** Derived from 2-hydroxybenzaldehyde.
- **HL-4:** Derived from 2-hydroxy-1-naphthaldehyde.
- **HL-5:** Derived from vanillin (4-hydroxy-3-methoxybenzaldehyde).
- **HL-6:** Derived from 4-hydroxybenzaldehyde

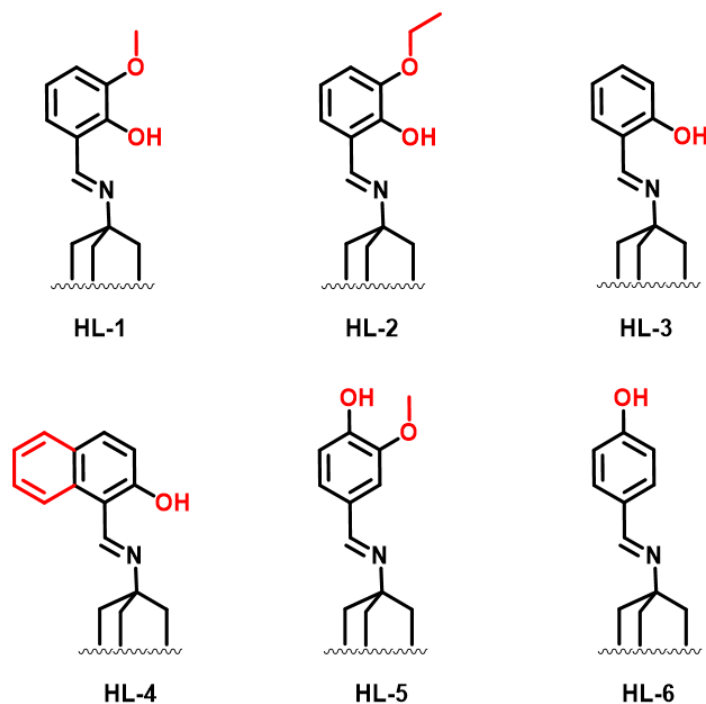


Figure 6.3. Representation of organic counterparts of hydroxy-functionalized POM hybrid linkers

In particular for the linker **HL-1**, three different types were identified by crystal structure determination and are labelled as **HL-1a**, **HL-1a** and **HL-1a**. These distinctions were ignored when this linker was used for the synthesis of POMCPs later and the label **HL-1** was used ambiguously.

Coordination chemistry of Schiff base complexes based on *o*-vanillin^[153] has been of wide interest. The chemistry involving the 3-methoxy and 2-hydroxy groups with the coordination with lanthanide ions as well as transition metal ions have been well explored and have given rise to different homo- and heterometallic compounds with interest in applications like magnetism.^[154] Hence the hybrid linker **HL-1** was chosen as a start to try the coordination with La^{3+} ions to make the coordination polymers.

6.3.1. Crystallography

In the following section, each hybrid linkers are described according to the single crystal X-ray diffraction (SCXRD) data. The full composition of each hybrid linkers from the crystallographic data is given in Table 6.1.

Table 6.1. Short name and full formula of the hybrid linkers.

<u>Hybrid Linker</u>	<u>Short name</u>	<u>Full Chemical Formula</u>
HL-1a	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$
HL-1b	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot \text{DMF}$
HL-1c	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 0.3\text{DMF} \cdot 1.3\text{H}_2\text{O} \cdot 0.3\text{Et}_2\text{O}$
HL-2	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}\}_2] \cdot \text{DMF}$
HL-3	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_4)(2\text{-OH})\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})\}\}_2] \cdot 2\text{DMF}$
HL-4	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2] \cdot 0.5\text{DMF}$
HL-5	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(3\text{-OCH}_3)(4\text{-OH})\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(3\text{-OCH}_3)(4\text{-OH})\}\}_2] \cdot \text{DMF} \cdot \text{CH}_3\text{CN}$
HL-6	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_4)(4\text{-OH})\}\}_2]$	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(4\text{-OH})\}\}_2] \cdot 2\text{DMF}$

6.3.1.1. $(n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]$ or **HL-1**

The compound **HL-1** is obtained by the Schiff base reaction of one equivalent of $\text{MnMo}_6(\text{TRIS})_2$ with two equivalents of *o*-vanillin in DMF. The synthesis has been done multiple times at different weather conditions and the DMF used for the reactions were not dried. DMF easily absorb water from atmosphere and water is produced as a by-product during the Schiff base reaction. The moisture content in DMF can alter the crystal packing of the products and this was visible with the case of hybrid linker **HL-1** where 3 different crystal systems has been identified (*vide infra*).

When the hybrid linkers are in solution, the C-N bond of the TRIS ligand attached to the inorganic MnMo_6 core can freely rotate. (Figure 6.4). However, upon crystallization, this rotation is restricted, and the organic moieties arrange themselves to maximize packing efficiency in the crystal lattice. The presence of solvent molecules in the lattice plays a significant role in this arrangement.

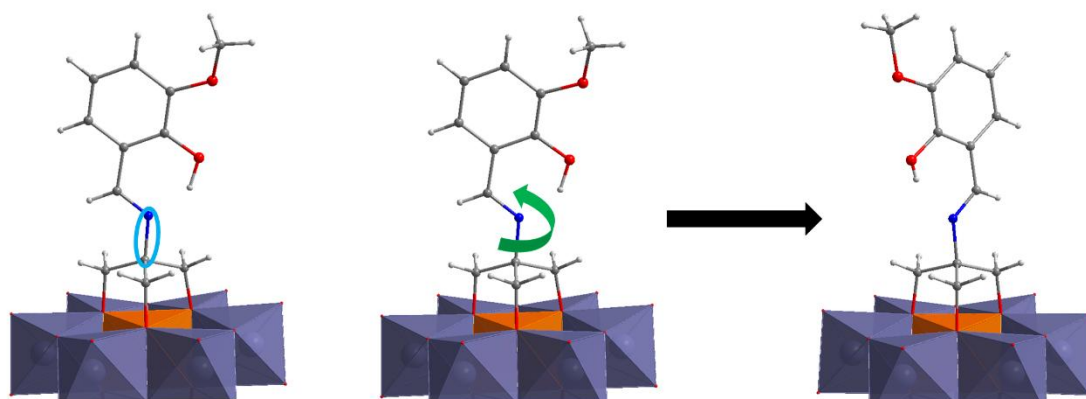


Figure 6.4. Free rotation across the C-N bond of the TRIS ligand attached to the inorganic MnMo_6 core. Color code: Blue-grey octahedra: molybdenum, orange octahedra: manganese, dark-grey spheres: carbon atoms, red spheres: oxygen atoms, blue spheres: nitrogen, pale-grey spheres: hydrogen atoms.

The two organic parts (aromatic rings with functional groups like -OH, -OMe etc.) in the hybrid can be arranged either '*cis*' or '*trans*' to each other with respect to a pseudo mirror plane along the MnMo_6 inorganic core (Figure 6.5). For the *cis*-form of the hybrid, there is no centre of symmetry, while for the *trans*-form, the inversion centre lies on the central Mn^{3+} ion.

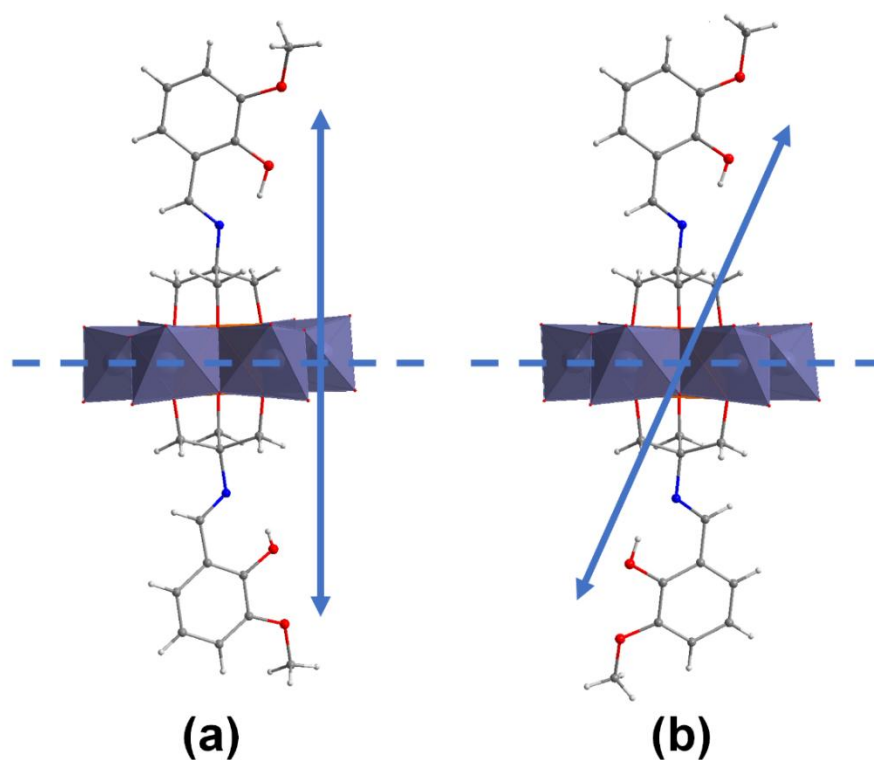


Figure 6.5. Aromatic rings (with OH and -OMe groups) oriented (a) ‘cis’ and (b) ‘trans’ to each other with respect to the MnMo₆ inorganic core in **HL-1**.

Table 6.2. Unit cell parameters of **HL-1a**, **HL-1b** and **HL-1c**.

Hybrid Linker	HL-1a	HL-1b	HL-1c
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pna</i> 2 ₁
a (Å)	23.4458(8)	16.4624(2)	28.6588(2)
b (Å)	15.0720(3)	23.6007(3)	45.5828(3)
c (Å)	27.8115(8)	24.9252(3)	23.1199(2)
α (°)	90	87.616(1)	90
β (°)	94.075(3)	87.717(1)	90
γ (°)	90	85.369(1)	90
V (Å ³)	9803.04(48)	9637.6(2)	30202.6 (4)
Z	4	4	12

For the hybrid linker **HL-1**, three types of crystals have been identified, depending on which isomers are present in the crystal lattice: **HL-1a**, **HL-1b** and **HL-1c**. In **HL-1a**, the hybrid molecules are in the 'cis' form in the crystal lattice. In **HL-1b**, this arrangement is entirely 'trans'. The crystals of **HL-1c** features both isomers in the same unit cell. The variable amount of DMF and water in the lattice could be reason for different crystal packings and hence different space groups for each form (Table 6.2).

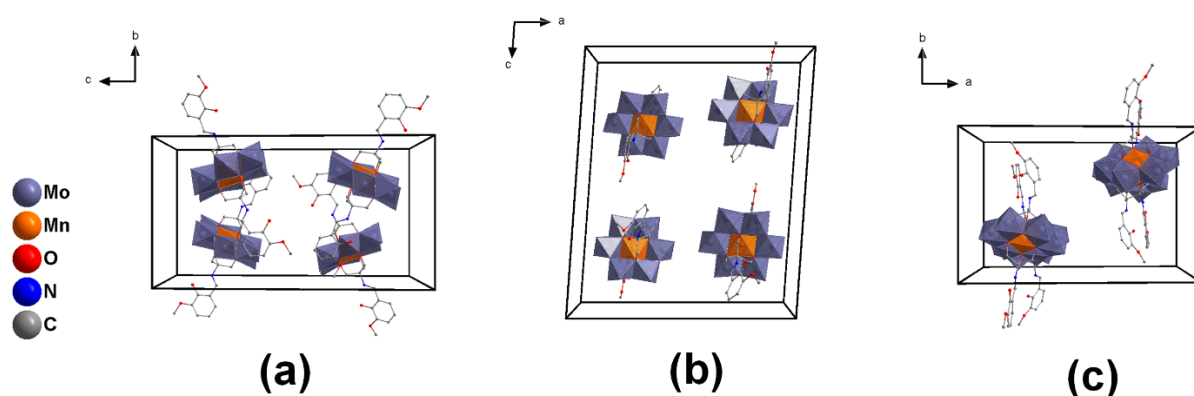


Figure 6.6. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-1a** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}^+$) cations, lattice solvent and hydrogen atoms are omitted for clarity.

HL-1a crystallizes in the monoclinic centrosymmetric space group $P2_1/c$. Even though the hybrid molecule is itself non-centrosymmetric, the crystal lattice is centric. Each anionic $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]^{3-}$ unit, is associated with three tertabutylammonium ($n\text{Bu}_4\text{N}^+$) counter cations. In the unit cell there are four anionic units ($Z=4$) (Figure 6.6) and associated counter cations, with two DMF molecules per anionic unit as lattice solvents.

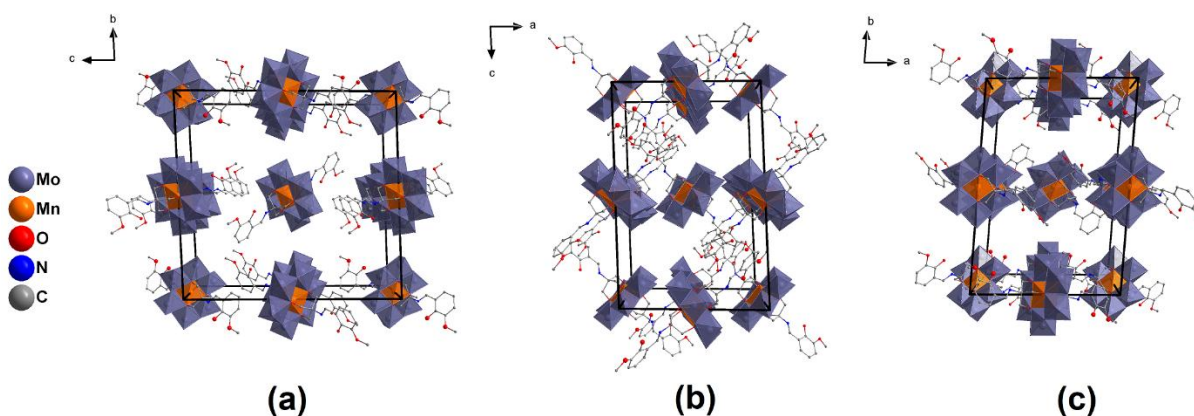


Figure 6.7. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-1b** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}^+$) cations, lattice solvent and hydrogen atoms are omitted for clarity.

In the case of **HL-1b**, the hybrid linker crystallizes in the triclinic space group $P\bar{1}$. In the unit cell there are four anionic units ($Z=4$) (Figure 6.7) and associated ($n\text{Bu}_4\text{N}$)⁺ counter cations, and a DMF per anionic unit.

HL-1c which features both *cis* and *trans* isomers has a relatively larger cell volume of 30202.6(4) Å³ and is crystallised in acentric space group $Pna2_1$. In a unit cell there are 12 anionic units ($Z=12$), and associated ($n\text{Bu}_4\text{N}$)⁺ counter cations, and a DMF, three water and a diethyl ether. Out of the 12 units, 8 are of *cis* form and 4 are of *trans* form (Figure 6.8).

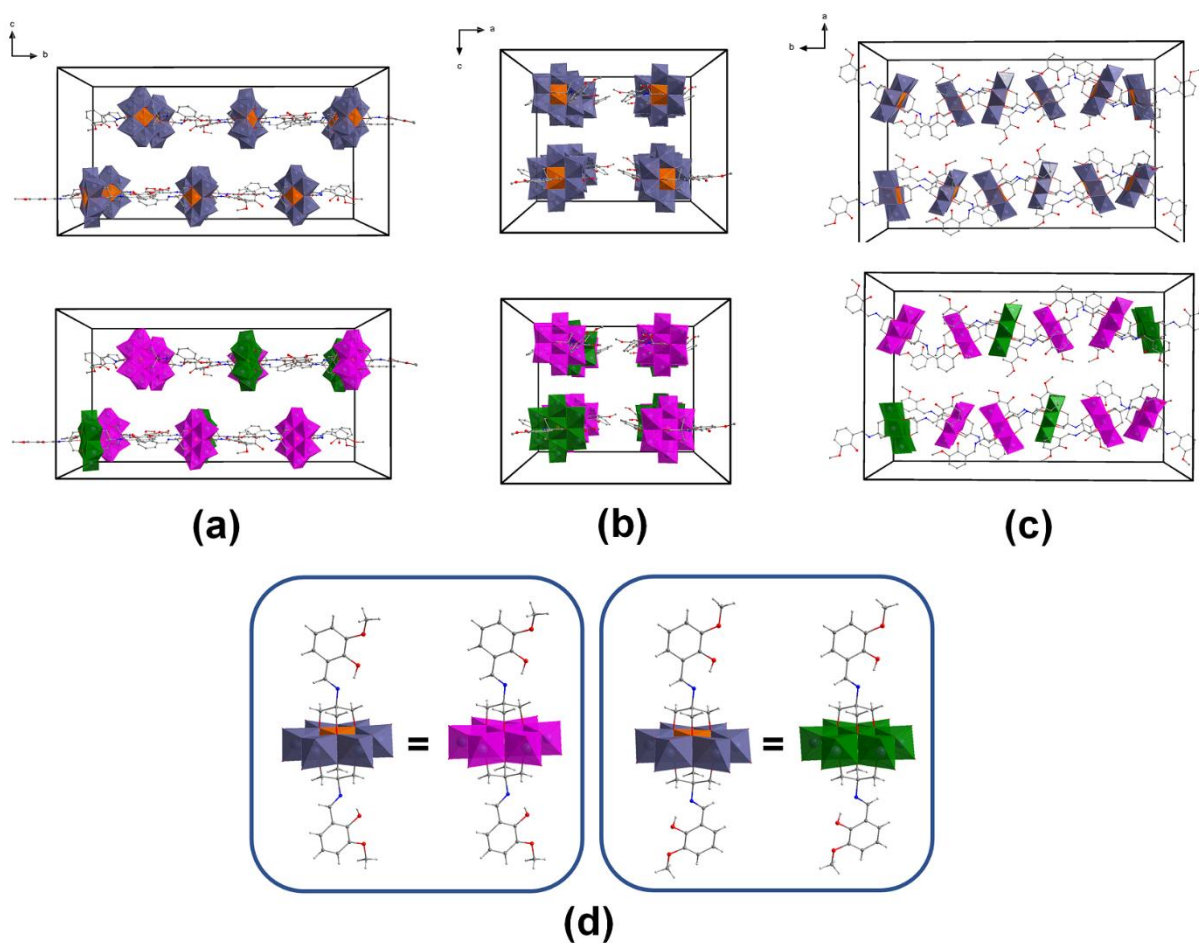


Figure 6.8. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-1c** in the unit cell when viewed along a, b, c axes (top: regular representation of the polyanions; bottom: representation distinguishing the *cis* and *trans* forms of the Anderson-Evans polyanions in the unit cell). ($n\text{Bu}_4\text{N}$)⁺ cations, lattice solvent and hydrogen atoms are omitted for clarity; (d) Representation of Anderson-Evans polyanions, the *cis* form: pink polyhedra and the *trans* form: green polyhedra.

Apart from the structural difference of the arrangement of organic part in the crystal structure, the variants in compound **HL-1** does not have any significant difference in the

context of using as linker for the synthesis of POMCPs in solution phase. The label **HL-1** was used ambiguously hereafter.

6.3.1.2. ($n\text{Bu}_4\text{N}$)₃[(MnMo₆O₁₈){((OCH₂)₃CN=CH{(C₆H₃)(2-OH)(3-OC₂H₅))}}₂] or **HL-2**

In crystal lattice of **HL-2** (Figure 6.9) for each [(MnMo₆O₁₈){((OCH₂)₃CN=CH{(C₆H₃)(2-OH)(3-OC₂H₅))}}₂]³⁻ unit, there are three tertabutylammonium ($n\text{Bu}_4\text{N}$)⁺ counter cations and DMF lattice solvent. The organic groups in the anionic unit exist in *trans* form in the crystal lattice. The ethoxy group on the aromatic ring is disordered (Figure 6.11).

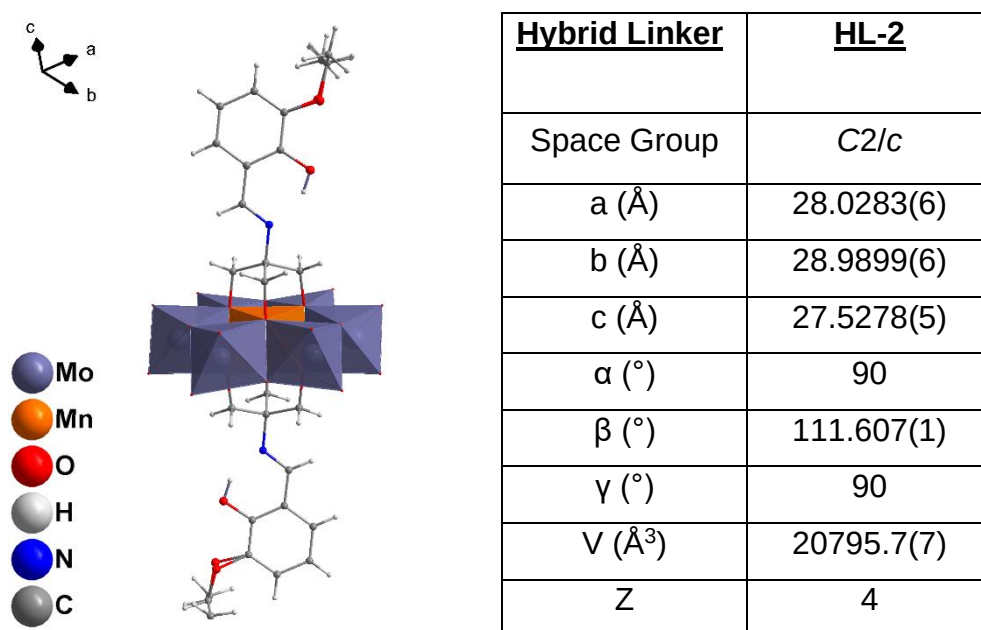


Figure 6.9. Polyanion and unit cell parameters for the crystals in **HL-2**.

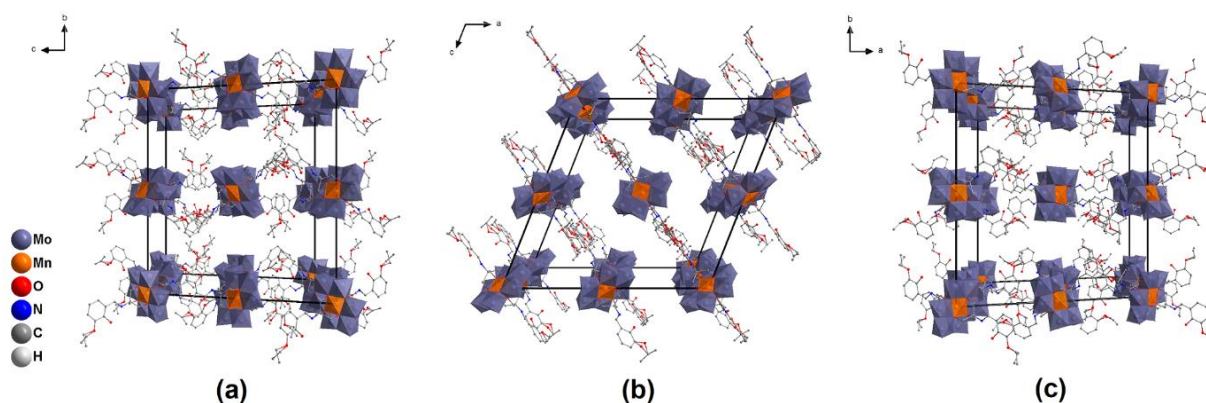


Figure 6.10. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-2** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}$)⁺ cations, lattice solvent and hydrogen atoms are omitted for clarity.

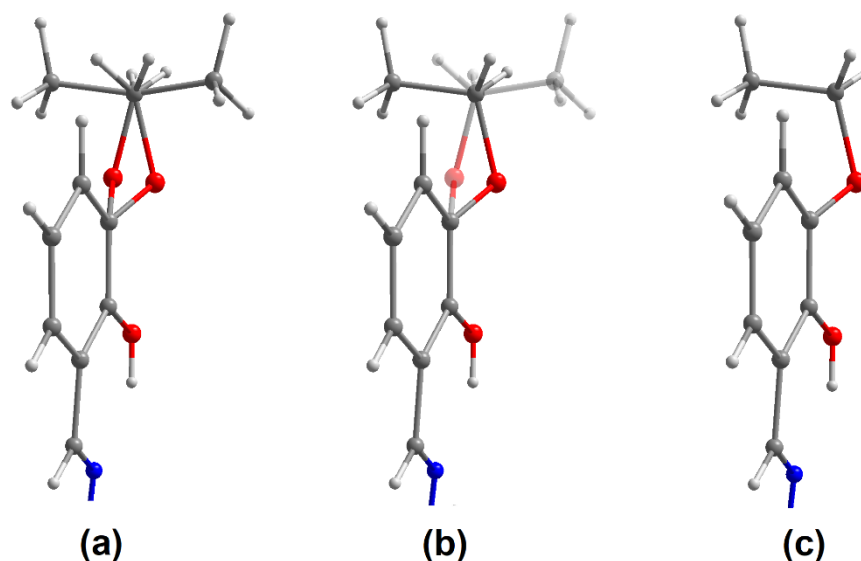
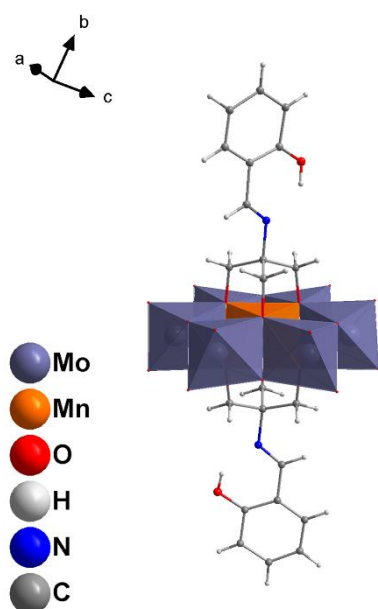


Figure 6.11. (a) The disordered ethoxy group on the aromatic ring in **HL-2**; (b) Atoms with lower occupancy is shown as transparent; (c) Ethoxy group with atoms with higher occupancy.

6.3.1.3. ($n\text{Bu}_4\text{N}$)₃[(MnMo₆O₁₈){((OCH₂)₃CN=CH{(C₆H₄)(2-OH))}}₂] or **HL-3**

The compound **HL-3** crystallizes in the monoclinic space group $P2_1/c$. There are twelve anionic units ($Z=12$) in the unit cell with three ($n\text{Bu}_4\text{N}$)⁺ cations per anion and DMF as lattice solvent. The organic groups in the anionic unit exist in *trans* form in the crystal lattice.



<u>Hybrid Linker</u>	<u>HL-3</u>
Space Group	$P2_1/c$
a (Å)	22.7361(2)
b (Å)	43.0724(3)
c (Å)	27.9725(3)
α (°)	90
β (°)	96.693(1)
γ (°)	90
V (Å ³)	27206.7(9)
Z	12

Figure 6.12. Polyanion and unit cell parameters for the crystals in **HL-3**.

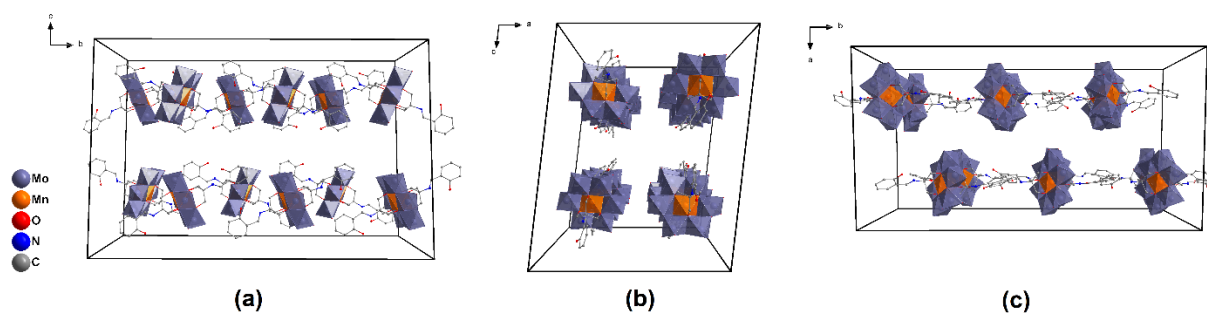


Figure 6.13. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-3** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}^+$) cations, lattice solvent and hydrogen atoms are omitted for clarity.

6.3.1.4. ($n\text{Bu}_4\text{N}$)₃[($\text{MnMo}_6\text{O}_{18}$)₃{(OCH_2)₃ $\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2]$ or **HL-4**

The compound **HL-4** crystallizes in the monoclinic space group $P2_1/c$. For each [$(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2\}^{3-}$ unit, there are three tertabutylammonium ($n\text{Bu}_4\text{N}^+$) counter cations. In the unit cell there are four anionic units ($Z=4$), and associated counter cations, with DMF molecule as lattice solvent. Here also the organic groups in the anionic unit exist in *trans* form. Even though the naphthyl groups are capable of π - π stacking, there is no such effective stacking in the crystal lattice of **HL-4** (Figure 6.15).

<u>Hybrid Linker</u>	<u>HL-4</u>
Space Group	$P2_1/c$
a (Å)	15.2602(5)
b (Å)	24.8325(11)
c (Å)	24.2613(10)
α (°)	90
β (°)	93.959(1)
γ (°)	90
V (Å ³)	9171.9(6)
Z	4

Figure 6.14. Polyanion and unit cell parameters for the crystals in **HL-4**.

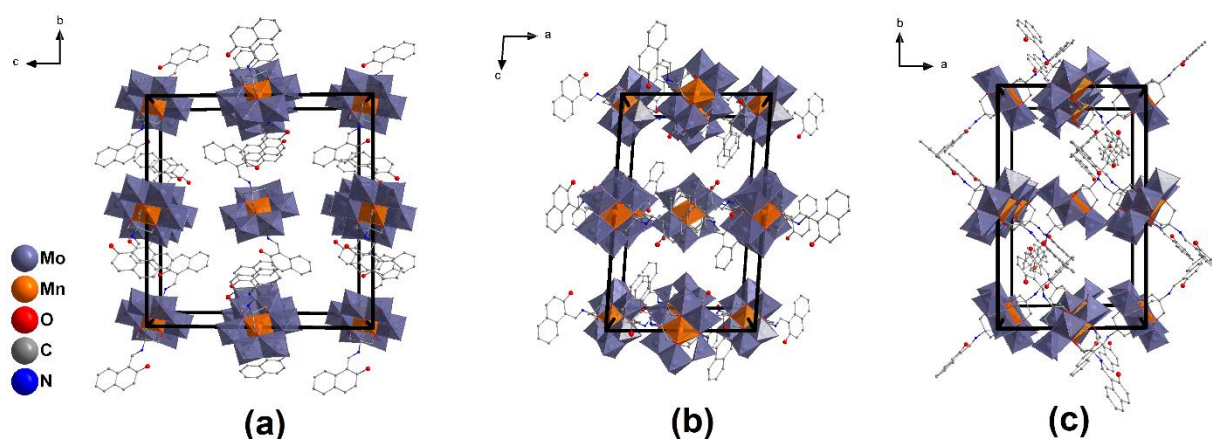
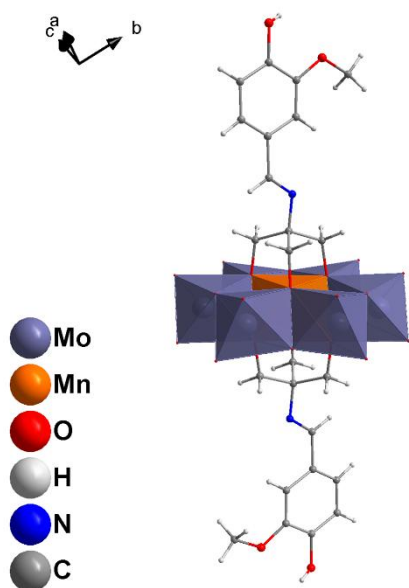


Figure 6.15. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-4** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}^+$) cations, lattice solvent and hydrogen atoms are omitted for clarity.

6.3.1.5. $(n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(3\text{-OCH}_3)(4\text{-OH})\}\}_2]$ or **HL-5**



<u>Hybrid Linker</u>	<u>HL-5</u>
Space Group	$P2_1/c$
a (Å)	25.1452(12)
b (Å)	17.0521(6)
c (Å)	22.5390(9)
α (°)	90
β (°)	97.326(4)
γ (°)	90
V (Å ³)	9585.3(7)
Z	4

Figure 6.16. Polyanion and unit cell parameters for the crystals in **HL-5**.

In the crystal structure of **HL-5**, for each $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(3\text{-OCH}_3)(4\text{-OH})\}\}_2]^{3-}$ anionic unit, has three tertabutylammonium ($n\text{Bu}_4\text{N}^+$) counter cations. In the unit cell there are four formula units ($Z=4$), with two DMF molecule, water and acetonitrile as lattice solvent per asymmetric unit. The acetonitrile has come from the starting material **MnMo₆(TRIS)₂** which was used as its crystallizing solvent.

It is worth mentioning that among all the hybrid linkers synthesized, the stability of **HL-5** in the crystallising medium was the lowest. Hydrolysis of the -C=N- bond in the imine linker was frequently observed and the single crystals chosen for SCXRD was sometimes the starting material $\text{MnMo}_6(\text{TRIS})_2$. This was the case even when excess of the aldehyde (vanillin) was considered for the synthesis. In order to get the structure of **HL-5**, the crystal structure determination had to be done within 2 days since its formation.

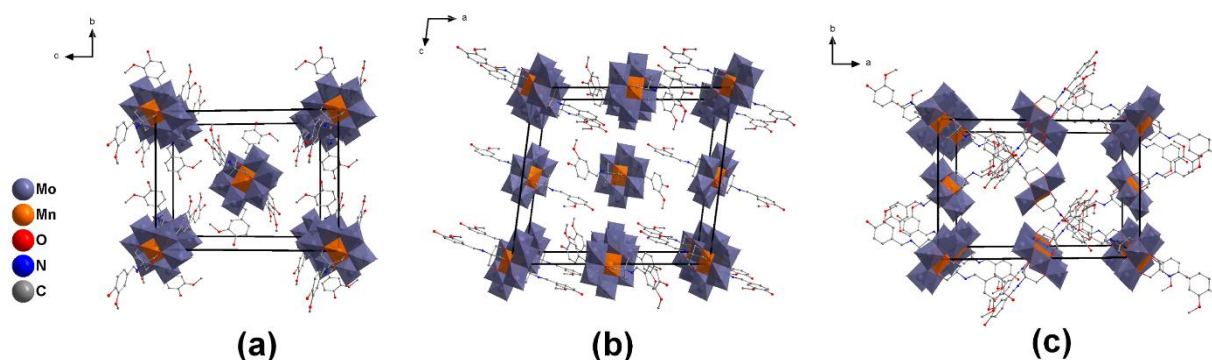


Figure 6.17. (a), (b), (c) Polyhedral representation of packing of anionic part of **HL-5** in the unit cell when viewed along a, b, c axes. ($n\text{Bu}_4\text{N}^+$) cations, lattice solvent and hydrogen atoms are omitted for clarity.

6.3.1.6. ($n\text{Bu}_4\text{N}$) $_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_4)(4\text{-OH})\}\}_2]$ or **HL-6**

Hybrid Linker	HL-5
Space Group	$P2_1/n$
a (Å)	14.4009(2)
b (Å)	28.8848(5)
c (Å)	23.1983(3)
α (°)	90
β (°)	$\beta = 93.938(1)$
γ (°)	90
V (Å ³)	9626.9(3)
Z	4

Figure 6.18. Polyanion and unit cell parameters for the crystals in **HL-6**.

The compound **HL-6** For each $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(4\text{-OH})\}\}_2]^{3-}$ unit, there are three tertbutylammonium ($n\text{Bu}_4\text{N}^+$) counter cations. In the unit cell there are

four anionic units ($Z=4$), and associated counter cations, with DMF molecule as lattice solvent. The anionic unit is centrosymmetric.

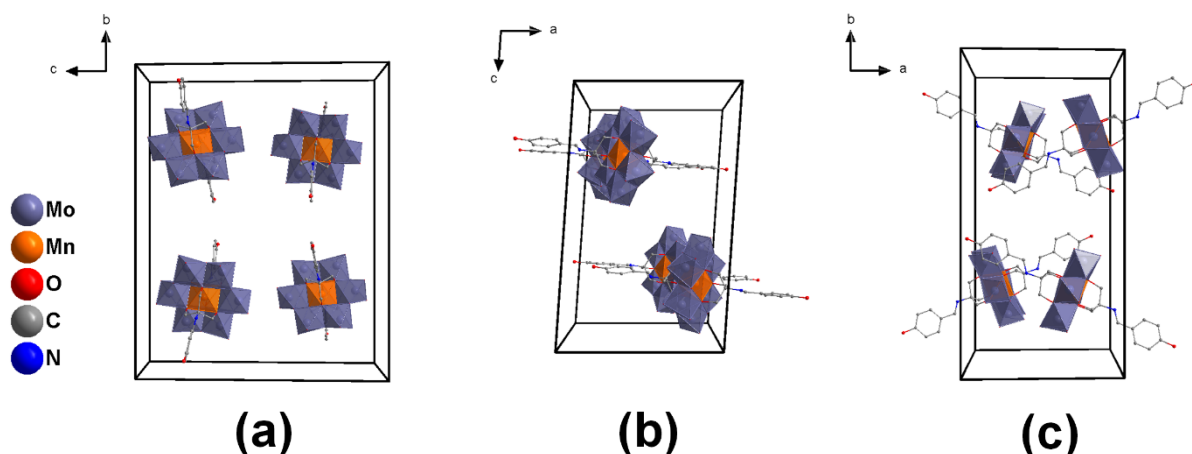


Figure 6.19. (a), (b), (c). Polyhedral representation of packing of anionic part of **HL-6** in the unit cell when viewed along a, b, c axes. $(n\text{Bu}_4\text{N})^+$ cations, lattice solvent and hydrogen atoms are omitted for clarity.

The anionic units of **HL-6** are arranged in the unit cell in such a way that the hydrogen atom of the -OH group at the 4- position of the aromatic ring in a unit point towards the terminal oxygen of the molybdate unit in the $\text{MnMo}_6\text{O}_{24}$ core of a neighbouring unit (Figure 6.20). The distances between the hydrogen atom and terminal oxygen atom from the nearby units are about 1.89 Å and 1.96 Å.

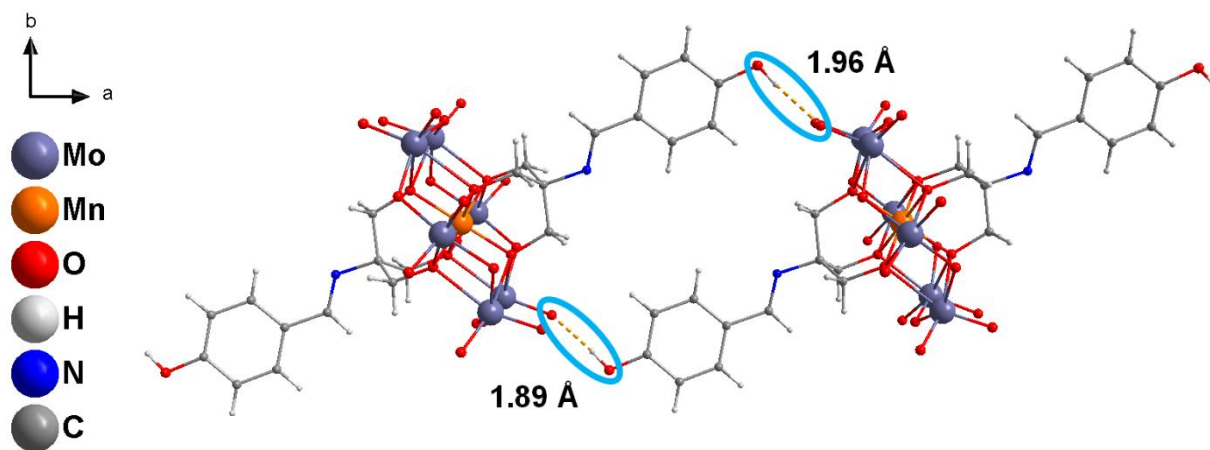


Figure 6.20. Arrangement of anionic units of **HL-6** in the unit cell. The phenolate hydrogen atom of one unit point toward molybdate oxygen of neighbouring unit.

6.3.2. Solid-state UV-Vis Spectroscopy of Hybrid Linkers

The solid-state UV-Vis spectra (Figure 6.20) of hybrid linkers **HL-1**, **HL-2**, **HL-3**, **HL-4**, **HL-5** and **HL-6**, exhibits a common absorption band around 520 to 530 nm, which can be attributed to the d-d transition within the Mn^{3+} ion (from the HOMO t_{2g} to the LUMO e_g) present in the Anderson-Evans polyanion.^[155] The absorption maxima around 300 nm are from the electron transfers from the ligand to metal charge transfer (LMCT), i.e., from the highest occupied molecule orbitals (HOMOs) of oxygen atoms (ligand) to the lowest unoccupied molecular orbitals (LUMOs) of metal (molybdenum) atoms. These high-energy transitions are typical for polyoxometalates with the absorption bands observed in ultra violet region of the spectrum.

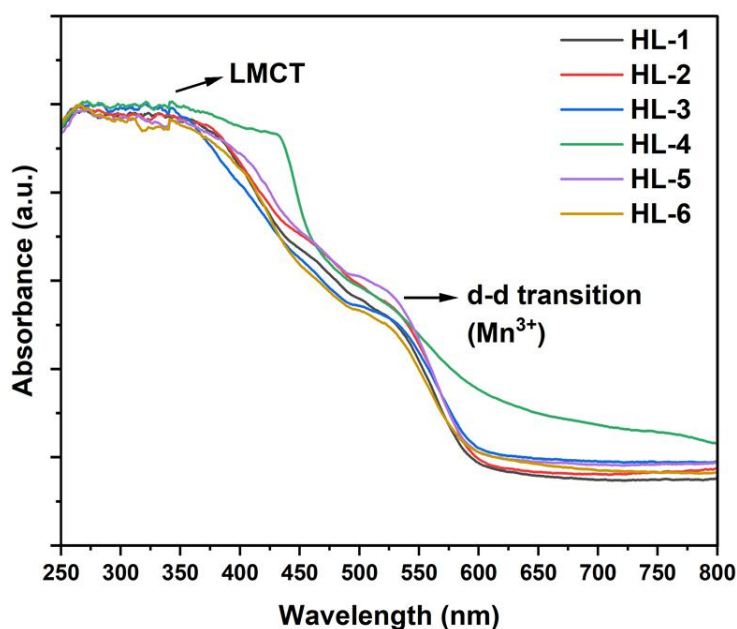


Figure 6.21. Solid state UV-Vis absorption spectra in the range of 250 to 800 nm for the hybrid linkers.

For all the hybrid linker except **HL-4**, there are phenyl groups in the organic part. In **HL-4**, this is the naphthyl group (Figure 6.22). The π - π^* transitions in these groups also contribute to the broad absorption band in ultra violet region for the hybrid linkers. Furthermore, the naphthyl group absorbs more towards visible region compared to the phenyl group as visible in the spectrum.

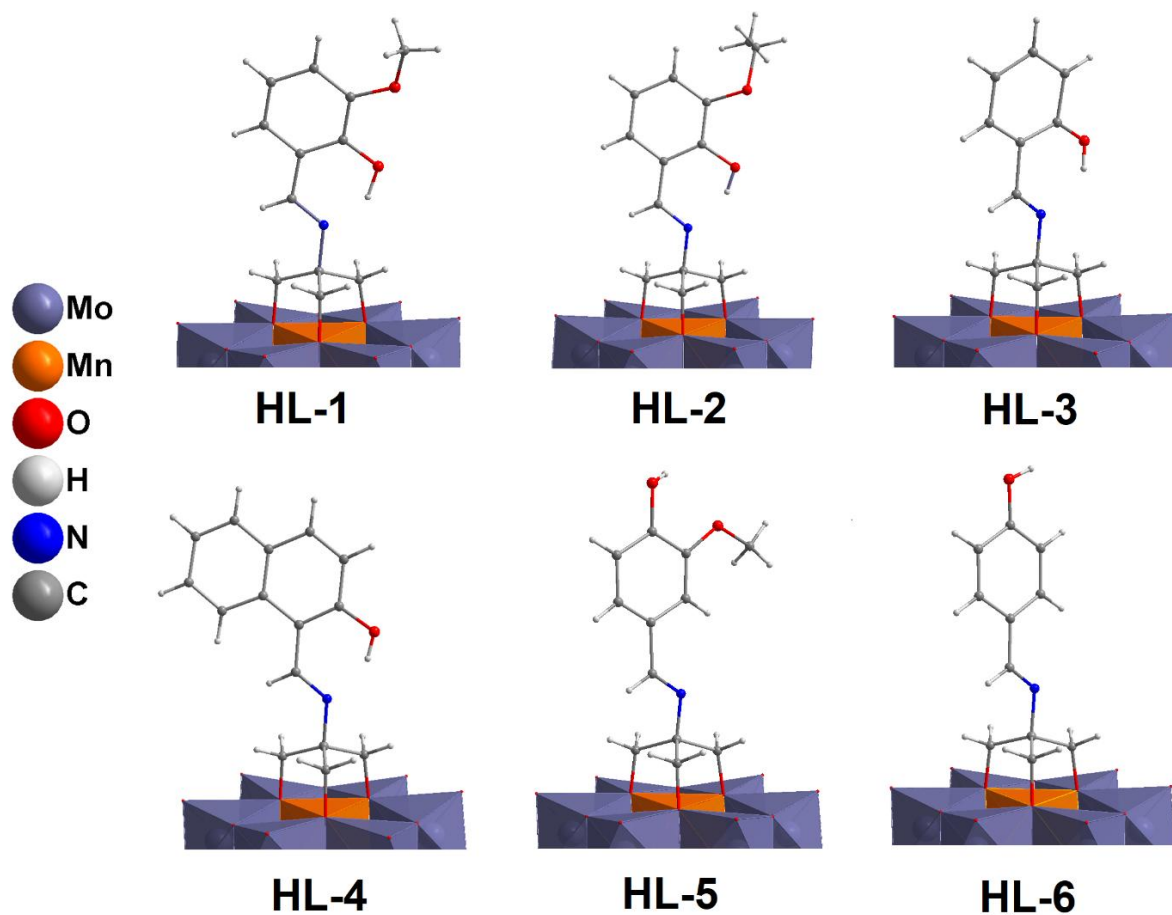


Figure 6.22. Aromatic rings in the hybrid linkers featuring phenyl groups in **HL-1**, **HL-2**, **HL-3**, **HL-5** and **HL-6** and naphthyl group in **HL-4**.

6.4. Synthetic Strategies for Polyoxometalate-Based Coordination Polymers (POMCPs)

Among the six synthesized hybrid linkers, the four 2-hydroxy-functionalized imine hybrid linkers **HL-1**, **HL-2**, **HL-3** and **HL-4** were selected for reaction with La^{3+} ions to synthesize Polyoxometalate-based Coordination Polymers (POMCPs).

All linkers feature oxygen-containing groups (-OH) at the 2-positions of the phenyl ring. The first two linkers additionally bear alkoxy groups at the 3-position, which can promote effective chelation of the La^{3+} ions. **HL-3** and **HL-4**, which lack these alkoxy substituents, are included for comparative analysis (Figure 6.22). Moreover, the naphthyl group present in **HL-4** offers potential for π - π stacking interactions, which are also investigated in the respective POMCP.

The syntheses of POMCPs were carried out using two widely adopted methods; ether diffusion and the layering technique, both commonly utilized in the synthesis of Polyoxometalate-based Metal-Organic Frameworks (POMOFs).^[67]

6.4.1. Synthesis via Ether Diffusion Method

In this method, a volatile solvent, in which the compound is insoluble, is gradually diffused into the solvent containing the sample to be crystallized. In this case, both the hybrid linker and the resultant coordination polymer are soluble in DMF, but insoluble in diethyl ether, which serves as the volatile solvent.

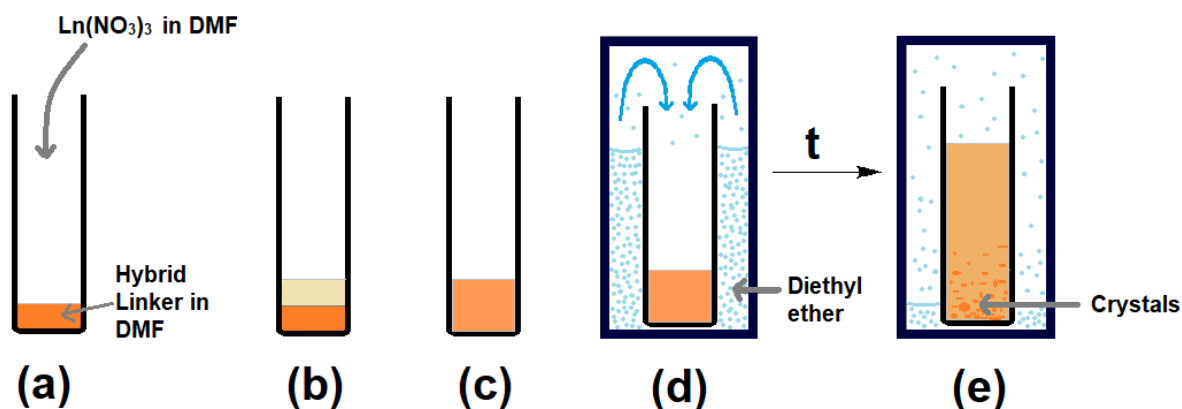


Figure 6.23. Ether diffusion method.

The hybrid linker was first dissolved in 1 mL of DMF in a narrow GC vial, followed by the addition of $\text{La}(\text{NO}_3)_3$, also dissolved in 1 mL DMF. The resultant mixture is made uniform by stirring (Figure 6.23a to c). The vial was then placed in a closed container saturated

with diethyl ether vapours. Over several days, the volatile ether slowly diffused into the DMF solution. This gradual diffusion reduces the solubility of the product, leading to its slow precipitation. Due to the controlled and slow nature of the process, the product crystallizes out of the solution (Figure 6.22d, e).

An optimised molar ratio of HL to La^{3+} (1 : 6.5) was used for all reactions, and 0.046 mmol hybrid linkers (HL) were dissolved in 2 mL DMF.

6.4.2. Synthesis via Layering Method

The synthesis was carried out using a three-layer solvent diffusion method. In a narrow vial, 1 mL of DMF containing the hybrid linker was added as the bottom layer (Figure 6.24a). A middle layer comprising 2 mL of a 1:1 (v:v) DMF/MeOH mixture was then slowly introduced above it (Figure 6.24b). Finally, 1 mL of a methanolic solution of $\text{La}(\text{NO}_3)_3$ was carefully layered on the top (Figure 6.24c). The slow interdiffusion of the solvent layers and their dissolved components allowed the reaction to proceed gradually, leading to the formation of the product as crystals due to its poor solubility (Figure 6.24d).

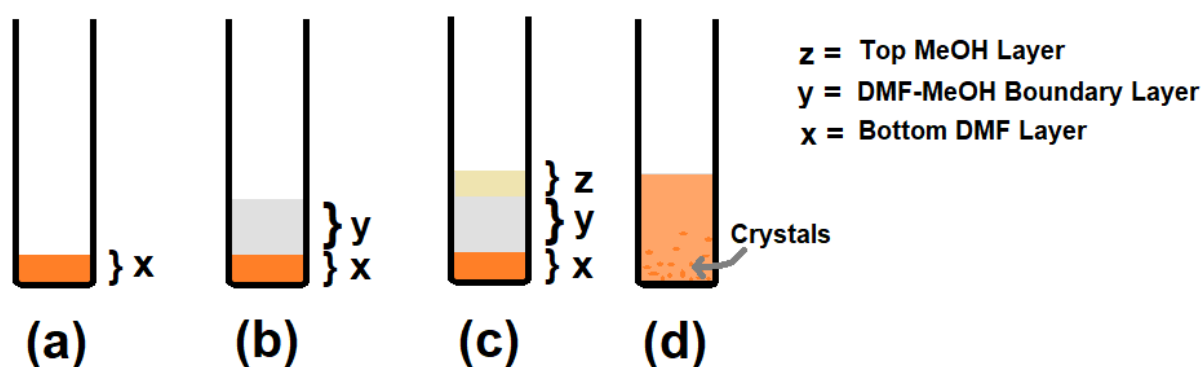


Figure 6.24. Layering method.

All reactions were carried out using a reagent ratio of $\text{HL} : \text{La}^{3+} = 1 : 6.5$. In each case, 0.025 mmol of the hybrid linker (HL) was dissolved in 1 mL of DMF and 0.16 mmol of $\text{La}(\text{NO}_3)_3$ was dissolved in 1 mL of methanol.

Depending on the synthesis approach and the structure of the hybrid linkers, several La^{3+} -based one-dimensional Polyoxometalate-based Coordination Polymers (POMCPs) were obtained. While the charge of the polyanionic hybrid linkers is typically balanced by tetrabutylammonium ($n\text{Bu}_4\text{N}^+$) cations, in the case of the POMCPs, La^{3+} ions serve as both charge-balancing and coordinating species. These La^{3+} ions coordinate with oxygen atoms from the hybrid linkers as well as solvent molecules such as DMF, methanol, or water, exhibiting coordination numbers of 8 or 9. Based on the coordination mode of La^{3+} ions with the hybrid linkers, the resulting POMCPs are categorized into two types: Type 1 and Type 2.

Figure 1 displays two crystal structures. (a) shows the structure of $[-\text{La}(\text{X})-\text{O}(\text{POM})\text{O}-\text{La}(\text{X})-]$, featuring a central POM unit (orange) bridged by O atoms (red) to La(X) units (blue). (b) shows the structure of $[-\text{La}(\text{X})-\text{R}(\text{POM})\text{R}-\text{La}(\text{X})-]$, where the POM unit is bridged by R groups (purple) to La(X) units. Both structures are shown with thermal ellipsoids at the 50% probability level.

- **O(POM)O**, represents the hybrid linker unit coordinated to the La^{3+} ion via the terminal oxygen of MoO_6 octahedra of the MnMo_6 (POM) core (see example in Figure 6.25a).
- **R(POM)R**, represents the hybrid linker unit coordinated to the La^{3+} ion via its organic moiety, specifically through aromatic rings with functional groups such as

–OH or –OMe. Coordination involves one or more atoms from the R-group interacting directly with the La^{3+} ion (example shown in Figure 6.25b).

- **La(X)** represents the La^{3+} ion along with the coordinated ligands like DMF methanol, water etc. (Figure 6.26).

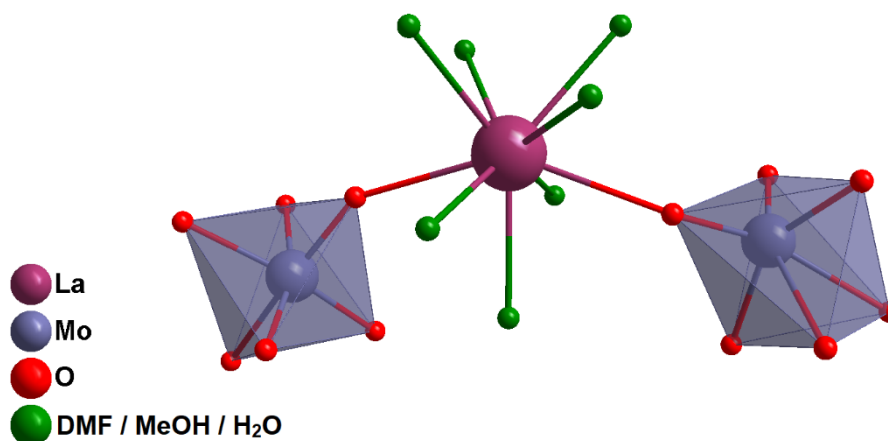


Figure 6.26. A La^{3+} ion which is coordinated by solvent ligands such as DMF and water, and is also bridged to terminal oxygen atoms of the MoO_6 octahedra from two hybrid linkers forming a $-\text{O}(\text{POM})\text{O}-\text{La}(\text{X})-\text{O}(\text{POM})\text{O}-$ unit.

6.5.1. Type-1 $[-\text{O}(\text{POM})\text{O}-\text{La}(\text{X})-]$ System

In this structure, the La^{3+} ions are coordinated exclusively to the terminal oxygen atoms of the MoO_6 octahedra within the hybrid linker, forming a one-dimensional $[-\text{O}(\text{POM})\text{O}-\text{La}(\text{X})-]$ coordination polymer. There is no coordination between La^{3+} and the organic component of the hybrid linker. This polymeric chain can be visualised as La^{3+} , along with their coordinated ancillary ligands, interconnected by free anionic hybrid linkers in an alternating arrangement.

6.5.2. Type-2 $[-\text{R}(\text{POM})\text{R}-\text{La}(\text{X})-\text{O}(\text{POM})\text{O}-\text{La}(\text{X})-]$ System

In this case, each La^{3+} ions are coordinated to two hybrid linkers via two distinct modes. One mode involves coordination through the terminal oxygen atoms of the MoO_6 octahedra from one linker, forming a $[-\text{La}(\text{X})-\text{O}(\text{POM})\text{O}-]$ fragment as seen in type 1. The other mode involves coordination via the functional group(s) on the aromatic rings of another hybrid linker, resulting in the formation of a $[-\text{R}(\text{POM})\text{R}-\text{La}(\text{X})-]$ fragment. Together, these interactions give rise to a one-dimensional coordination polymer composed of repeating $[-\text{R}(\text{POM})\text{R}-\text{La}(\text{X})-]$ units, interconnected by free anionic hybrid linkers in an alternating pattern. The two types of POMCPs are explained with examples in the following sections.

6.6. Synthesis of POMCPs

Different POMCPs were synthesized by reacting the four 2-hydroxy-functionalized imine hybrid linkers (**HL-1**, **HL-2**, **HL-3**, and **HL-4**) with $\text{La}(\text{NO}_3)_3$ using either the ether diffusion or layering method. The results are summarized in Figure 6.27.

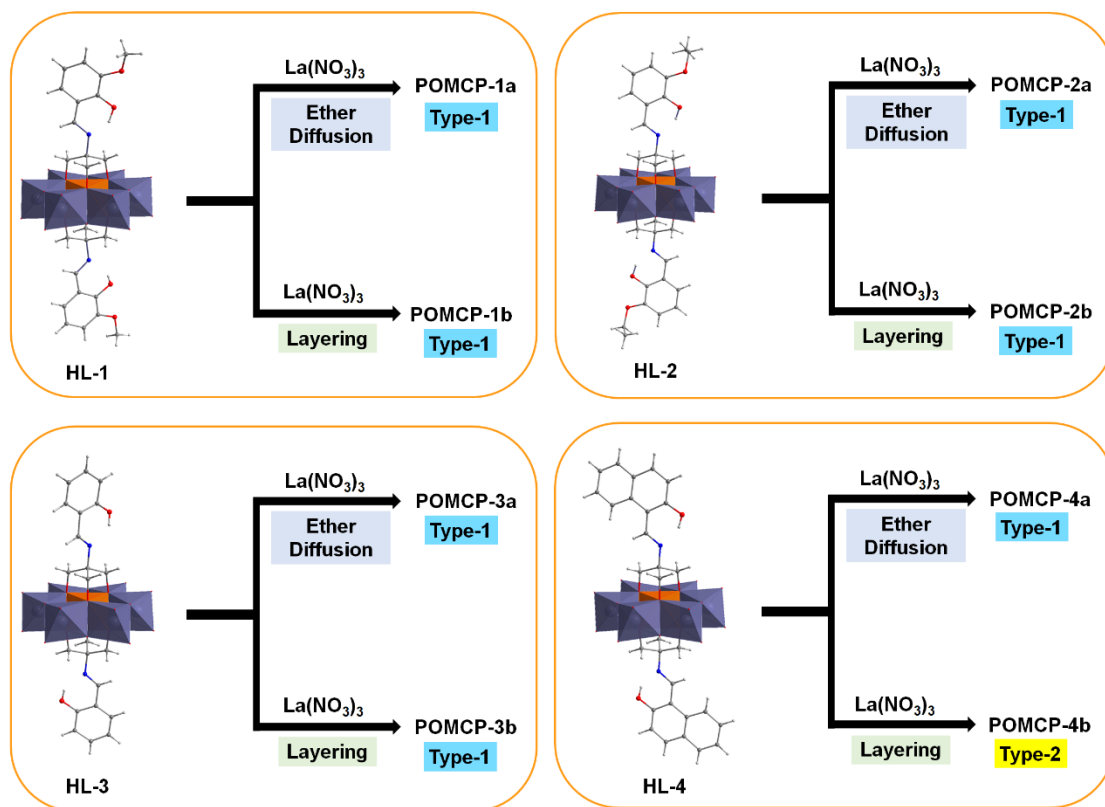


Figure 6.27. Different types of POMCPs were obtained from each of the four hybrid linkers with La^{3+} ions using either diffusion or the layering method.

The formula of the POMCPs obtained in each method is given in Table 6.3. The crystal structures of compounds obtained from the hybrid linker **HL-2** via the ether diffusion method (**POMCP-2a**) and from linker **HL-3** via the layering method (**POMCP-3b**) could not be fully refined. Although the overall structural framework could be resolved and assigned to the POMCP type, significant disorder in the vicinity of the La^{3+} coordination environment and inferior quality of the crystals prevented accurate refinement of the coordinated ligands. Therefore, these details are not discussed further. An approximate formula is provided where relevant.

Table 6.3. POMCPs obtained from various hybrid linkers through ether diffusion and layering methods.

<u>POMCP</u>	<u>Hybrid Linker & Method</u>	<u>Full Chemical Formula</u>
POMCP-1a	HL-1, Ether diffusion	$[\text{La}(\text{DMF})_7]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$
POMCP-1b	HL-1, Layering	$[\text{La}(\text{DMF})_4(\text{MeOH})_2]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$
POMCP-2a	HL-2, Ether diffusion	$[\text{La}(\text{X})]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}\}_2] \cdot y\text{DMF}$
POMCP-2b	HL-2, Layering	$[\text{La}(\text{DMF})_6(\text{MeOH})]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}\}_2] \cdot 2\text{DMF}$
POMCP-3a	HL-3, Ether diffusion	$[\text{La}(\text{DMF})_6(\text{H}_2\text{O})]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})\}\}_2] \cdot 2\text{DMF}$
POMCP-3b	HL-3, Layering	$[\text{La}(\text{X})]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})\}\}_2] \cdot y\text{DMF}$
POMCP-4a	HL-4, Ether diffusion	$[\text{La}(\text{DMF})_6]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2] \cdot 2\text{DMF}$
POMCP-4b	HL-4, Layering	$[\text{La}(\text{DMF})_6(\text{MeOH})]_2$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2]$ $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CNH}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-O})\}\}_2] \cdot 2\text{DMF} \cdot 2\text{MeOH}$

6.7. POMCPs obtained by Ether Diffusion Method

The coordination polymers **POMCP-1a**, **POMCP-2a**, **POMCP-3a** and **POMCP-4a** were synthesised from the hybrid linkers **HL-1**, **HL-2**, **HL-3** and **HL-4** respectively. For all POMCPs presented in this work, La^{3+} ions compensate the 3-unit negative charge associated with the hybrid linker anions.

Table 6.4. Unit cell parameters of POMCPs obtained from various hybrid linkers by ether diffusion method.

POMCP	POMCP-1a	POMCP-2a	POMCP-3a	POMCP-4a
Type of POMCP	Type-1	Type-1	Type-1	Type-1
Space Group	<i>P1</i>	<i>P1</i>	<i>C2/c</i>	<i>P$\bar{1}$</i>
a (Å)	16.4624(2)	13.884(1)	25.719(2)	12.7459(13)
b (Å)	23.6007(3)	13.8742(9)	13.5705(10)	16.1566(15)
c (Å)	24.9252(3)	20.7856(14)	22.8196(14)	20.795(2)
α (°)	87.616(1)	95.201(5)	90	86.343(8)
β (°)	87.717(1)	95.119(6)	119.270(5)	74.139(8)
γ (°)	85.369(1)	104.720(5)	90	69.734(8)
V (Å³)	9637.6(2)	3830.3(5)	6947.6(9)	3862.0(7)
Z	1	2	4	1

6.7.1. POMCP-1a

The one-dimensional coordination polymer **POMCP-1a** crystallizes in the triclinic space group *P1*. Each hybrid anion $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]^{3-}$ is coordinated to a La^{3+} ion, which is further coordinated by seven DMF molecules, resulting in the formation of a type-1 POMCP. The asymmetric unit comprises one hybrid anion, one La^{3+} ion ($Z = 1$) and two lattice DMF molecules. Accordingly, the molecular formula of **POMCP-1a** is $[\text{La}(\text{DMF})_7][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$.

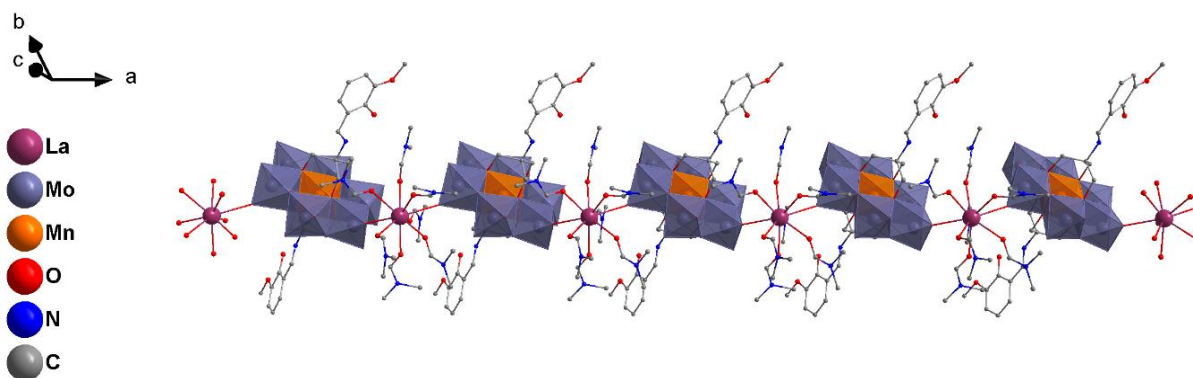


Figure 6.28. One-dimensional arrangement in **POMCP-1a**.

Crystallization in the acentric space group *P1* indicates the absence of an inversion center in the molecular structure. This is evident from the coordination pattern of the La^{3+} ion with the MoO_6 octahedra of the two hybrid linker molecules. In each hybrid linker, the first and third MoO_6 octahedra are coordinated to the La^{3+} ion (Figure 6.29). The structure of the coordination polymer can be visualised as the La^{3+} ion being coordinated to only one side of the hybrid linker, which rule out the presence of any inversion centre in the structure.

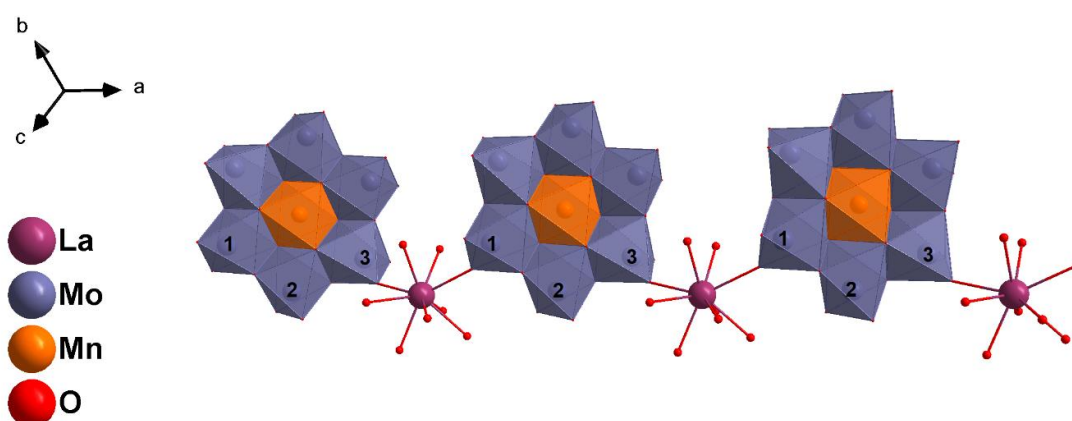


Figure 6.29. Representation of La^{3+} coordination with first and third MoO_6 octahedra of the hybrid linker in **POMCP-1a**. Carbon and nitrogen atoms on hybrid linker and DMF removed for clarity.

6.7.2. POMCP-2a

The one-dimensional coordination polymer **POMCP-2a** crystallizes in the triclinic space group *P1*. As stated earlier, the absolute structure could not be refined and will not be discussed further.

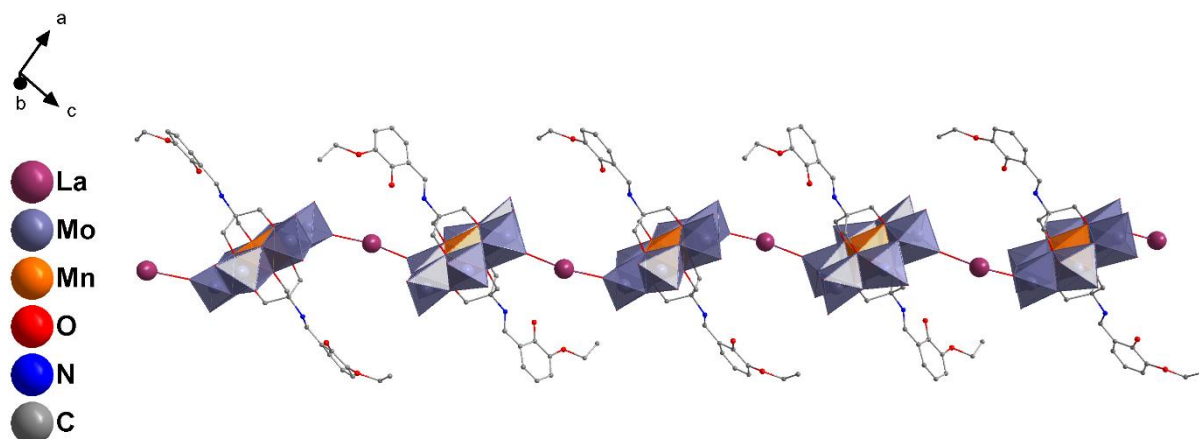


Figure 6.30. One-dimensional arrangement in **POMCP-2a**. All hydrogen atoms, lattice solvents and disordered coordination sphere around the La^{3+} omitted for clarity.

6.7.3. POMCP-3a

POMCP-3a forms a type-1 coordination polymer and crystallizes in the monoclinic space group $C2/c$. Each $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]^{3-}$ hybrid unit, is coordinated to a La^{3+} ion which is further ligated by 6 DMF molecules. In the unit cell there are two DMF molecules as lattice solvent. Thus, the molecular formula of **POMCP-3a** is $[\text{La}(\text{DMF})_6(\text{H}_2\text{O})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$.

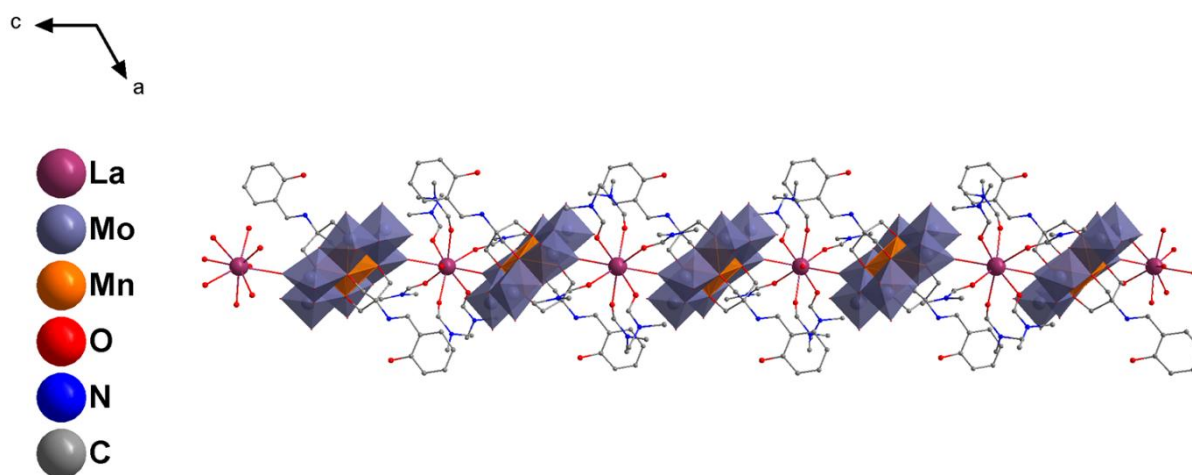


Figure 6.31. One-dimensional arrangement in **POMCP-3a**.

In the coordination polymer, La^{3+} ion is coordinated to the MoO_6 octahedra of two hybrid linker molecules. In each hybrid linker, the first and fourth MoO_6 octahedra are coordinated to the La^{3+} ion (Figure 6.32). An inversion centre can be visualised on the Mn^{3+} ion in the Anderson Evans POM.

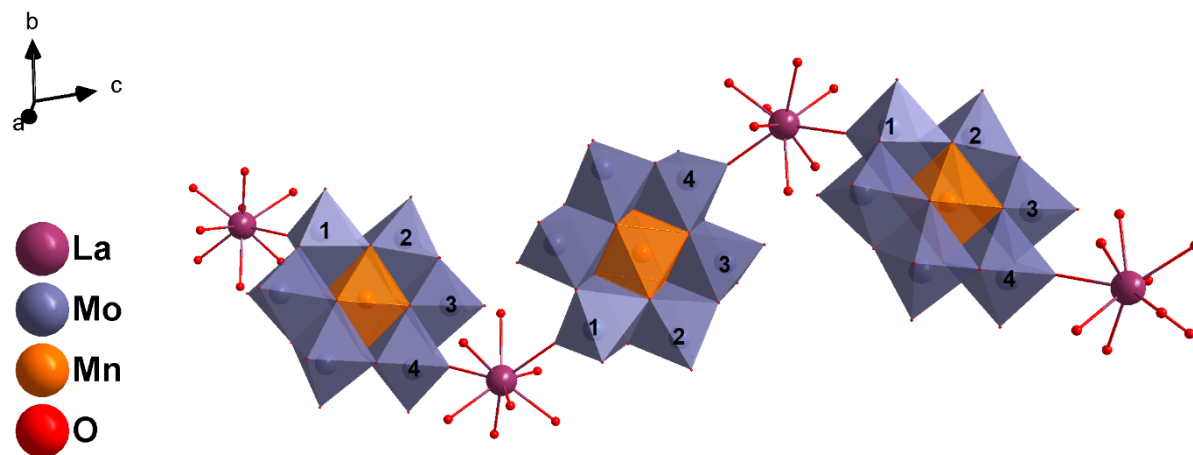


Figure 6.32. Representation of La^{3+} coordination with first and fourth MoO_6 octahedra of the hybrid linker in **POMCP-3a**. Here there is an inversion centre on the Mn^{3+} ion in the Anderson Evans POM. Carbon and nitrogen atoms on hybrid linker and DMF removed for clarity.

6.7.4. POMCP-4a

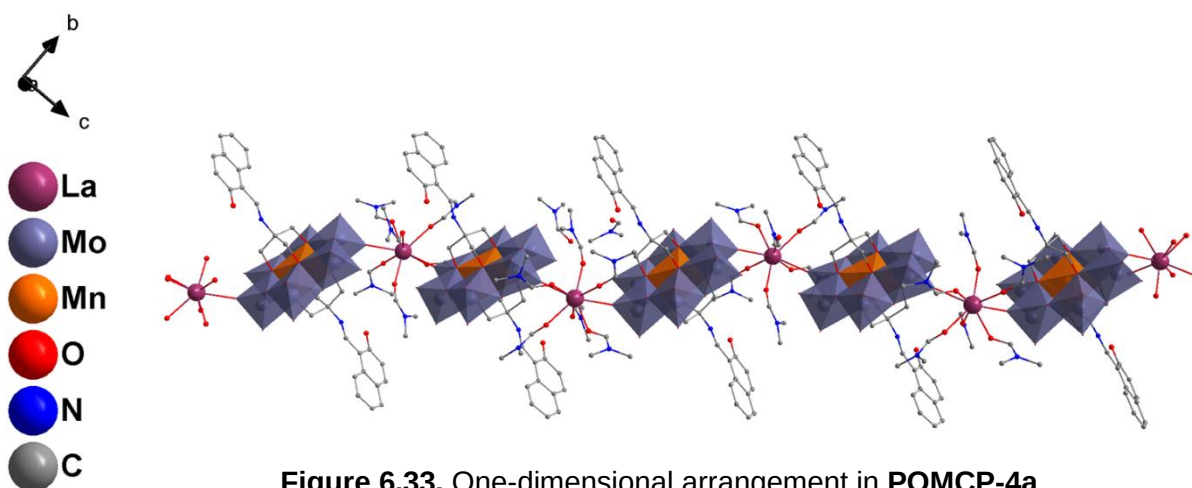


Figure 6.33. One-dimensional arrangement in **POMCP-4a**.

POMCP-4a forms type-1 coordination polymer and crystallizes in the triclinic space group $P\bar{1}$. Each of the eight-coordinated La^{3+} ion is attached to two $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2]$ units and 6 DMF molecules. Within the unit cell, the coordination polymer chains are arranged nearly parallel to each other. The packing pattern prevents any possibility of π – π stacking interactions between the naphthyl groups of adjacent chains (Figure 6.34).

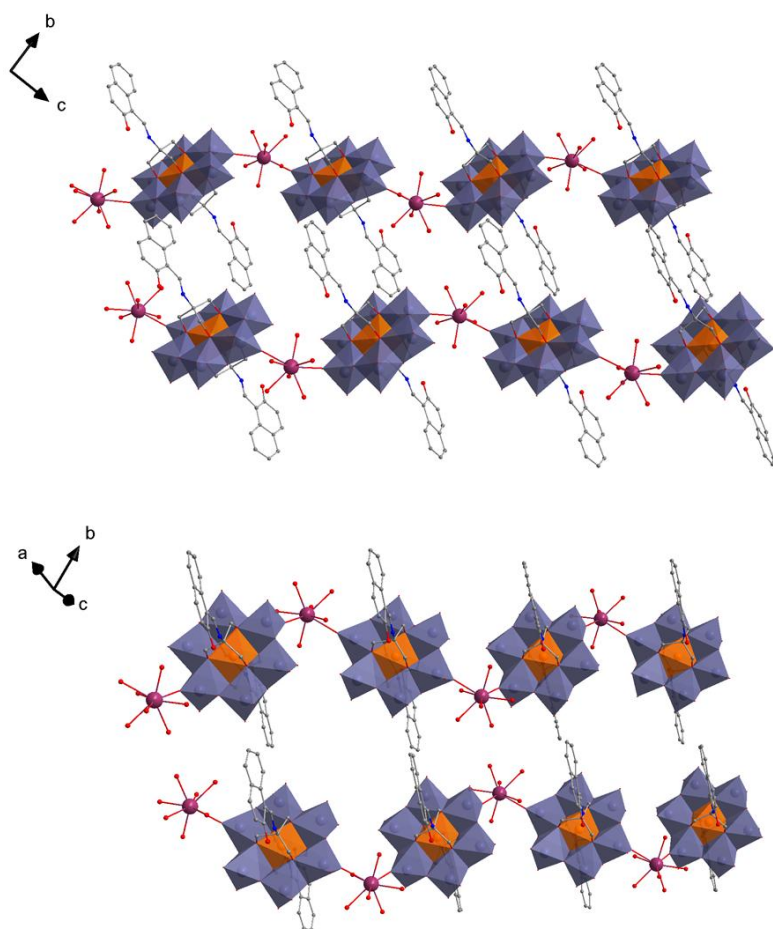


Figure 6.34. Packing of coordination polymer chains in **POMCP-4a**.

The molecular formula of **POMCP-4a** is $[\text{La}(\text{DMF})_6] [(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2] \cdot 2\text{DMF}$.

6.8. POMCPs obtained by Layering Method

Table 6.5. Unit cell parameters of POMCPs obtained from various hybrid linkers by layering method.

POMCP	POMCP-1b	POMCP-2b	POMCP-3b	POMCP-4b
Type of POMCP	Type-1	Type-1	Type-1	Type-2
Space Group	Cc	$P2_1/n$	$C2/c$	$P\bar{1}$
a (Å)	22.0004(4)	17.4339(4)	21.1988(4)	12.7592(2)
b (Å)	14.7409(3)	21.7523(5)	13.7340(3)	14.3962(3)
c (Å)	18.9884(4)	20.6125(5)	23.9079(5)	23.8288(5)
α (°)	90	90	90	92.207(2)
β (°)	96.300(2)	97.969(2)	105.579(1)	90.435(2)
γ (°)	90	90	90	115.167(1)
V (Å ³)	6120.9(2)	7741.3(3)	6704.9(2)	3957.14(14)
Z	4	4	1	1

The coordination polymers **POMCP-1b**, **POMCP-2b**, **POMCP-3b** and **POMCP-4b** were synthesised by the reaction of La^{3+} ions with the hybrid linkers **HL-1**, **HL-2**, **HL-3** and **HL-4** respectively.

6.8.1. POMCP-1b

The one-dimensional coordination polymer **POMCP-1b** crystallizes in the monoclinic space group Cc. Each hybrid unit of the type $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2]^{3-}$ is coordinated to La^{3+} ion, which is further coordinated to 4 DMF and 2 methanol ligands, resulting in the formation of a Type-1 POMCP. The unit cell contains four such anionic units, four La^{3+} ion (Z=4), and two DMF molecules as lattice solvent. The molecular formula of **POMCP-1b** is $[\text{La}(\text{DMF})_4(\text{MeOH})_2][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}\}_2] \cdot 2\text{DMF}$.

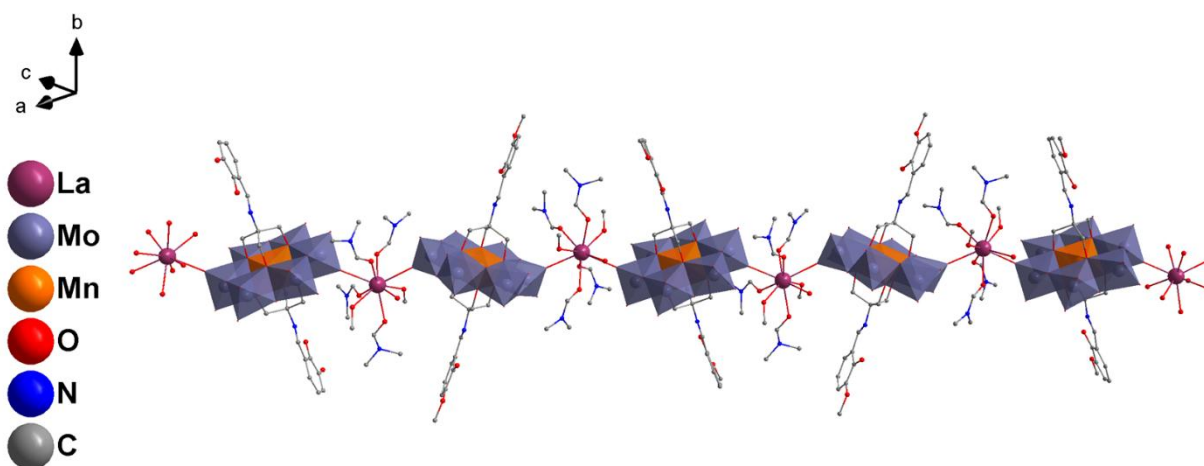


Figure 6.35. One-dimensional arrangement in **POMCP-1b**.

The arrangement of the La^{3+} ion and linker units in the crystal lattice of **POMCP-1b** is similar to that observed in **POMCP-3a**, with La^{3+} ions coordinating to the first and fourth MoO_6 octahedra (Figure 6.35a). However, due to the orientation of the organic segments of the hybrid linkers, an inversion centre is not observed at the Mn^{3+} ion within the AE POM in **POMCP-1b** (Figure 6.36b). As a result, the crystal structure of **POMCP-1b** is acentric.

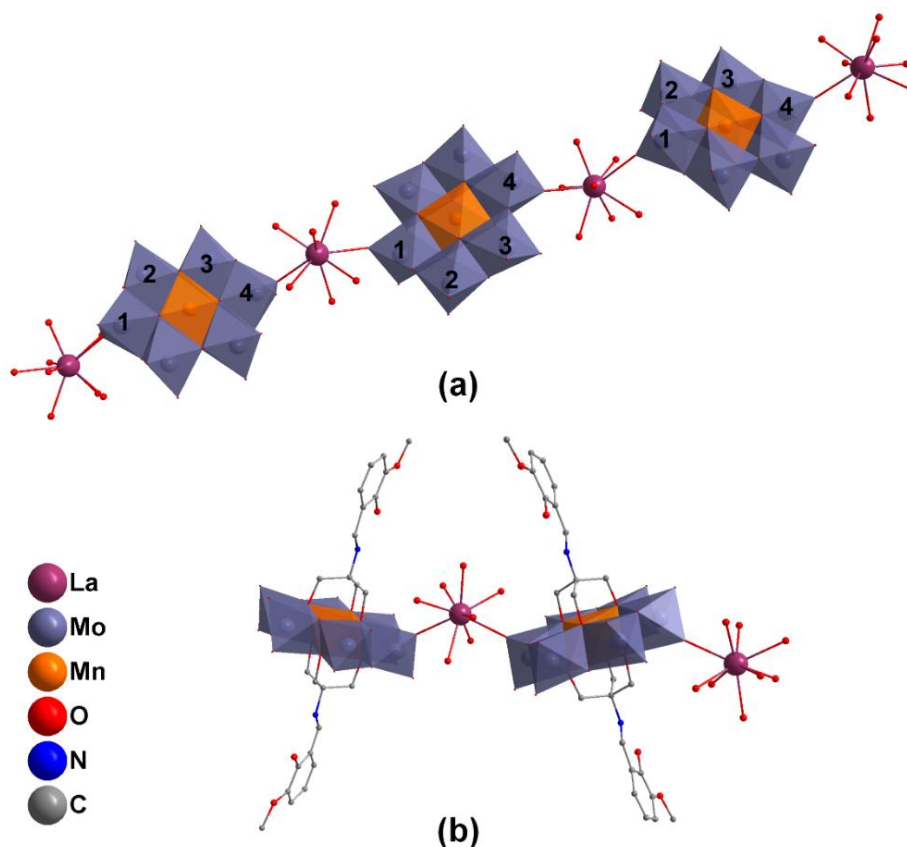


Figure 6.36. One-dimensional arrangement in **POMCP-1b**.

6.8.2. POMCP-2b

The compound **POMCP-2b** crystallizes in the monoclinic centrosymmetric space group $P2_1/n$. The Type-1 POMCP structure is formed by a one-dimensional arrangement of alternating La^{3+} and POM hybrid units. Each La^{3+} ion is coordinated to two POM units through the terminal oxygen atoms in MoO_6 octahedra. The coordination sphere of the La^{3+} ion is completed by 6 DMF and 1 methanol ligand. The molecular formula of **POMCP-2b** is $[\text{La}(\text{DMF})_6(\text{MeOH})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}\}_2]\cdot 2\text{DMF}$.

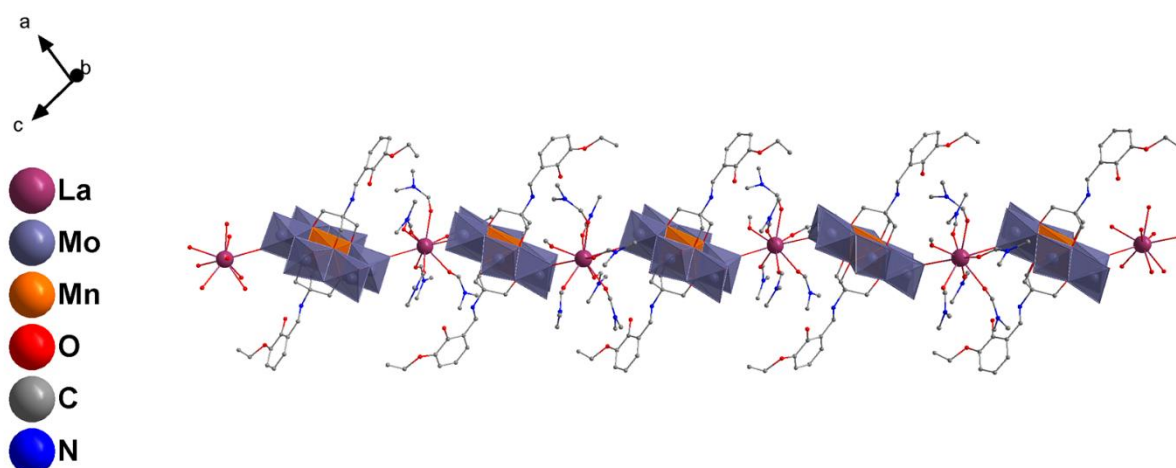


Figure 6.37. One-dimensional arrangement in **POMCP-2b**.

6.8.3. POMCP-3b

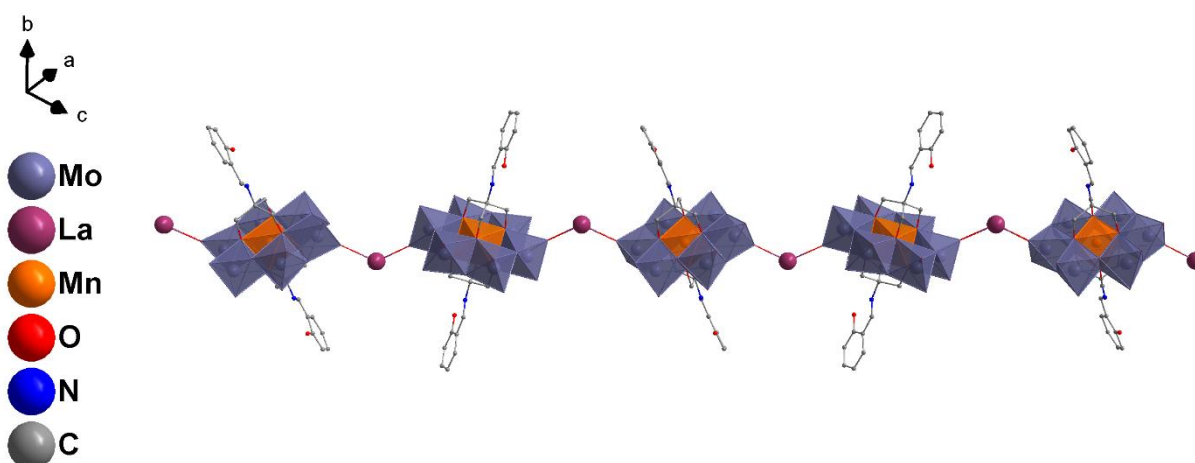


Figure 6.38. One-dimensional arrangement in **POMCP-2b**.

The one-dimensional coordination polymer **POMCP-3b** crystallizes in the monoclinic centrosymmetric space group $C2/c$. Each La^{3+} ion is coordinated with two hybrid units, in an alternate pattern to form the Type-1 coordination polymer. Like mentioned earlier,

the absolute structure refinement of the coordination environment around La^{3+} was impossible and is not discussed further.

6.8.4. POMCP-4b

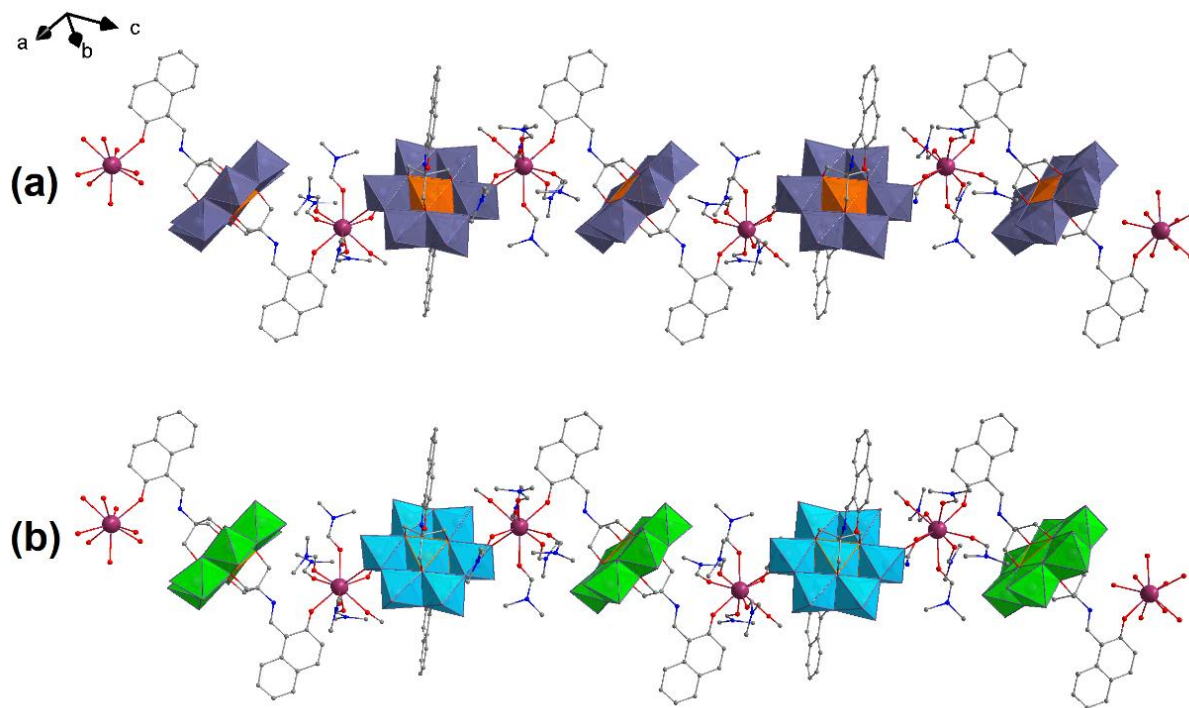


Figure 6.39. (a) One-dimensional chain structure in **POMCP-4b**; (b) Simplified representation showcasing different coordination modes of hybrid linker with La^{3+} ions where the Anderson-Evans POMs are represented in green and blue colour.

By the layering method, the compound **POMCP-4b** was obtained by the reaction of the linker **HL-4** with lanthanum nitrate. This is a type-2 POMCP and is crystallises in triclinic space group $P\bar{1}$. Each La^{3+} ions are coordinated with 6 DMF, 1 methanol ligands and two hybrid linker units in two coordination modes (Figure 6.39a). The structure is simplified as shown in Figure 6.39b, where Anderson-Evans POM unit of the hybrid linker with different coordination modes are marked in different colours. The green coloured Anderson-Evans POM represents the linker which coordinates the La^{3+} ion via the organic functional side (oxygen on the naphthyl ring) forming the $[-R(POM)R-La(X)-]$ unit. The blue coloured Anderson-Evans POM represents the linker which is connected to the La^{3+} ion via the terminal oxygen atoms of the MoO₆ octahedra which forms the $[-O(POM)O-La(X)-]$ unit. A detailed representation of these coordination modes of La^{3+} ion is shown in Figure 6.40a.

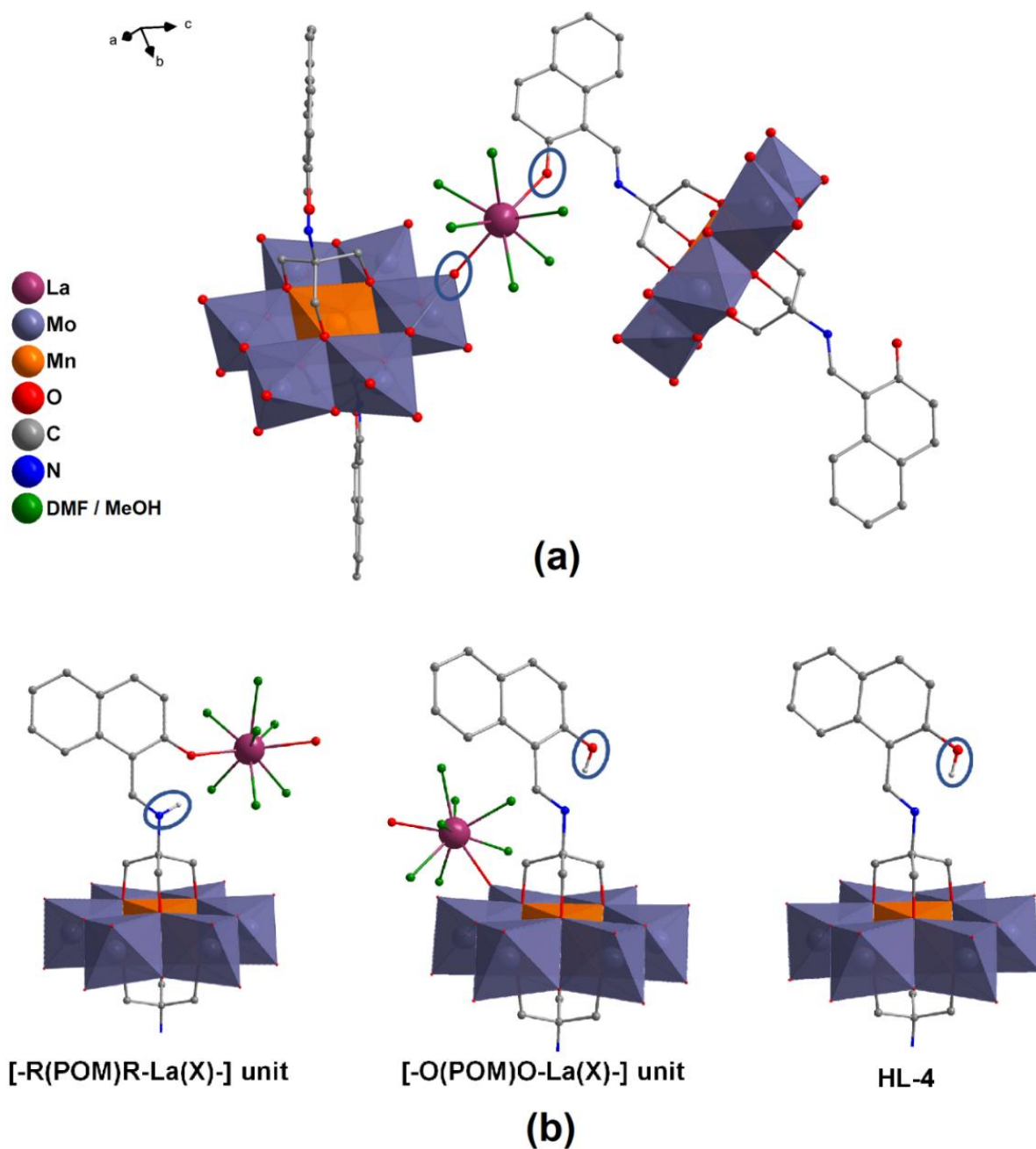


Figure 6.40. (a) Different coordination modes of the La³⁺ ion to the hybrid linker units in **POMCP-4b** (terminal oxygen in the Anderson Evans POM are shown with an enlarged radius in the polyhedral representation for clarity); (b) Difference in protonation on N/O atoms in [-R(POM)R-La(X)-] and [-O(POM)O-La(X)-] units.

In the [-R(POM)R-La(X)-] unit, the hydroxyl group on the naphthyl group is deprotonated and this oxygen (-O⁻) is involved in coordination with the La³⁺ ion. At the same time, the nitrogen atom from tris ligand in the hybrid linker is in protonated form (NH⁺) (Figure 6.40b, left). Hence this unit can be formulated as [(MnMo₆O₁₈){[(OCH₂)₃CN(H)=CH{(C₁₀H₅)(2-O))}]₂]-La(X)-. For the [-O(POM)O-La(X)-]

unit, the hydroxy group is protonated (Figure 6.40b, middle) as in the original hybrid linker **HL-4** (Figure 6.40b, right) and this unit can be formulated as $[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2]\text{-La(X)-}$. In both cases, the hybrid linker units have three-unit negative charge which is balanced by the La^{3+} ions.

Considering the attached solvent molecules on the La^{3+} ion and combining both these two units and with lattice solvents, the entire formula of **POMCP-4b** is given by $[\text{La}(\text{DMF})_6(\text{MeOH})_2][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}\}_2][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CNH}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-O})\}\}_2] \cdot 2\text{DMF} \cdot 2\text{MeOH}$.

6.9. Topological Aspects of the Investigated POMOFs

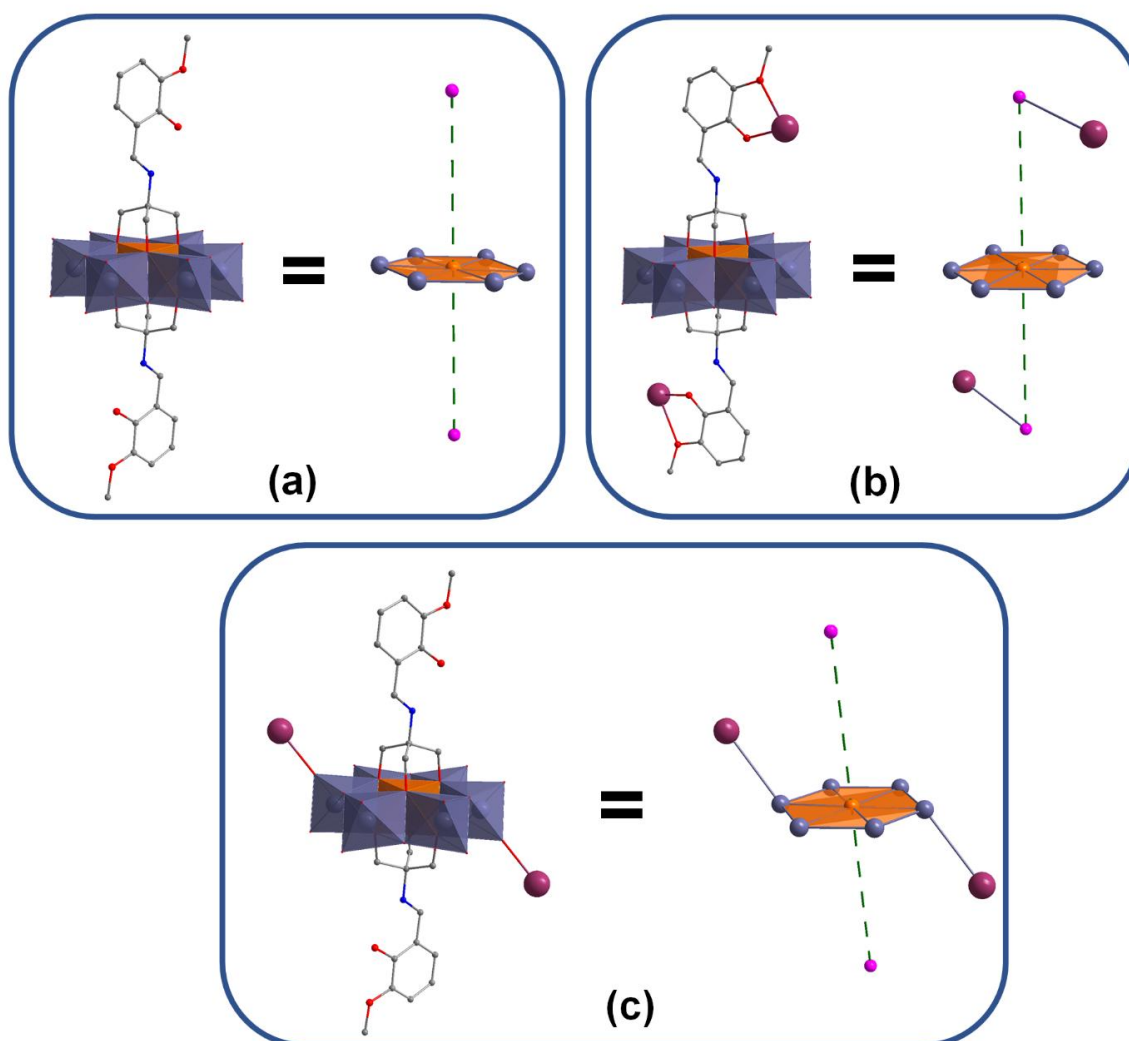


Figure 6.41. Simplified representation of (a) hybrid linker; (b) and (c) different coordination modes of La^{3+} with hybrid linker.

Type-1 POMCPs were predominantly obtained from reactions of hybrid linkers with lanthanum nitrate salt using ether diffusion and layering methods. Only in one case, the formation of Type-2 POMCPs was observed. In Type-1 POMCPs, although the coordination environments around the La^{3+} ions varied in terms of the coordination number and the nature of coordinated solvent molecules, all compounds are topologically similar.

The topological aspects of various POMCPs will be investigated here. For simplification, the $\{\text{MnMo}_6\text{O}_{24}\}$ inorganic POM unit is represented as a hexagon. The aromatic ring of the hybrid linker which contains the functional groups such as -OH, -OMe, is represented as a pink sphere, while the remaining organic group is indicated by dotted green lines. A representative structure incorporating **HL-1** is shown in Figure 6.41a. The two

coordination modes, $[-R(POM)R-La(X)-]$ and $[-O(POM)O-La(X)-]$ are shown in Figure 6.41b and c, respectively. The topological representations of POMCPs obtained by the ether diffusion and layering method are summarised below.

Type-1 POMCPs by Ether Diffusion Method

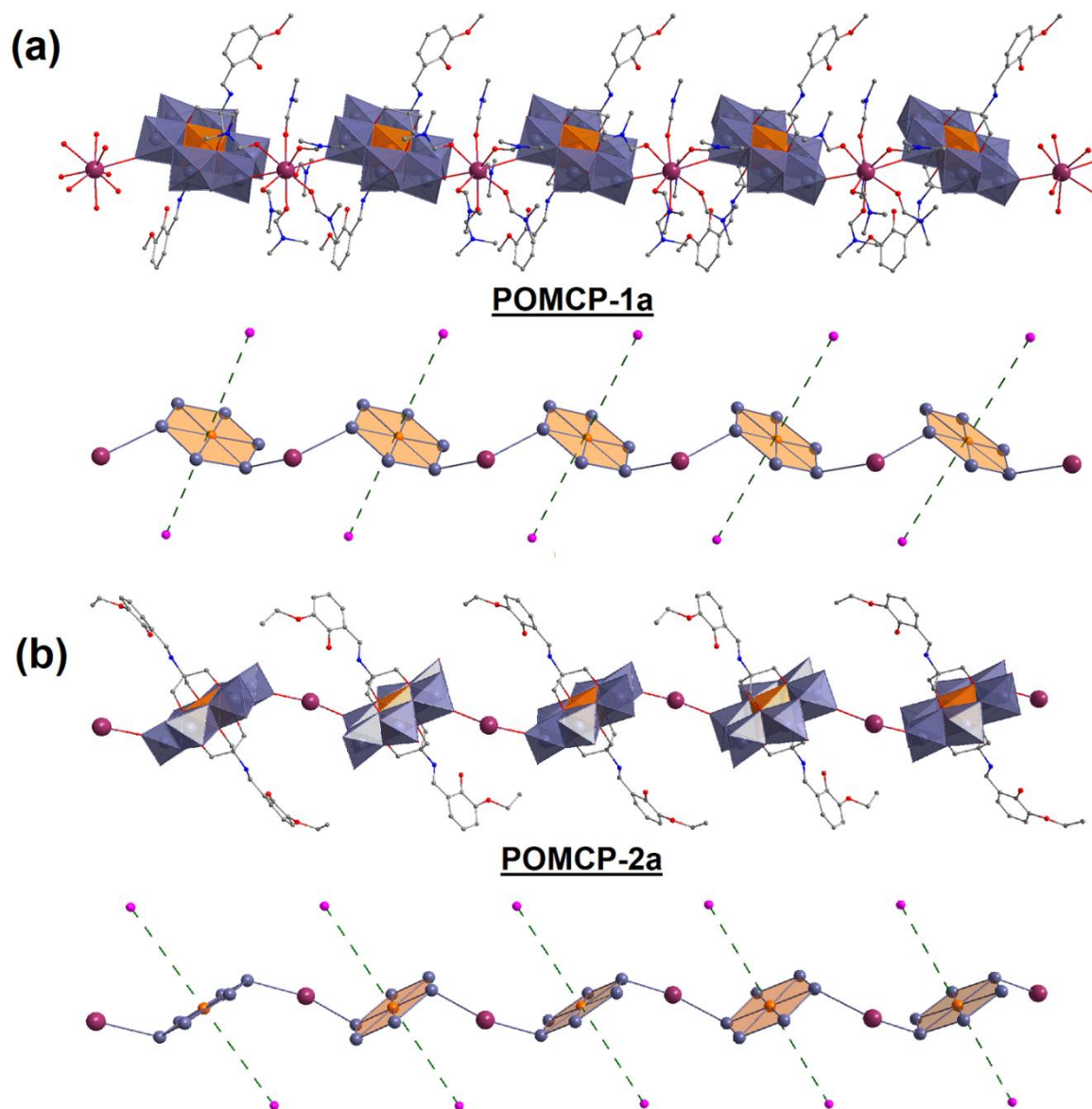


Figure 6.42. Representation for topological understanding in (a) **POMCP-1a** and **POMCP-2a**.

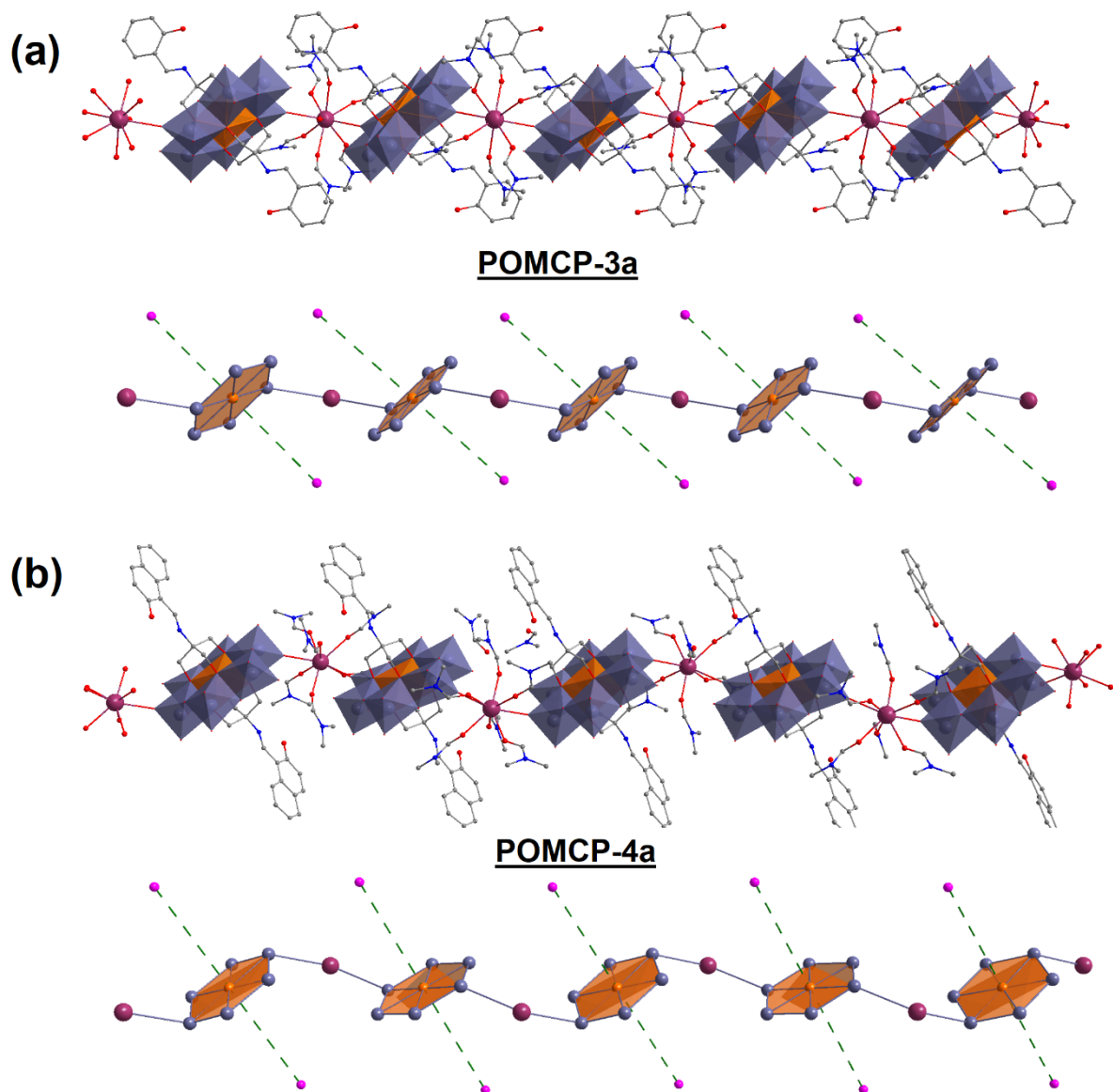


Figure 6.43. Topological representations of (a) **POMCP-3a** and **POMCP-4a**.

Type-1 POMCPs by Layering Method

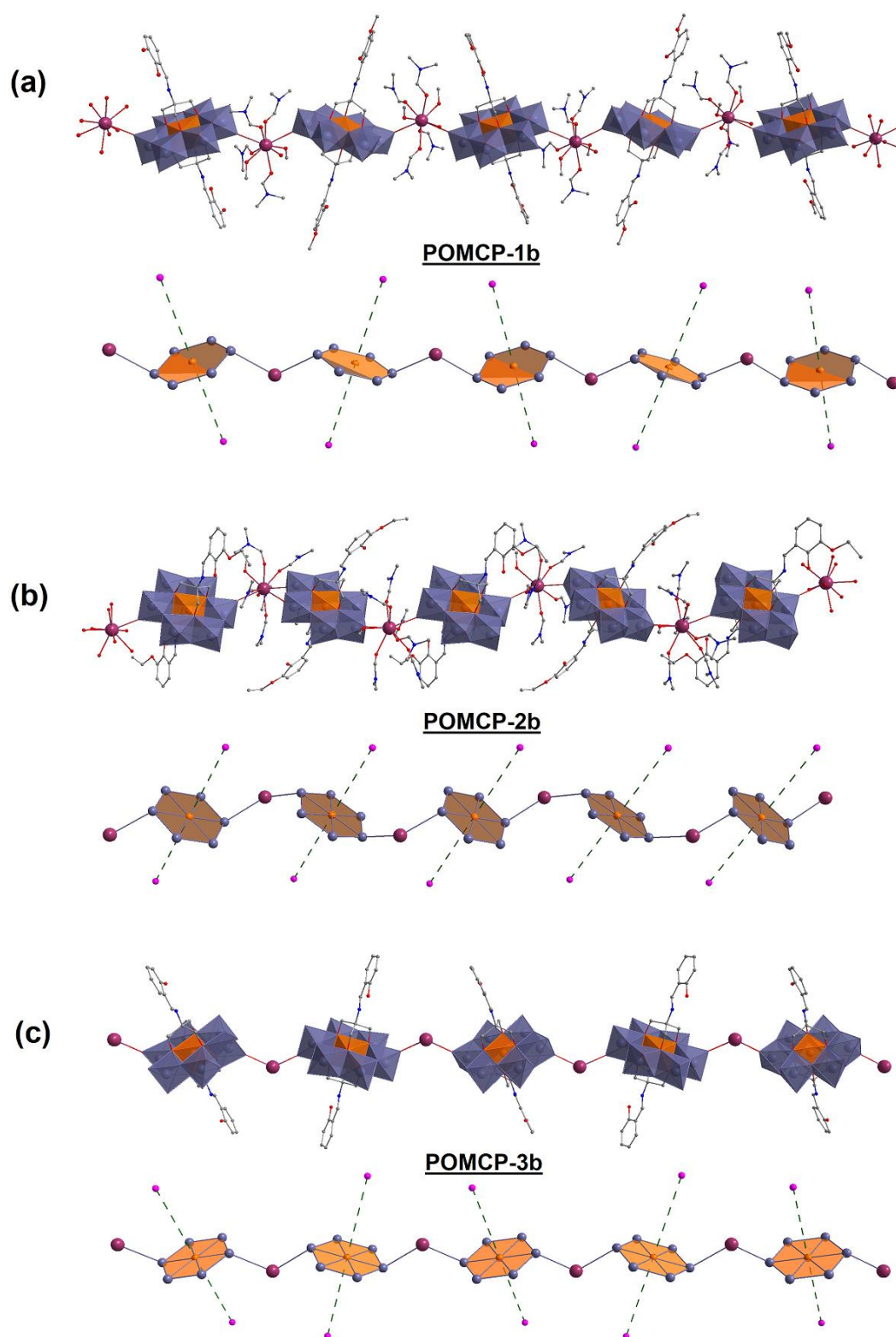


Figure 6.44. Topological representations of (a) **POMCP-1b**, **POMCP-2b** and **POMCP-3b**.

Type-2 POMCPs by Layering Method

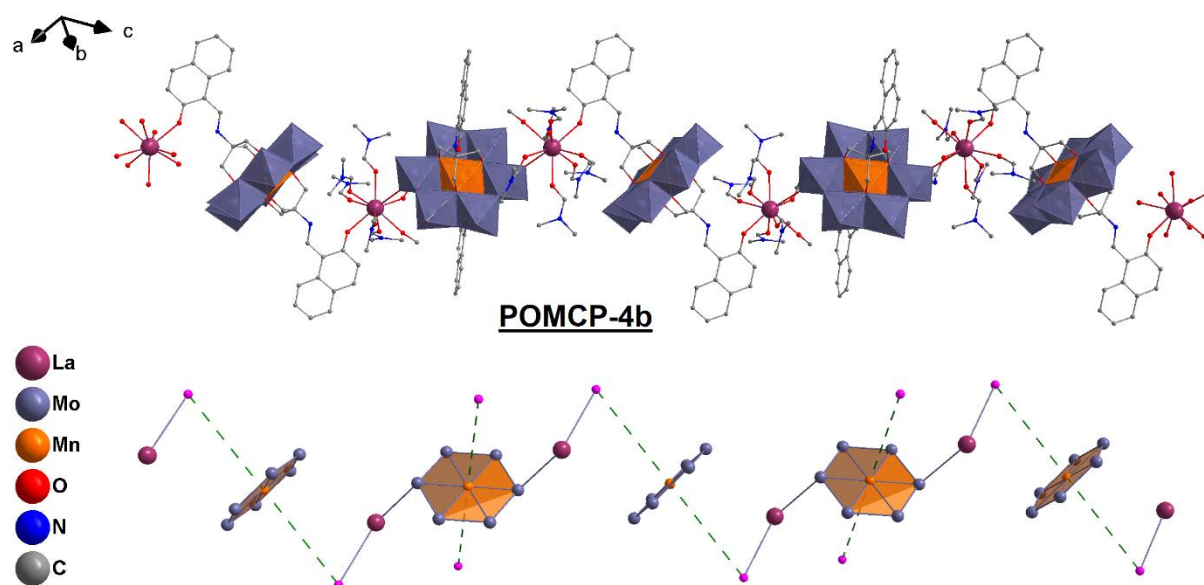


Figure 6.45. Topological representations of **POMCP-4b**.

6.10. Conclusion and Outlook

In this chapter, six new POM hybrid linkers (**HL-1** to **HL-6**) were synthesised by the Schiff base reaction between the amino-functionalised Anderson-Evans POM hybrid ($(n\text{Bu}_4\text{N})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{C-NH}_2\}_2]$ (**MnMo₆(TRIS)₂**) and six hydroxy-functionalized aromatic aldehydes. The crystal structures of these hybrids were analysed in detail, highlighting the symmetry features arising from the arrangement of the organic moieties within the crystal lattice. UV-Vis spectroscopy confirmed the presence of characteristic electronic transitions, including the d-d transitions of the Mn^{3+} centres.

Among the six synthesized hybrid linkers, those with 2-hydroxy substituted ones were considered for the synthesis of Polyoxometalate-based Coordination Polymers (POMCPs). By successfully applying ether diffusion and layering crystallization techniques under mild conditions, high-quality single crystals of La^{3+} -containing POMCPs were obtained. The tetrabutylammonium ($n\text{Bu}_4\text{N}^+$) counter cations that balanced the charge of the polyanion in the hybrid linkers were replaced by the La^{3+} ions in the coordination polymers. Two distinct types of POMCPs (Type 1 and Type 2) were identified based on the coordination modes of the La^{3+} ions and the connectivity of the hybrid linkers. Despite variations in coordination patterns and crystallographic space groups, compounds classified within the same type exhibited consistent

topological features. These findings highlight the critical role of ligand design and synthetic strategy in controlling the structure and dimensionality of POM-based coordination frameworks.

In the next stage of this work, the extension of the one-dimensional coordination polymers into multidimensional structures using ancillary organic ligands will be investigated. Investigation using other lanthanide ions besides La^{3+} especially those with unpaired electrons such as Gd^{3+} , Dy^{3+} , Er^{3+} and Tb^{3+} is planned. These will be useful in studies related to the magnetic properties of the resulting compounds and may lead to materials that show interesting magnetic behaviour, such as forming chains with magnetic interactions.

Redox-active lanthanides like Ce^{3+} will also be explored. These elements can change their oxidation states and might be useful for applications in electrocatalysis or as components in electrode materials. Selected compounds will also be tested for their light-emitting (photoluminescent) properties to understand how the metal and the structure affect the emission of light (e.g., Eu^{3+}). In all cases, parallel studies of the hybrid linker molecules will also be carried out. The physical and chemical properties of the free linkers will be compared with those of the final metal-containing products. This will be useful to understand the influence of the lanthanide ion and the type of structure formed on the overall properties of the materials.

7. TRIS-Ligand Decorated Cobalt-Containing Polyoxomolybdates

7.1. Introduction

Many organic-functionalized Anderson-Evans polyoxometalates with different heteroatoms in various oxidation states (E.g., Fe^{3+} , Co^{3+} , Cr^{3+} , Al^{3+} , Ga^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} etc.) have been synthesised with different triol organic ligands $(\text{CH}_2\text{OH})_3\text{C-R}$ (where $-\text{R} = -\text{NH}_2$, $-\text{OH}$, $-\text{CH}_2\text{OH}$, $-\text{NO}_2$, etc.).^[52] A majority of tris(hydroxymethyl)aminomethane (TRIS)-functionalized Anderson-Evans (AE) type polyoxometalates $[\text{MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ is reported for $\text{M} = \text{Mn}^{3+}$ or Cr^{3+} .^[60] A small number of examples of cobalt containing structures are known and the ones with TRIS ligand decoration are amongst the least studied ones.^[156]

This chapter focuses on the synthesis of TRIS-ligand decoration in Co-Containing polyoxomolybdates. Isomerism in Triol-ligand decoration in the Anderson-Evans POMs family is discussed in terms of the already known $(n\text{Bu}_4\text{N})_3[\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ($\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$)^[156] and newly synthesised $(n\text{Bu}_4\text{N})_3[\text{Co}^{\text{II}}\text{Mo}_6\text{O}_{17}(\text{OH})\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ ($\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$). A new cluster molecule $[\text{Co}^{\text{II}}\text{Mo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3]$ (**CoMo₃(TRIS)₃**) was also synthesised, which is one of the smallest heteropolyoxomolybdate hybrid molecule to be ever reported. The structural features of each compound are discussed along with their optical properties.

In **CoMo₃(TRIS)₃**, the divalent cobalt ion is interesting in terms of magnetic properties^[157] and hence the magnetism in dc and ac fields were evaluated. In addition, this molecule is a good candidate to be used as a single atom catalyst test-bed for photocatalytic hydrogen evolution reaction (HER). These were also examined in this chapter. Whereas the synthesis of MOF structures is not discussed in this chapter, the synthesis of novel hybrid Co-POM molecules is discussed here with an outlook towards novel POMOFs.

7.2. Background on Triol-Ligand Functionalized Cobalt based-Anderson-Evans POM Hybrids

The synthesis of organically functionalised Anderson-Evans (AE) POM hybrids was first reported in 2002 by Hasenknopf *et al.* This was achieved by refluxing octamolybdate ($(n\text{Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$, acetylacetonate (acac) or acetate (OAc) complexes of various transition metals ($\text{M}=\text{Mn}^{3+}$, Fe^{3+} , Ni^{2+} and Zn^{2+}) and different tris(alkoxo) ligands ($(\text{HOCH}_2)_3\text{C-R}$, where $\text{R}=\text{CH}_3$, NO_2 , CH_2OH) in acetonitrile.^[56] Different hybrids were isolated from the solution as tetrabutylammonium salts using slow ether diffusion. In order to understand the structural difference in these hybrids formed during the organic functionalisation, the structure of protonated B-type Anderson ($[\text{M}^{n+}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{(6-n)-}$) can be used as a reference. Here, M^{n+} are the transition metal ions which constitute the heteroatom in the AE POM.

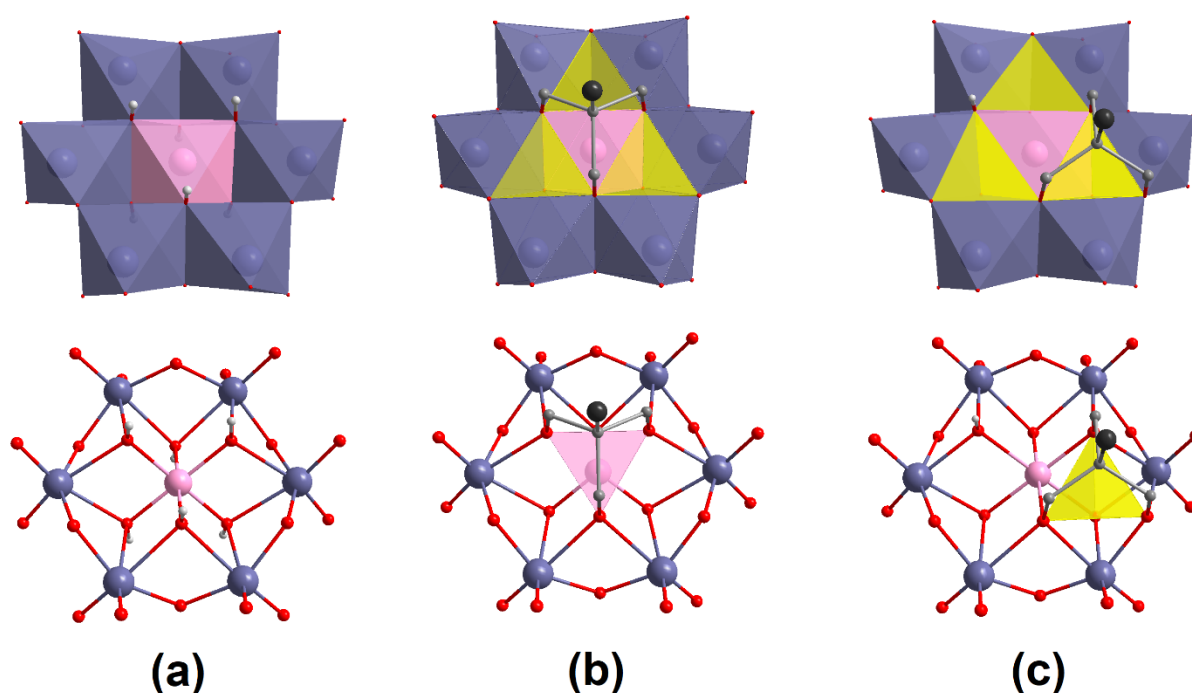


Figure 7.1. Polyhedral (top) and ball-and-stick (bottom) representation of (a) B-type Anderson-Evans POM with protonated $\mu_3\text{-O}$ atoms; (b) organic tripodal alkoxide capping the triangular faces of MO_6 octahedra in δ -form of hybrid; (c) organic tripodal alkoxide capping one of the tetrahedral cavities (shown in yellow) in χ -form of hybrid. Colour code = Blue-grey sphere and octahedra = the addenda atoms M, rose spheres and octahedron = the hetero atoms M, dark-grey spheres = carbon atoms, red spheres = oxygen atoms, pale-grey spheres = hydrogen atoms, black spheres = R-group on the tripodal ligand.

In the B-type Anderson POM, the six μ_3 -O atoms, which are shared between the central MO_6 octahedron and the six surrounding MO_6 octahedra are protonated. (Figure 7.1a). The Anderson hybrid is termed the δ -form when six μ_3 -hydroxide groups are replaced by organic tripodal alkoxide groups from the triol ligand $((\text{HOCH}_2)_3\text{C}-\text{R})$, which attach to the POM and cap the triangular faces of the MO_6 octahedra (Figure 7.1b). In the case of the other isomer, the tripodal alkoxide groups of organic ligands do not cap the triangular faces of the central MO_6 octahedron, but caps the tetrahedral cavity and is called the χ -form (Figure 7.1c). Usually, the tripodal ligand anchor at both sides of the MnMo_6 plane forming symmetric double sided δ/δ and χ/χ isomers. Threefold symmetry is observed in the δ -isomer (approximate D_3 symmetry) and is absent in the χ -isomer (which exhibits approximate C_{2v} symmetry).^[57] Thus, different isomers of functionalised AE structures were obtained depending on the tris(alkoxo) ligands and metal ion M (as explained in Chapter 3).

The organic functionalisation concept was then applied using tris-(hydroxymethyl) aminomethane $[(\text{HOCH}_2)_3\text{C}-\text{NH}_2]$, commonly known as the TRIS ligand.^[57] The choice of this ligand opens up possibilities of developing different binding sites via the post functionalization of the amino ($-\text{NH}_2$) group. δ/δ isomers of the Anderson hybrids $(^n\text{Bu}_4\text{N})_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (**MnMo₆(TRIS)₂**) and $(^n\text{Bu}_4\text{N})_3[\text{FeMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (**FeMo₆(TRIS)₂**) were obtained by using trivalent metal salts $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Fe}(\text{acac})_3]$ respectively.

Since the first report in 2002^[56] further AE hybrids featuring single-sided and double-sided decoration patterns in both δ and χ forms have been identified (as explained in Chapter 3). These incorporate various heteroatoms and triol ligands.^[36, 57-59] However, organic modification was first reported in 2017 in cobalt-centered AE POMs by Wang, Streb *et al.* for the functionalized $\text{Co}^{2+/3+}$ -centered ones produced under different reaction conditions.^[60] Here, the decoration of the parent polyanion $[\text{Co}^{\text{II/III}}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-/3-}$ with triol ligands resulted in the formation of different δ and χ isomers. In the same year, Schönweiz *et al.* synthesized the δ/δ - isomer AE hybrid of the Co^{3+} analogue, $(^n\text{Bu}_4\text{N})_3[\text{CoMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ (δ/δ -**CoMo₆(TRIS)₂**) using a similar approach with $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ as the metal (heteroatom) source. Although the reaction was initiated with a divalent cobalt salt, the Co-centre in the resulting hybrid was found to be in the trivalent state.^[156] In all reported cases of organic functionalised

AE hybrids, the compounds were isolated from the mother liquor using the ether diffusion or evaporation methods.

7.3. TRIS Ligand-Decoration in Cobalt-containing POM Hybrids

Despite trivalent cobalt having an ionic radius comparable to that of trivalent manganese and iron, the organic modification of cobalt-centred AE POMs remains relatively underexplored, as mentioned in the previous section 7.2.

In particular, functionalisation using the tris-(hydroxymethyl) aminomethane (TRIS) ligand is limited to the δ/δ -**CoMo₆(TRIS)₂** example, which has subsequently been post-functionalised into new derivatives.^[59] Such POM molecules have been used as photosensitizers for light-driven hydrogen evolution, as well as electrode material for energy storage, among other applications.^[60, 158-159] Furthermore, divalent cobalt ions are of catalytic interest in processes such as hydrogen evolution and CO₂ reduction,^[160] as well as in molecular magnetism.^[157]

For the tris(alkoxo)-functionalized AE POMs, different synthetic routes have been previously explored, each yielding different isomers. Key pathways for functionalization include the rearrangement of octamolybdate and the use of pre-synthesized Anderson–Evans POMs.^[52]

This section discusses the synthesis of tris-(hydroxymethyl) aminomethane-functionalized cobalt-containing POMs using different polyoxomolybdate salts. The first reported example, δ/δ -**CoMo₆(TRIS)₂**, employed the octamolybdate salt (*n*Bu₄N)₄[α -Mo₈O₂₆] as the source of Mo⁶⁺ ions. This reaction is served as the reference for subsequent studies. Given the structural similarity between the hexamolybdate [Mo₆O₁₉]²⁻ (Lindqvist anion) and the [α -Mo₈O₂₆]⁴⁻ anion^[161], the former was selected for comparative purposes.

7.3.1. Octamolybdate as the Source of Mo⁶⁺ Ions

For the synthesis of δ/δ -**CoMo₆(TRIS)₂**, octamolybdate (*n*Bu₄N)₄[α -Mo₈O₂₆], cobalt acetate and tris(hydroxymethyl)-aminomethane [(HOCH₂)₃C-NH₂] were refluxed in acetonitrile. After the reaction, the suspension obtained was cooled to room temperature and centrifuged. The green crystals of δ/δ -**CoMo₆(TRIS)₂** were obtained by slow diffusion of diethyl ether into the supernatant, as reported in reference 2 (Figure 7.2).

There are no subsequent reports of further studies on the precipitate obtained after the centrifugation of the crude reaction mixture.

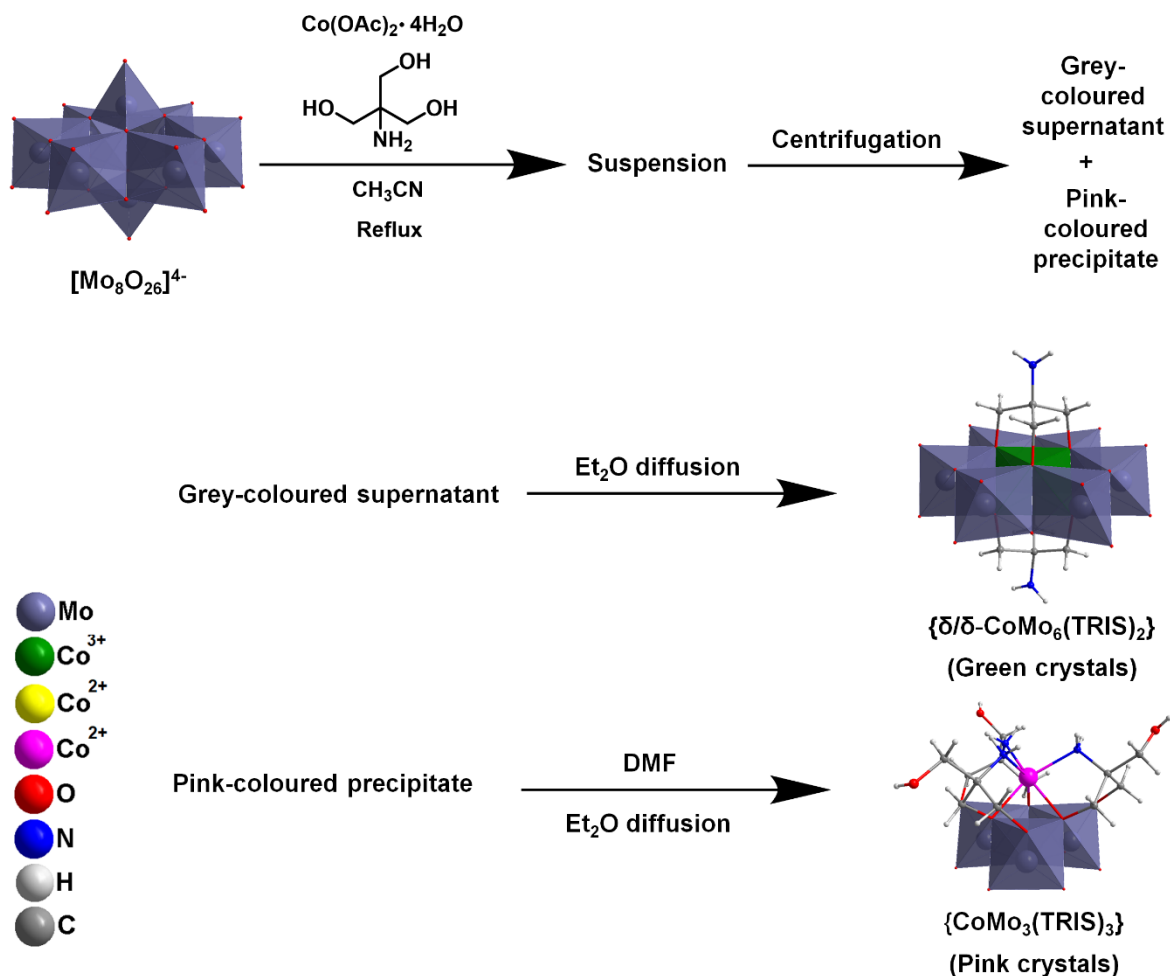


Figure 7.2. Reaction scheme for the synthesis of cobalt-containing polyoxomolybdates from octamolybdate.

The crude pink precipitate obtained after filtration was characterised by infrared spectroscopy. The spectra exhibited the characteristic features of bridged molybdate units and TRIS ligand (Figure 7.3).

The precipitate was then dissolved in DMF and slow diffusion of diethyl ether into this solution over the course of a week yielded pink crystals of varying sizes. X-ray crystallographic analysis revealed that this compound is a divalent cobalt-containing trimolybdate hybrid cluster with three TRIS ligands, **CoMo₃(TRIS)₃** (Figure 7.2).

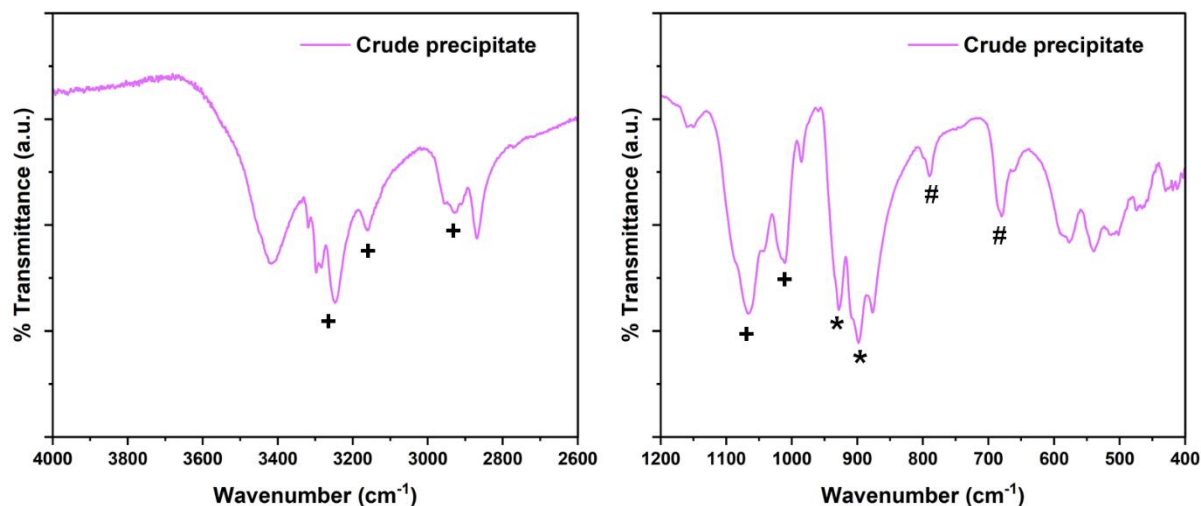


Figure 7.3. FT-IR spectra of crude precipitate obtained during the synthesis of the Anderson hybrid δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ are shown in two separate ranges: 1200–400 cm^{-1} and 4000–2500 cm^{-1} , indicating the presence of bridged molybdate units and TRIS ligand. Peak representations are + for the O-C, O-N or O-H units from TRIS ligand, * for the terminal Mo=O units, # for the terminal bridging Mo-O-Mo units.

The difference in the moisture content in the crystallisation solvent DMF led to the isolation of two solvate forms of $\text{CoMo}_3(\text{TRIS})_3$. If the DMF was nearly dry, pale pink block crystals of $[\text{CoMo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 5.5\text{DMF}$ ($\text{CoMo}_3(\text{TRIS})_3\text{-1}$) were isolated. In contrast, the use of DMF containing a higher water content yielded $[\text{CoMo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$ ($\text{CoMo}_3(\text{TRIS})_3\text{-2}$). Although the two compounds crystallized in different unit cell packings, the $\text{CoMo}_3(\text{TRIS})_3$ core structure was nearly identical in both cases.

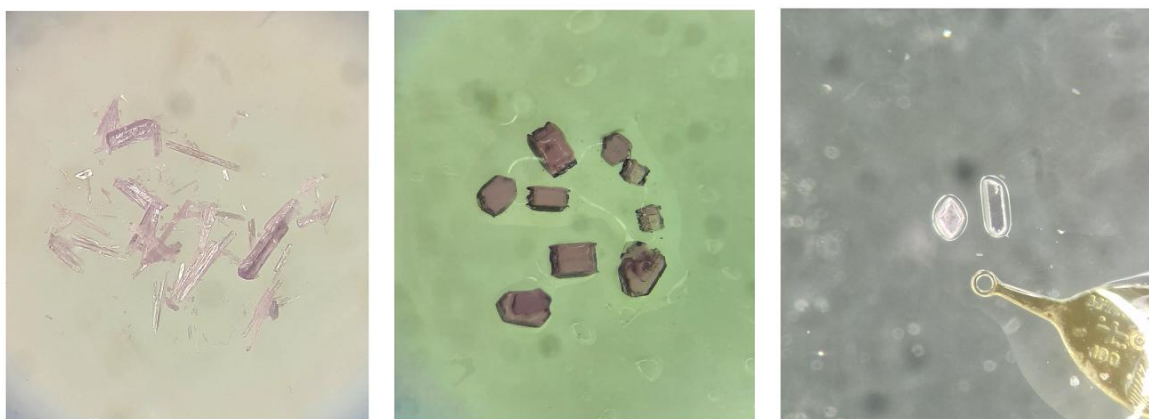


Figure 7.4. Crystals of $\text{CoMo}_3(\text{TRIS})_3$ in air, mother liquor and perfluorinated polyether (PFPE) oil. The colours of the crystals appear different depending on the lighting and background.

7.3.2. Lindqvist Hexamolybdate as the Source of Mo⁶⁺ Ions

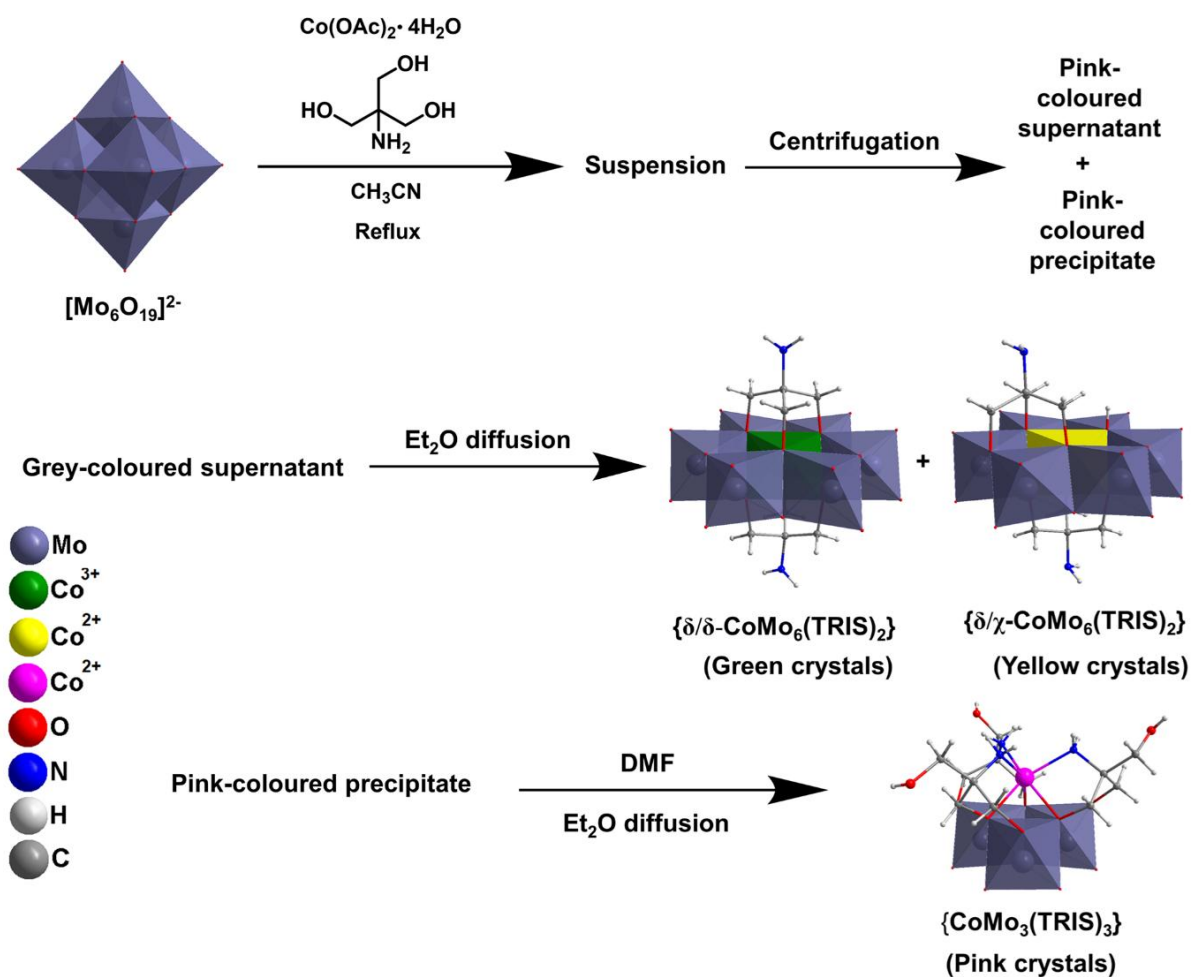


Figure 7.5. Reaction scheme for the synthesis of cobalt-containing polyoxomolybdates from Lindqvist hexamolybdate. The Co^{2+} in different coordination environment in two compounds $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ and $\text{CoMo}_3(\text{TRIS})_3$ are shown in yellow and pink respectively.

When Lindqvist hexamolybdate ($(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$) was used instead of octamolybdate as the source of Mo^{6+} ions, a suspension was obtained. Following centrifugation, the supernatant was exposed to an ether atmosphere, resulting in the formation of a mixture of green crystals of $\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$ crystals and yellow crystals of $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$. This represents the first report of a δ/χ -isomer incorporating TRIS ligand.⁷ The pink precipitate obtained after the centrifugation was of higher yield, compared to when octamolybdate was used. It was dissolved in DMF and subsequent crystallization via ether diffusion yielded $\text{CoMo}_3(\text{TRIS})_3$ (Figure 7.5).

7.4. Structural Features of TRIS-Functionalised Cobalt-Containing POMs

7.4.1. $\text{CoMo}_3(\text{TRIS})_3$

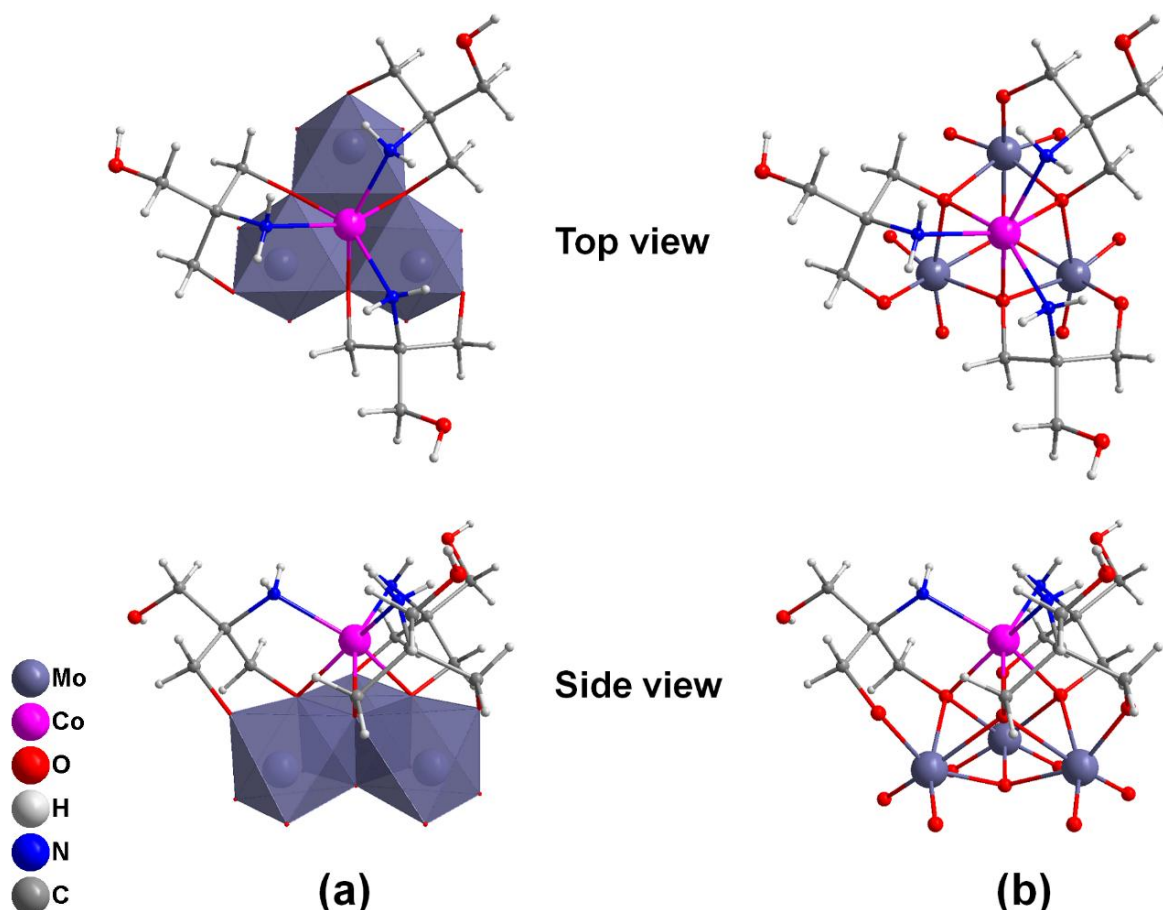


Figure 7.6. (a) Polyhedral and (b) ball-and-stick representation and of the $\text{CoMo}_3(\text{TRIS})_3$ core, shown from side and top views. Hydrogen atoms and disordered atoms removed for clarity.

The compound $[\text{CoMo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 5.5\text{DMF}$ **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** crystallizes in the monoclinic space group $P2_1/c$, whereas $[\text{CoMo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$ **$\text{CoMo}_3(\text{TRIS})_3\text{-2}$** crystallises in the triclinic space group $P\bar{1}$ with $Z = 4$. The two compounds only differ in their crystal packing due to variations in solvation, but both contain the same $\text{CoMo}_3(\text{TRIS})_3$ central core, which is described below.

The $\text{CoMo}_3(\text{TRIS})_3$ core comprises a 6-coordinated divalent cobalt ion and three edge-shared $\{\text{MoO}_6\}$ polyhedra and three doubly-deprotonated TRIS ligands. The structure has a Co^{2+} in a geometry lying between idealised octahedral and trigonal prismatic with three $-\text{NH}_2$ groups positioned above and three μ_3 -oxo ligands below (Figure 7.6). The

bridging oxygen atoms, together with the non-bridging O atoms from other -OCH₂- groups of the TRIS ligands contribute to stabilizing the edge-shared [Mo₃O₁₃]⁸⁻ unit. One of the three -CH₂-OH arms of the TRIS ligands in the core exhibits slight disorder.

The three edge-shared {MoO₆} octahedra that forms the [Mo₃O₁₃]⁸⁻ unit can be viewed as one half of a hexamolybdate [Mo₆O₁₉]²⁻ Lindqvist structure (Figure 7.7a, b). The Co²⁺ ion caps the resulting tetrahedral void in this fragment (Figure 7.7c).

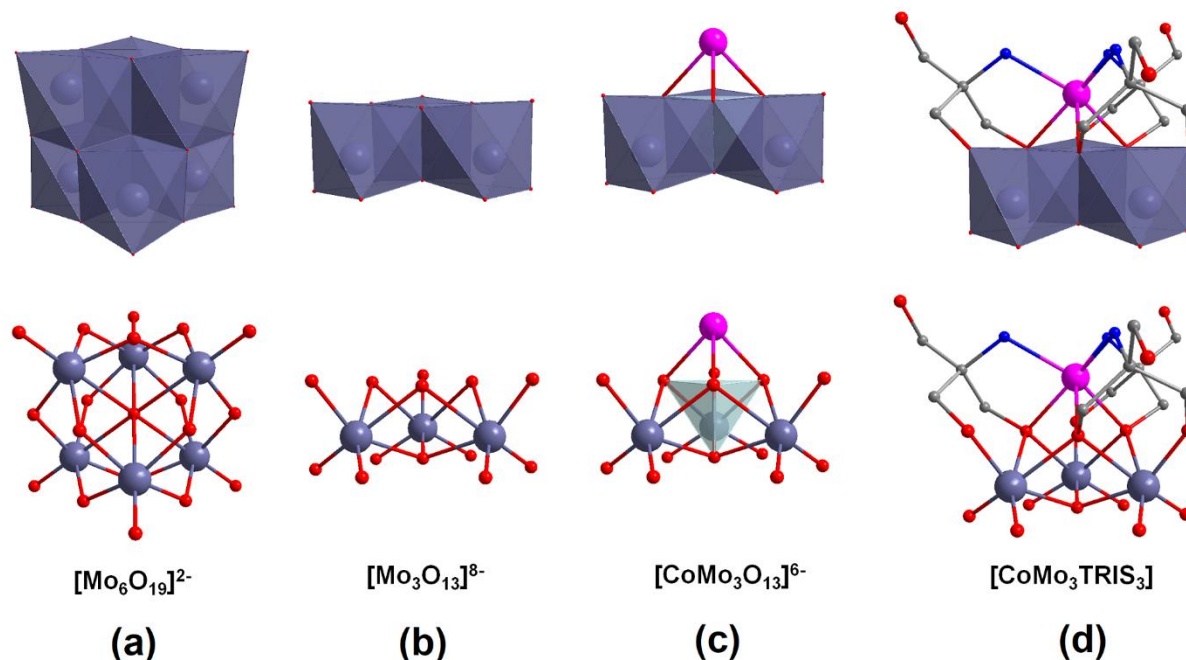


Figure 7.7. Polyhedral (top) and ball-and-stick (bottom) representation of (a) hexamolybdate anion; (b) [Mo₃O₁₃]⁸⁻ unit; (c) Co²⁺ ion capping the tetrahedral void in [Mo₃O₁₃]⁸⁻ unit; (d) **CoMo₃(TRIS)₃** core. Hydrogen atoms and disordered atoms removed for clarity. (Blue-grey spheres and octahedra = molybdenum; pink spheres = cobalt; dark-grey spheres = carbon atoms = red spheres = oxygen atoms; blue spheres = nitrogen atoms).

The central Co²⁺ ion is coordinated to three nitrogen atoms and three oxygen atoms, forming an intermediate structure between octahedron and trigonal prism. The Co–N bond lengths are 2.14 Å (2.13 Å), 2.14 Å (2.14 Å) and 2.14 Å (2.16 Å), and the Co–O bond lengths are 2.11 Å (2.10 Å), 2.11 Å (2.12 Å) and 2.13 Å (2.13 Å) respectively in **CoMo₃(TRIS)₃-1** (and **CoMo₃(TRIS)₃-2**).

The Continuous SHAPE Measurements for the 6-coordinated Co^{2+} ion reveal a deviation from ideal octahedral (O_h) and trigonal prism (D_{3h}) geometry (Table 7.1). The coordination geometry can be visualised as roughly the half-way point between an ideal octahedral and trigonal prism geometry. The torsional angle (ϕ) is useful in understanding the distortion by trigonal rotation. For octahedron $\phi = 60^\circ$ and for trigonal prisms $\phi = 0^\circ$. In **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**, the three N atoms and O atoms surrounding the divalent Co^{2+} ion form two triangular planes which are oriented at a torsional angle (ϕ) of approximately 31° and 30.5° respectively, which are almost exactly intermediate between the two ideal values (Figure 7.8).

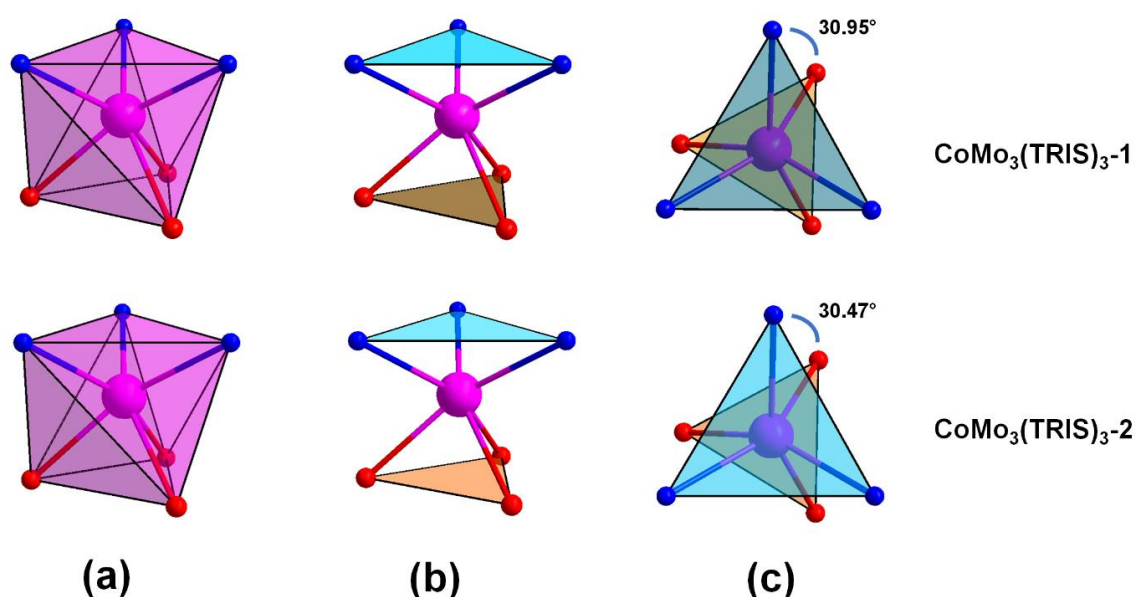


Figure 7.8. Coordination environment around Co^{2+} in **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**. (a) 6-vertex coordination polyhedra around Co^{2+} ; (b) the triangular planes in the coordination polyhedral to compare the torsional angle; (c) torsional angle for the triangular planes (Pink spheres = divalent cobalt; red spheres = oxygen atoms; blue spheres = nitrogen).

Table 7.1. Continuous Shape Measurements (CShM) for the six- coordinated cobalt atoms in **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**.

Compound	Atom	Shape	Ideal Value	Continuous Shape Measurements (CShM)
CoMo₃(TRIS)₃-1	Co1	OC-6 Octahedron	0	4.68
		TPR-6 Trigonal prism	0	5.45
CoMo₃(TRIS)₃-2	Co1	OC-6 Octahedron	0	4.59
		TPR-6 Trigonal prism	0	5.64

For comparative study of torsional angle in 6-coordinated cobalt ion in **CoMo₃(TRIS)₃**, a new complex was synthesized by the reaction of CoCl₂·6H₂O with TRIS ligand in DMF (i.e., without Mo⁶⁺). A binuclear cobalt-TRIS complex [Co₂{(NH₂)C(CH₂O)₃}{(NH₂)C(CH₂OH)₃}][(NH₃)C(CH₂OH)]Cl₄ (**Co(TRIS)₃**) was obtained as hexagonal shaped crystals over the period of 3 weeks (Figure 7.9a).

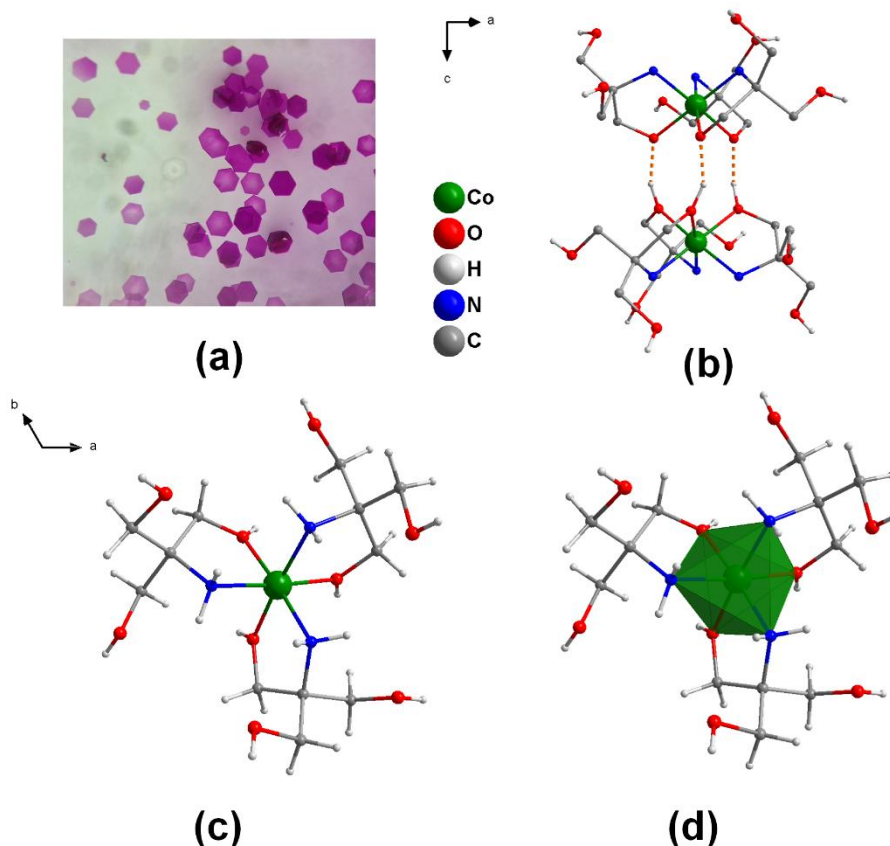


Figure 7.9. (a) Hexagonal shaped pink crystals of **Co(TRIS)₃**; (b) Hydrogen bonds between two units of cobalt-TRIS complex molecules; (c) Ball and stick and (d) polyhedral representation of trivalent cobalt centre in **Co(TRIS)₃**.

The compound **Co(TRIS)₃** crystallises in *R*32 trigonal space group and the crystal structure reveal a binuclear unit made from [Co{(NH₂)C(CH₂O)₃}] and [Co{(NH₂)C(CH₂OH)₃}] core units. The protons on oxygen atoms (of three -CH₂O- groups) attached on cobalt centres are disordered over the two units and can be placed at the midpoint of the hydrogen bond (Figure 7.9b). The Co-O bond lengths vary between 1.90 and 1.91 Å and suggests that the cobalt ion is trivalent. In the lattice, there are two Cl⁻ and a disordered protonated TRIS ligand per cluster. This compound is structurally similar to the previously reported cobalt-aminoethanol complex featuring a binuclear cobalt complex.^[162] Only the structural features of 6-coordinated cobalt in the **Co(TRIS)₃** complex (trivalent) and **CoMo₃(TRIS)₃** cluster (divalent) are compared.

As shown in Figure 7.10, the coordination environment of cobalt ions in the central core unit of $\text{Co}^{\text{II}}\text{Mo}_3(\text{TRIS})_3$ and $\text{Co}^{\text{III}}(\text{TRIS})_3$ are very similar, although their oxidation states are different. As described before, the complex $\text{Co}^{\text{III}}(\text{TRIS})_3$ has protons on the oxygen atoms (with half occupancy) of the three $-\text{CH}_2\text{O}-$ group attached on cobalt centres. If we ignore these hydrogen atoms and consider here an additional $[\text{Mo}_3\text{O}_7]$ unit attaching to the core via three $-\text{CH}_2\text{O}-$ group, the resultant structure is very similar to that of $\text{Co}^{\text{II}}\text{Mo}_3(\text{TRIS})_3$. Here, the coordination polyhedra of cobalt can be compared now.

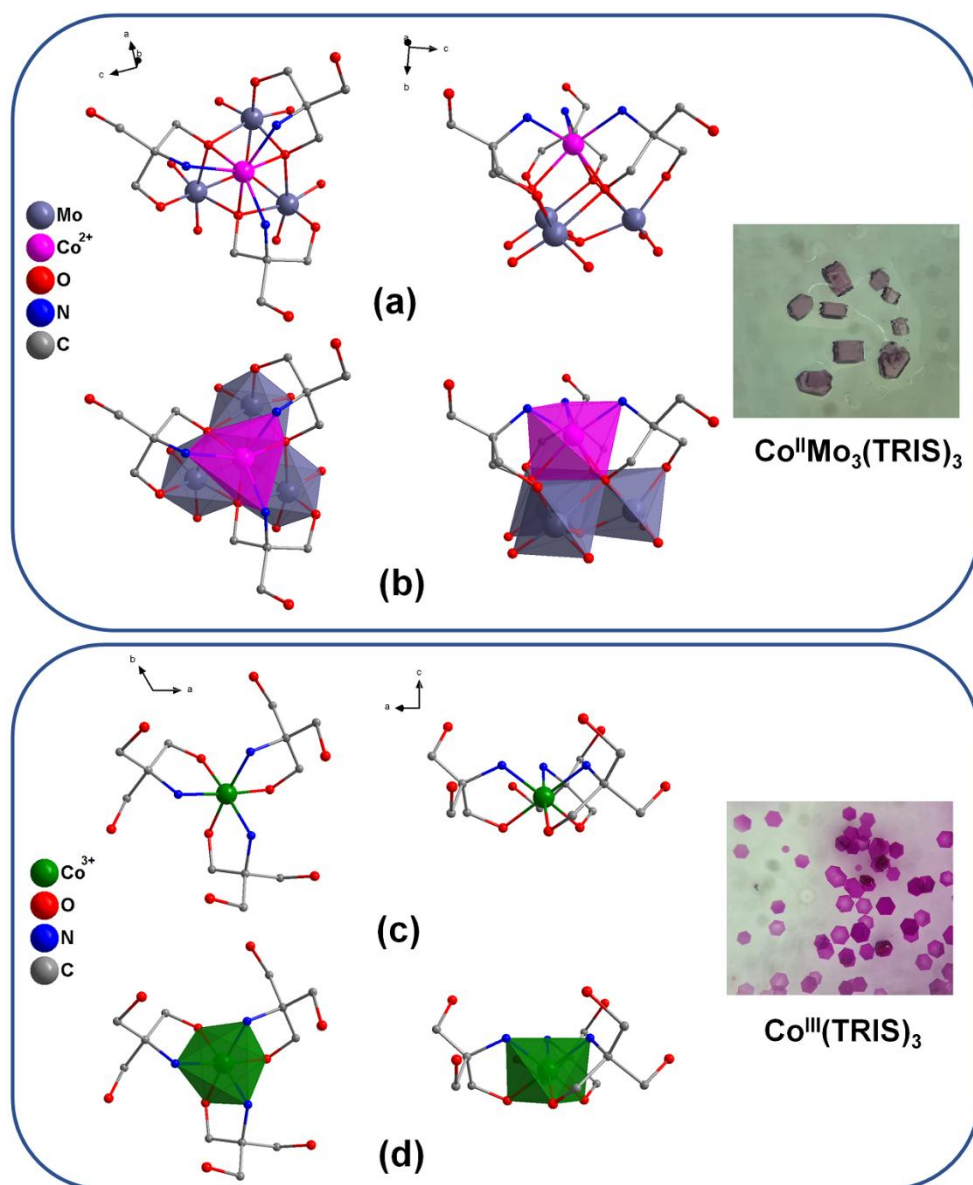


Figure 7.10. (a) Ball and stick and (b) polyhedral representation of metal centers in $\text{CoMo}_3(\text{TRIS})_3$ viewed along different directions; (c) Ball and stick and (d) polyhedral representation of cobalt center in $\text{Co}(\text{TRIS})_3$ viewed along different directions.

The Co^{2+} in $\text{Co}^{\text{II}}\text{Mo}_3(\text{TRIS})_3$ is in a geometry lying between idealised octahedral and trigonal prismatic as seen earlier. However, the Co^{3+} in $\text{Co}^{\text{III}}(\text{TRIS})_3$ is in a geometry close to idealised octahedral (Figure 7.11a). The torsional angle is close to 60° as described for an ideal octahedral geometry (Figure 7.11c).

Thus, it is inferred that the $[\text{Mo}_3\text{O}_7]$ unit is responsible for twisted coordination of cobalt ion away from ideal octahedral geometry in $\text{Co}^{\text{II}}\text{Mo}_3(\text{TRIS})_3$.

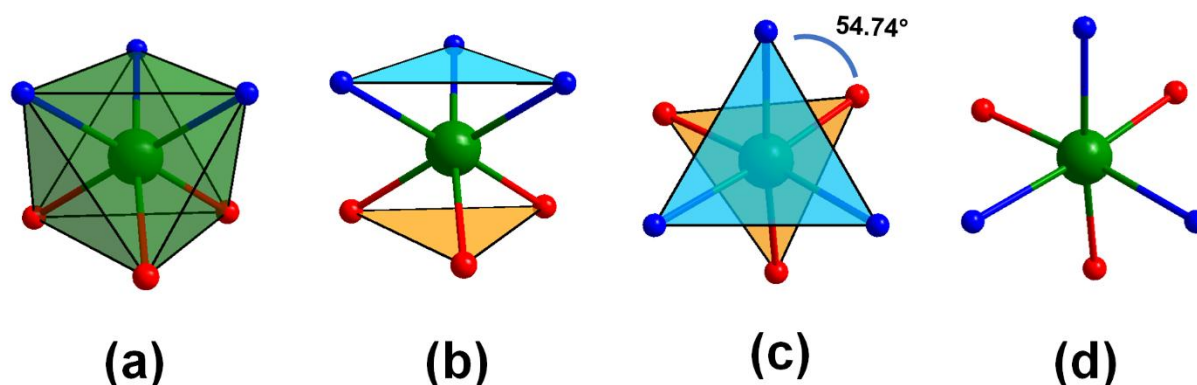


Figure 7.11. Coordination environment around Co^{3+} in $\text{Co}(\text{TRIS})_3$ (a) 6-vertex coordination polyhedral (octahedral) of Co^{3+} ; (b) the triangular planes in the coordination polyhedral to compare the torsional angle; (c) torsional angle for the triangular planes; (d) 6-coordinated Co^{3+} . (Green spheres = trivalent cobalt; red spheres = oxygen atoms; blue spheres = nitrogen).

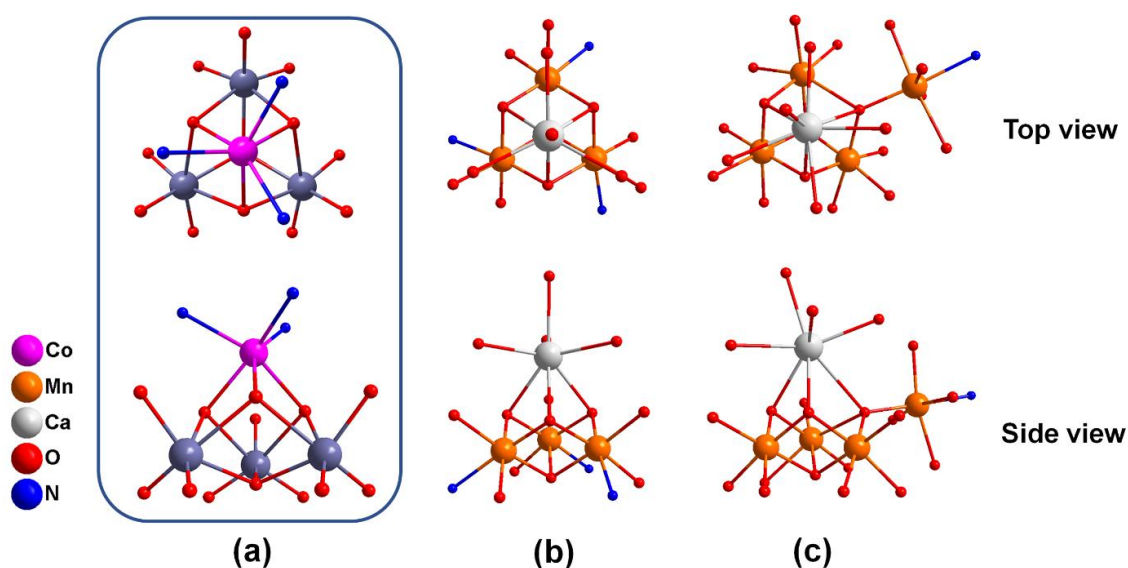


Figure 7.12. (a) CoMo_3 , (b) Mn_3Ca , (c) Mn_4Ca metal-oxide cubane cores that has been studied as closest mimic of the oxygen-evolving complex (OEC).^{15, 16}

The CoMo_3 inorganic unit along with bridging oxygen atoms, exhibits a structural motif comparable to metal-oxide cubane cluster, which has been recognized as close structural analogue of the Mn_4Ca oxygen-evolving complex (OEC) in photosystem II (Figure 7.12). [163-166]

$\text{CoMo}_3(\text{TRIS})_3$ represents one of the smallest heteropolyoxomolybdate-based hybrid molecules reported to date.^[167] It is a charge-neutral cluster that does not require any counter cations such as tetrabutylammonium ($n\text{Bu}_4\text{N}^+$) for stabilization. The solubility of the compound is limited and is soluble only in highly polar aprotic solvents like DMF at low concentrations (about 10 mg in 3 mL).

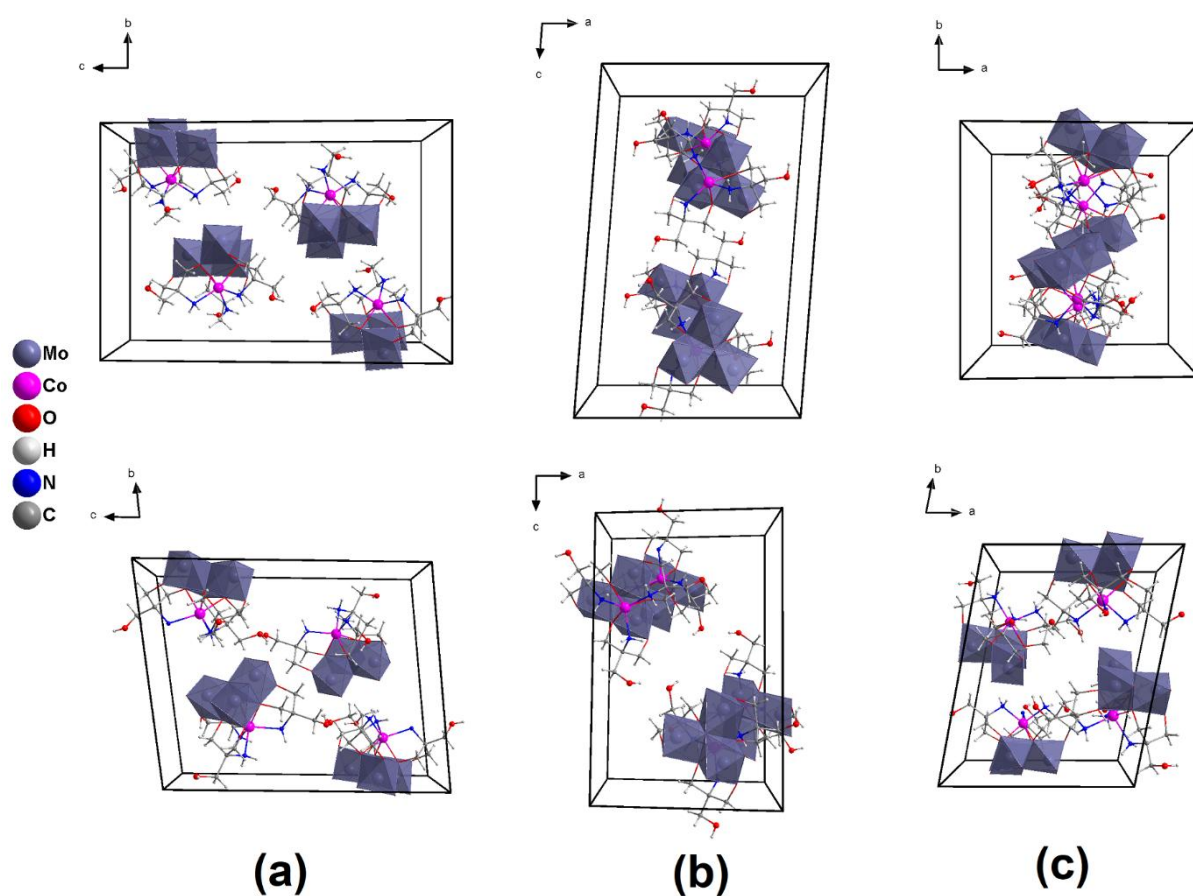


Figure 7.13. Crystal packing of core of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** (top) and **$\text{CoMo}_3(\text{TRIS})_3\text{-2}$** (bottom) in the unit cell viewed along the a, b, c axes. Lattice DMF, water and disordered atoms in TRIS ligand removed for clarity.

The two crystalline forms of **$\text{CoMo}_3(\text{TRIS})_3$** differ in the presence of water molecules alongside DMF within their crystal lattices (Figure 7.13). A summary of the unit cell parameters for **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** and **$\text{CoMo}_3(\text{TRIS})_3\text{-2}$** is provided in Table 7.2.

Table 7.2. Molecular formulas and unit cell parameters of **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**

<u>Compound</u>	CoMo₃(TRIS)₃-1	CoMo₃(TRIS)₃-2
<u>Formula</u>	$[\text{CoMo}_3\text{O}_7 \{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 5.5\text{DMF}$	$[\text{CoMo}_3\text{O}_7 \{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$
<u>Space Group</u>	$P2_1/c$	$P\bar{1}$
<u>a (Å)</u>	13.9822(3)	11.9990(4)
<u>b (Å)</u>	14.9610(3)	15.0259(6)
<u>c (Å)</u>	21.9247(6)	18.6165(6)
<u>α (°)</u>	90	83.126(3)
<u>β (°)</u>	94.498(2)	89.198(3)
<u>γ (°)</u>	90	78.944(3)
<u>V (Å³)</u>	4572.25(18)	3270.4(2)
<u>Z</u>	4	4

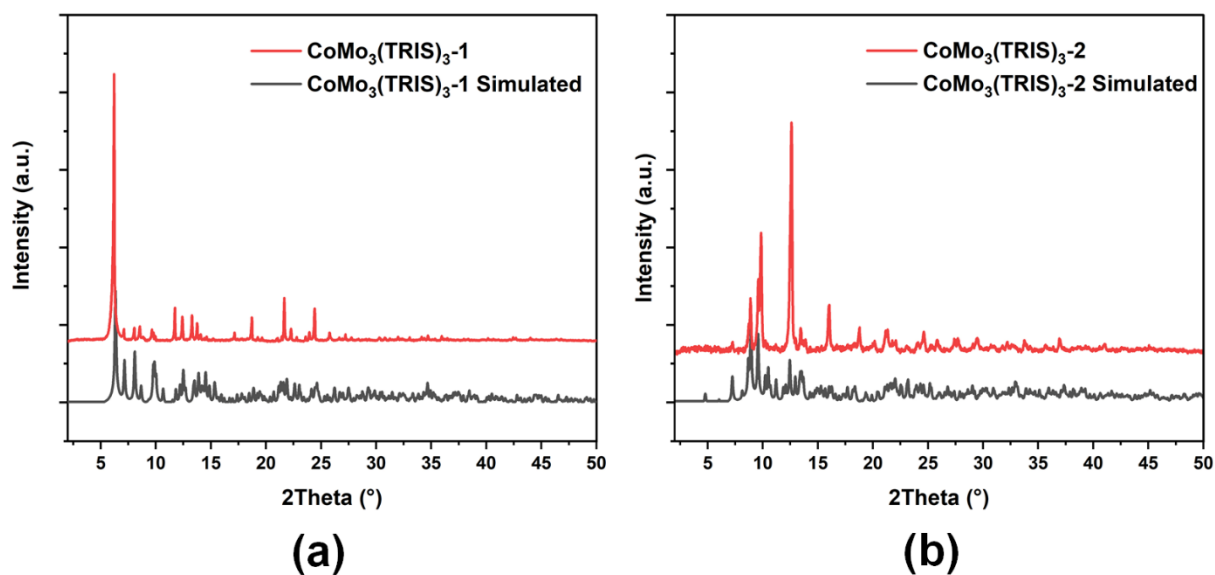


Figure 7.14. PXRD pattern of (a) **CoMo₃(TRIS)₃-1** and (b) **CoMo₃(TRIS)₃-2**.

The FT-IR spectra of **CoMo₃(TRIS)₃** offer structural information on both the metal-oxo core and the organic ligands (Figure 7.15). The region between 500 and 600 cm⁻¹ may be attributed to Co-O and Co-N stretching vibrations.^[60] Bands in the 1000–650 cm⁻¹ range are associated with Mo–O vibrational modes. The sharp peaks at 900, 933 and 966 cm⁻¹ are assigned to terminal Mo=O stretches, while lower energy bands at 661, 686 and 788 cm⁻¹ are characteristic of bridging Mo–O–Mo vibrations.^[60, 168]

Table 7.3. Summary for assignments of IR spectra of **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**

<u>IR Spectra Peak (cm⁻¹)</u>	<u>Assignment</u>
3450 (broad), 3340 (sharp)	Water
3301, 3277	O-H str.
3248, 3237, 3150	N-H str.
2939	CH ₂ asym. str.
2875	CH ₂ sym. str.
1592	NH ₂ rocking
1498, 1441, 1415	CH ₂ scissoring
1390, 1290, 1251, 1148, 1063, 1034, 1010	C-N, C-O, C-C
966, 933, 900	Mo=O
788, 686, 661	Mo–O–Mo
580	Co–N
466, 417	Co–O

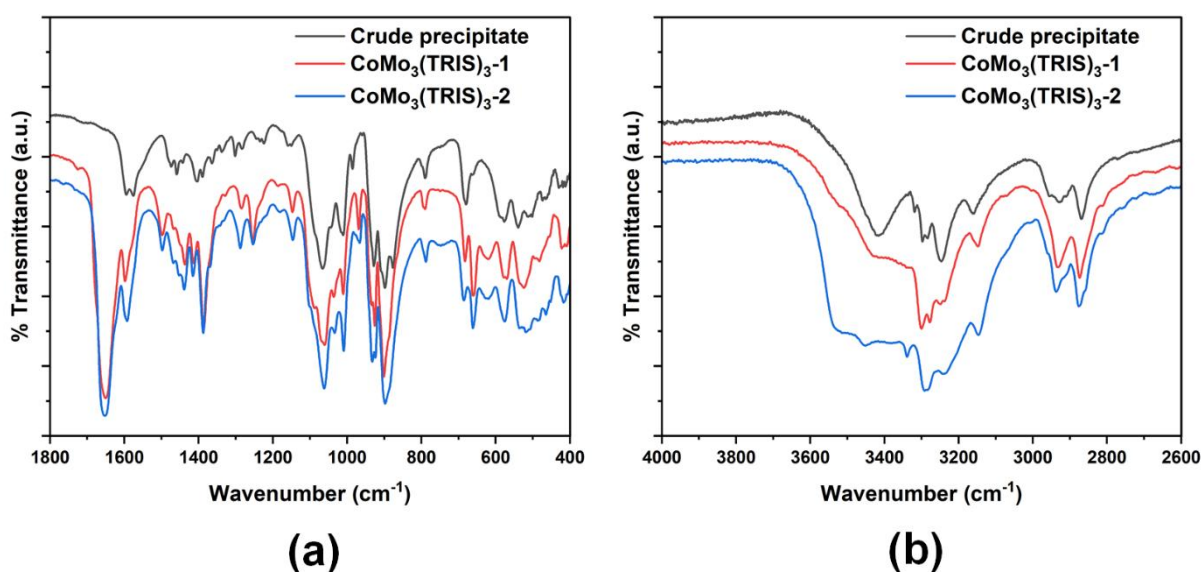


Figure 7.15. FT-IR spectra of **CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2** compared with the crude precipitate from which these are crystallized: (a) from 1800 cm⁻¹ and 400 cm⁻¹ and (b) 4000 cm⁻¹ to 2600 cm⁻¹.

Vibrational bands corresponding to the O–C, C–N, and C–C bonds of the TRIS ligand are primarily observed in the 1000–1700 cm^{-1} region. For instance, the O–C stretching vibrations are responsible for the bands at 1010, 1032, and 1062 cm^{-1} . A sharp peak at 1592 cm^{-1} accounts for the NH_2 deformation.^[169] The characteristic C–H stretching bands are visible at 2850–2950 cm^{-1} region and N–H, O–H bond vibrations are visible in 3100–3600 cm^{-1} .^[170]

7.4.2. δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ and δ/χ - $\text{CoMo}_6(\text{TRIS})_2$

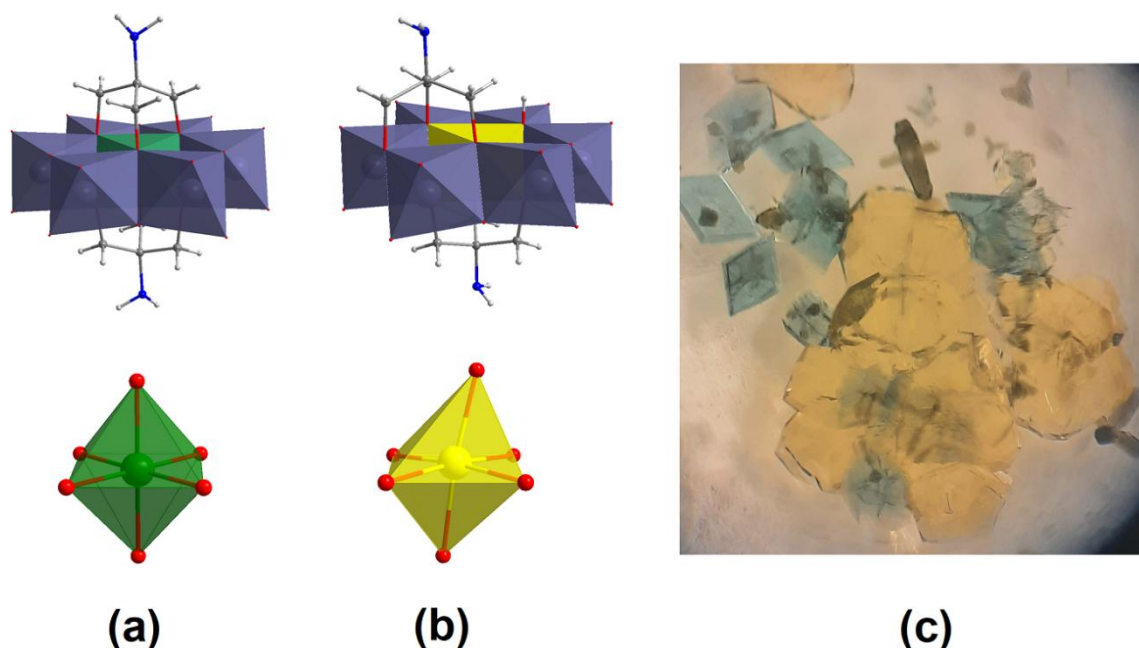


Figure 7.16. (a) Polyanion in δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ (top) and central $\text{Co}^{\text{III}}\text{O}_6$ polyhedron (bottom); (b) Polyanion in δ/χ - $\text{CoMo}_6(\text{TRIS})_2$ (top) and central $\text{Co}^{\text{II}}\text{O}_6$ polyhedron (bottom); (Blue-grey spheres and octahedra: molybdenum and the MoO_6 , green spheres and octahedra = Co^{3+} centres and the corresponding CoO_6 octahedra, yellow spheres and octahedra = Co^{2+} centres and the corresponding CoO_6 octahedra, dark-grey spheres = carbon atoms, red spheres = oxygen atoms, blue spheres = nitrogen atoms, light-grey spheres = hydrogen atoms). (c) Crystals of δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ (green) and δ/χ - $\text{CoMo}_6(\text{TRIS})_2$ (yellow).

The δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ has been previously reported² and only a basic structural description is discussed here. The $[\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]^{3-}$ polyanion consist of six edge-sharing MoO_6 octahedral units around a central $\text{Co}^{\text{III}}\text{O}_6$ octahedron. All six Co^{III} -O bonds are between 1.910 and 1.923 Å long. Three tetrabutylammonium cations balances the charge of the polyanion, and the molecular formula is $(^t\text{Bu}_4\text{N})_3[\text{CoMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$. The two NH_2 - $\text{C}(\text{CH}_2\text{O})_3$ groups of TRIS ligand

symmetrically coordinate to the central Co^{III} ion in the Anderson-Evans (AE) structure forming the δ/δ - isomer (Figure 7.16a).

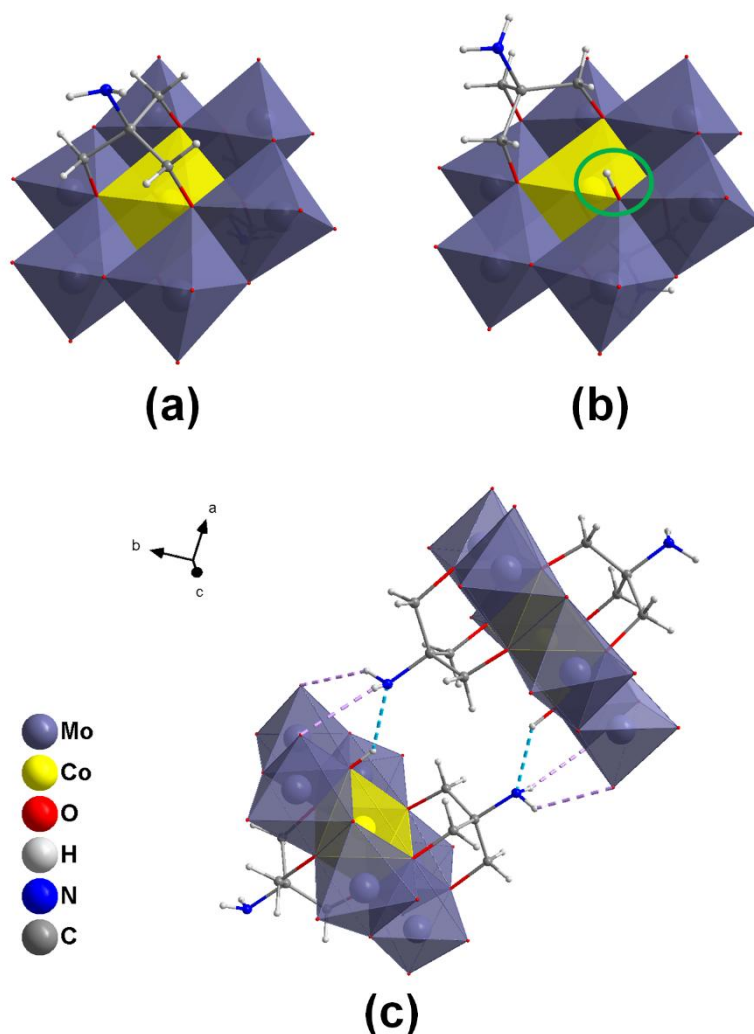


Figure 7.17. The planar side of the CoMo_6 inorganic core of $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ showing the TRIS ligand decoration as the (a) δ -form and (b) χ -form (with highlighted proton on the $\mu_3\text{-O}$); (c) Hydrogen bonds between two cluster units of $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$. Hydrogen bond between the $\mu_3\text{-O-H}$ of a POM unit and the amine lone pairs of another unit is shown in sky blue and that between the N-H of a unit and terminal Mo=O oxygens with the other unit is shown in lavender.

The compound $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ crystallises in the tetragonal space group $I4_1cd$. The molecule $(n\text{Bu}_4\text{N})_3[\text{Co}^{\text{II}}\text{Mo}_6\text{O}_{17}(\text{OH})\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ is an AE POM with a divalent cobalt centre. The planar side of the CoMo_6 inorganic core of the POM where the TRIS-ligand decoration is in χ -form, has an additional proton on the $\mu_3\text{-O}$ (Figure 7.17b). The

asymmetric unit contains a $[\text{Co}^{\text{II}}\text{Mo}_6\text{O}_{17}(\text{OH})\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$ trianionic POM, three $(n\text{Bu}_4\text{N})^+$ cations, a lattice water and an acetonitrile molecule.

Both the molecular unit and the space group are acentric. This isomer is one of the rarest structures seen in AE-type hybrids, especially with the TRIS ligand.^[58] In the crystal lattice, two POM hybrid clusters form a dimeric unit, with the O-H of a unit forming hydrogen bonds to the amine lone pairs of the nearby unit and while the N-H of a unit make intermolecular hydrogen bonds to terminal Mo=O oxygens with the other unit (Figure 7.17c).

The SHAPE analysis was performed on Co polyhedra in δ/δ -**CoMo₆(TRIS)₂** and δ/χ -**CoMo₆(TRIS)₂**. The Co^{3+} in the symmetric δ/δ - isomer is close to ideal octahedron (CShM = 0.22), while that in the asymmetric δ/χ - isomer (Co^{2+}) is more distorted (CShM = 0.68).

The FT-IR spectra of δ/δ -**CoMo₆(TRIS)₂** and δ/χ -**CoMo₆(TRIS)₂** show characteristic signals for these Anderson POM structures. The well-defined bands around 900-950 cm^{-1} account for the terminal Mo=O units and lower energy bands at 700 to 500 cm^{-1} for the bridging Mo-O groups. In the case of δ/χ -**CoMo₆(TRIS)₂**, some bands show splitting which seems to be a result of the reduction of the symmetry (shown in bold in Table 7.4) as described in reference^[56].

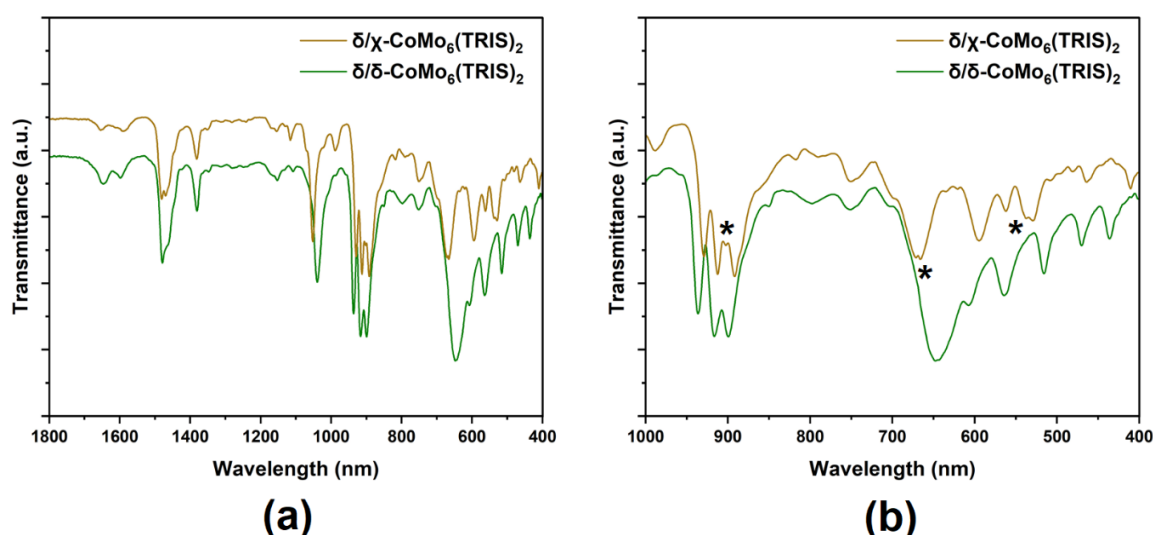


Figure 7.18. FT- IR spectra of δ/δ -**CoMo₆(TRIS)₂** and δ/χ -**CoMo₆(TRIS)₂** in (a)1800-400 cm^{-1} range and (b) 1000-400 cm^{-1} range. Asterisk (*) show the splitting of the bands in the δ/χ - isomer.

Table 7.4. Infrared spectral assignments for δ/δ - and δ/χ - $\text{CoMo}_6(\text{TRIS})_2$, showing key stretching and bending modes of the inorganic core ($\text{Mo}=\text{O}$, $\text{Mo}-\text{O}-\text{Mo}$, $\text{Co}-\text{O}-\text{Mo}$, $\text{Co}-\text{O}$) in cm^{-1} . (ν = stretching vibration, δ^{bend} = bending vibration, asym. = asymmetric, sym. = symmetric). Bands that are result of the reduction of the symmetry are given in bold.

Vibrational Mode	Assignment	δ/δ - $\text{CoMo}_6(\text{TRIS})_6$ (cm^{-1})	δ/χ - $\text{CoMo}_6(\text{TRIS})_2$ (cm^{-1})
$\nu(\text{O}-\text{H})$, hydrogen bonding	H_2O (stretching)	3450 (broad)	3500 (broad)
$\nu_{\text{as}}(\text{Mo}=\text{O}_\text{t})$	Terminal $\text{Mo}=\text{O}$ (asym. str.)	963, 916, 900	929, 912, 902 , 890
$\nu_{\text{sym/as}}(\text{Mo}-\text{O}-\text{Mo})$	$\text{Mo}-\text{O}-\text{Mo}$ (bridging str.)	750, 564	750, 562
$\nu(\text{Co}-\text{O}-\text{Mo})$, δ^{bend} ($\text{Co}-\text{O}-\text{Mo}$)	$\text{Co}-\text{O}-\text{Mo}$ (str. + bend)	646, 606, 564	672, 666 , 595, 537, 527
$\nu(\text{Co}-\text{O})$, δ^{bend} ($\text{Co}-\text{O}$)	$\text{Co}-\text{O}$ (str. + bend)	469, 435	463, 410

7.4.3 $\text{CoMo}_3(\text{TRIS})_3$ vs δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ and δ/χ - $\text{CoMo}_6(\text{TRIS})_2$

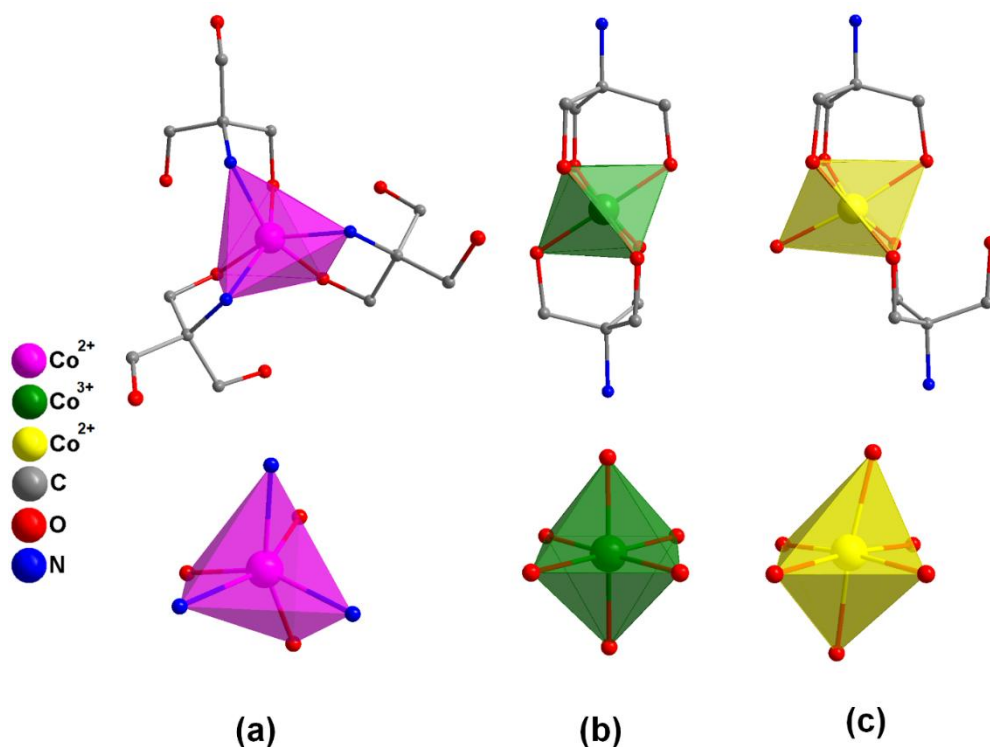


Figure 7.19. Coordination environment around cobalt ion in $\text{CoMo}_3(\text{TRIS})_3$ -1, δ/δ - $\text{CoMo}_6(\text{TRIS})_2$ and δ/χ - $\text{CoMo}_6(\text{TRIS})_2$.

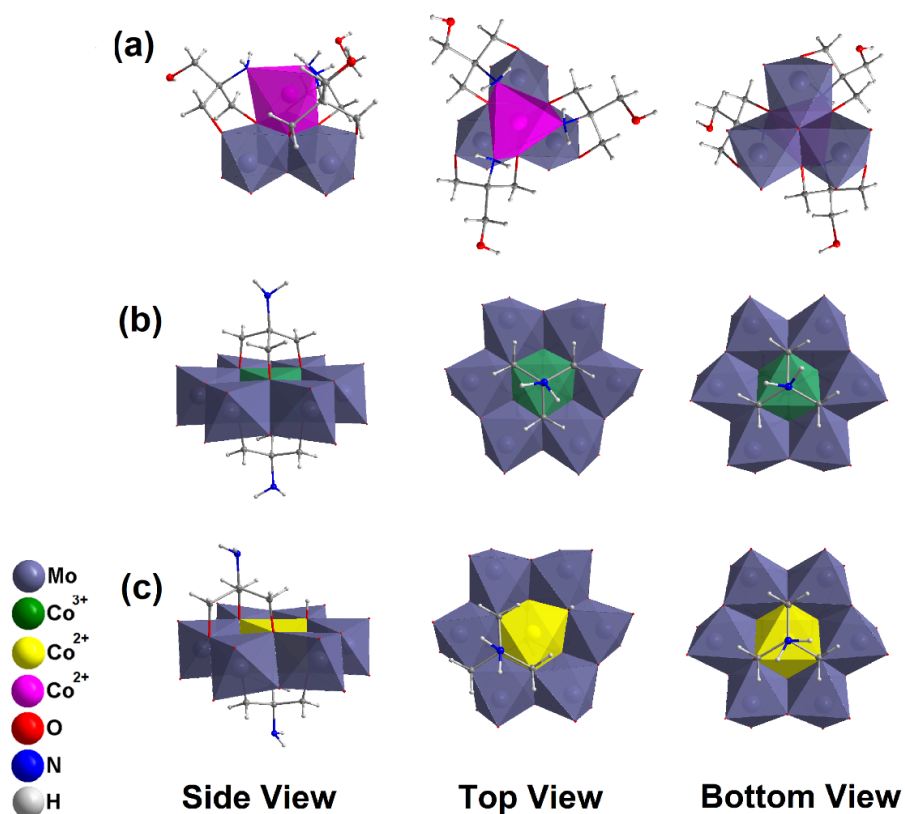


Figure 7.20. $\text{CoMo}_3(\text{TRIS})_3\text{-1}$, $\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$ and $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ viewed along different directions.

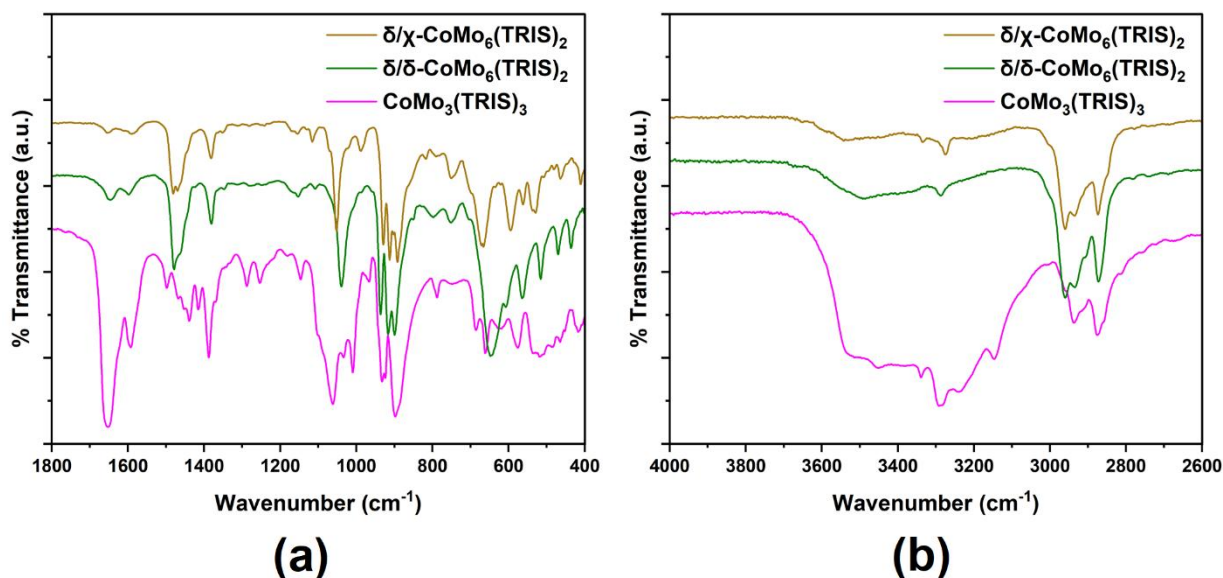


Figure 7.21. FT-IR spectra of $\text{CoMo}_3(\text{TRIS})_3\text{-1}$, $\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$ and $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ shown in two separate ranges: (a) 1800–400 cm^{-1} and (b) 4000–2600 cm^{-1} .

The structures of TRIS-functionalised cobalt-containing polyoxomolybdates discussed above differ with respect to the coordination environment around their respective cobalt ions. The cluster units in $\text{CoMo}_3(\text{TRIS})_3\text{-1}$, $\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$ and $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ are

shown in Figure 7.19. The coordination environment around the cobalt ions is distinct for each of these molecules, especially with respect to the coordinated TRIS ligands (Figure 7.20).

The infrared spectra give a good indication of differences in their molecular structures (Figure 7.21).

7.4.4. Overview About Synthetic Strategies for Isomers in AE POMs

As described in section 7.3.2, both δ/δ -**CoMo₆(TRIS)₂** (green crystals, containing Co³⁺) and δ/χ -**CoMo₆(TRIS)₂** (yellow crystals, containing Co²⁺) were obtained from the same reaction mixture. Although the reaction was initiated with a Co²⁺ source, a significant portion of the Co²⁺ ions was oxidized *in situ*, leading predominantly to the formation of the δ/δ -isomer. This is reflected in its higher yield compared to the δ/χ -isomer. The incomplete oxidation of Co²⁺, which allowed the formation of the less common χ -decoration, is not yet fully understood. However, a possible explanation may be drawn from observations on triol ligand decoration in Anderson-Evans POMs, as discussed in reference 3.

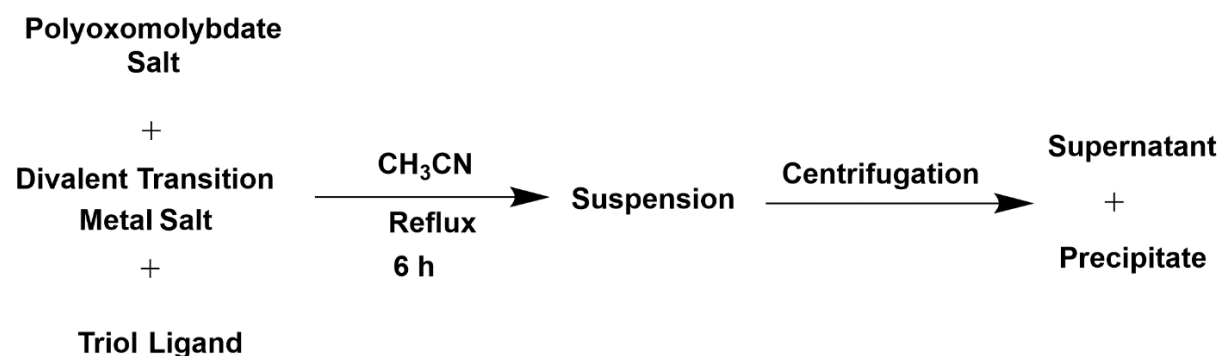
Several factors influence the formation of single- or double-sided isomers in triol-decorated Anderson-Evans POM hybrids. These include the solvent and acidic/basic conditions, the type and oxidation state of the central heteroatom, and the nature of the terminal group (R) in the triol ligand [(CH₂OH)₃C–R]. The main considerations are summarized below:

- a) In most cases, single-sided isomers tend to form in aqueous solutions, whereas double-sided isomers are more readily obtained in organic solvents.
- b) In protic environments, triol decoration of M²⁺-centered (M = transition metal) Anderson-Evans POMs typically results in the χ/χ -isomer. Protonation at the μ_2 -O site enhances its reactivity toward the triol ligand over the μ_3 -O site, leading to the formation of an asymmetric (malposition) structure.
- c) δ/χ -isomers are typically formed from M²⁺-centered clusters in nonacidic or aprotic environments. In less acidic conditions, protonation of the μ_2 -O atom is hindered, decreasing its reactivity. As a result, part of the triol grafting shifts to the μ_3 -O atom, leading to the formation of the δ/χ -isomer.
- d) Highly charged metal ions as heteroatoms, such as Mn³⁺, Cr³⁺, Fe³⁺ or Co³⁺ generally lead to the formation of δ - or δ/δ -isomers.

In the cases of δ/δ -**Co^{III}Mo₆(TRIS)₂** and δ/χ -**Co^{III}Mo₆(TRIS)₂**, the difference in the oxidation state of cobalt (Co²⁺ and Co³⁺) ions significantly influences the protonation of the μ_2 -O atom, which affects TRIS ligand attachment. Further studies should be carefully designed to isolate the rare δ/χ -isomer by precisely controlling the acidity/basicity of the reaction mixture and the reaction duration to prevent the oxidation of Co²⁺ to Co³⁺.

7.5. Synthetic Approaches Based on Variations in Reagents and Reaction Conditions

As discussed in previous sections, different TRIS-functionalised cobalt-containing polyoxomolybdates were obtained by the reaction of cobalt acetate and tris(hydroxymethyl)-aminomethane (TRIS) ligand with octamolybdate (ⁿBu₄N)₄[α -Mo₈O₂₆] or hexamolybdate (ⁿBu₄N)₂[Mo₆O₁₉] in acetonitrile. Anderson- Evans POM hybrids δ/δ -**CoMo₆(TRIS)₂** and δ/χ -**CoMo₆(TRIS)₂** were obtained from the filtrate and the **CoMo₆(TRIS)₂** cluster from the precipitate of the original reaction mixture. It is a well-established fact that the choice of reagents is an important factor that affects the structure and properties of the final products. This section discusses various trial reactions aimed at synthesising analogous polyoxomolybdate hybrid molecules containing transition metal heteroatoms, following a similar approach as previously described.



As a general reaction scheme shown above, a polyoxomolybdate salt, a divalent transition metal salt and triol ligand are refluxed in acetonitrile for 6 hours. The resulting suspension was centrifuged, and the separated components were subjected to different treatments. The supernatant obtained is kept in ether diffusion. The precipitate obtained is stirred with DMF with heating (80 °C) for 30 minutes, filtered and kept for ether diffusion.

Table 7.5. List of reagents used with an aim of synthesizing analogous compounds as **CoMo₃(TRIS)₃**.

<u>Polyoxomolybdate Salt</u>	<u>Co²⁺ Salt</u>	<u>Divalent Transition Metal Salt</u>	<u>Triol Ligand</u>
• (ⁿBu₄N)₂ [Mo₆O₁₉] • (ⁿBu₄N)₄ [α-Mo₈O₂₆] • (ⁿBu₄N)₂Na₂ [β-Mo₈O₂₆]	• Co(OAc)₂·4H₂O • CoCl₂·6H₂O • CoBr₂ • Co(NO₃)₂·6H₂O • Co(ClO₄)₂·6H₂O	• Mn(OAc)₂·2H₂O • Ni(OAc)₂·4H₂O • Cu(OAc)₂·H₂O • Zn(OAc)₂·2H₂O • Pd(OAc)₂	• TRIS • Tricine • Pentaerythritol • Dipentaerythritol • Tripentaerythritol • Bis-tris propane • Bicine • Triethanolamine

For the optimised reaction for **CoMo₆(TRIS)₂**, one equivalent of (ⁿBu₄N)₂[Mo₆O₁₉], 2 equivalents of Co(OAc)₂·4H₂O and 6 equivalent TRIS were used. This ratio was maintained in the new reactions, with one reagent altered at a time.

7.5.1. Variation of Polyoxomolybdate Source

Table 7.6. Reagents with variation of polyoxomolybdate source.

<u>Polyoxomolybdate Salts</u>	<u>Co²⁺ Salt</u>	<u>Triol Ligand</u>
• (ⁿBu₄N)₄ [α-Mo₈O₂₆] • (ⁿBu₄N)₂ [Mo₆O₁₉] • (ⁿBu₄N)₂Na₂ [β-Mo₈O₂₆]	• Co(OAc)₂·4H₂O	• TRIS

As discussed previously, Anderson Evans hybrids **δ/δ-CoMo₆(TRIS)₂** and a mixture of **δ/δ-CoMo₆(TRIS)₂** and **δ/χ-CoMo₆(TRIS)₂** were obtained from the mother liquor when (ⁿBu₄N)₄[α-Mo₈O₂₆] and (ⁿBu₄N)₂[Mo₆O₁₉] were used as the respective polyoxomolybdate-sources. In both cases, the **CoMo₃(TRIS)₃** cluster was obtained from the precipitate, but the yield was better when (ⁿBu₄N)₂[Mo₆O₁₉] was used. When the β-isomer of octamolybdate [β-Mo₈O₂₆]⁴⁻ was used, no crystals were isolated.

7.5.2. Variation of Co^{2+} Salts

Table 7.7. Reagents with variation of divalent cobalt source.

<u>Polyoxomolybdate Salt</u>	<u>Co^{2+} Salts</u>	<u>Triol Ligand</u>
$(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$	$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ CoBr_2 $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$	TRIS

The reflux reaction of $(^n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$, Co^{2+} salts and TRIS ligand in acetonitrile solvent is a key step during the synthesis of **$\text{CoMo}_3(\text{TRIS})_3$** . The contents of the reaction mixtures thus obtained are separated into supernatant and precipitate by centrifugation (Figure 7.22). The cobalt ions along with other molecular fragments that form the AE hybrids $\delta/\delta\text{-CoMo}_6(\text{TRIS})_2$ and $\delta/\chi\text{-CoMo}_6(\text{TRIS})_2$ will be in the supernatant solution. The atoms/molecular fragments that form the **$\text{CoMo}_3(\text{TRIS})_3$** cluster constitute the precipitate.

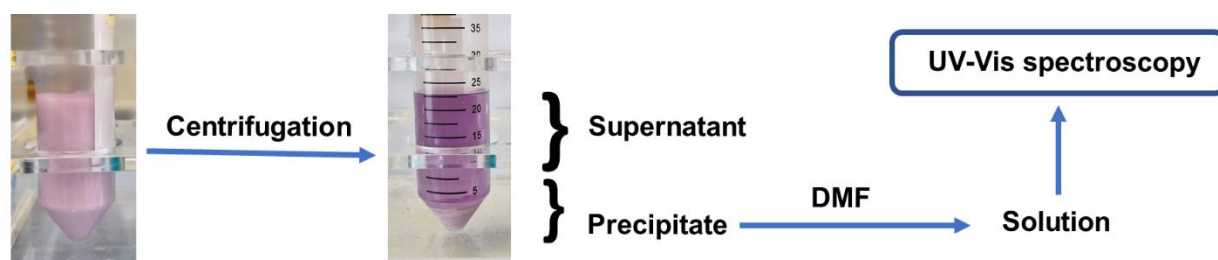


Figure 7.22. The phases involved during the synthesis of **$\text{CoMo}_3(\text{TRIS})_3$** .



Figure 7.23. The supernatant obtained during the reactions using different Co^{2+} salts: $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; CoBr_2 ; $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$.

Depending on the Co^{2+} salts used, the supernatant solutions had different colours with different intensities (Figure 7.23). This indicates that the Co^{2+} ions exist in different coordination environments (octahedral/tetrahedral) in the solution in each case. Those solutions which are colourless indicate the absence or very low concentration of Co^{2+} ions.

As for the interest in the synthesis of the **$\text{CoMo}_3(\text{TRIS})_3$** cluster, the crude precipitate obtained after the centrifugation are investigated further. In each case, the precipitate exhibit characteristic colours depending on the Co^{2+} salts used (Figure 7.24). Furthermore, the yields of the precipitate were also different.

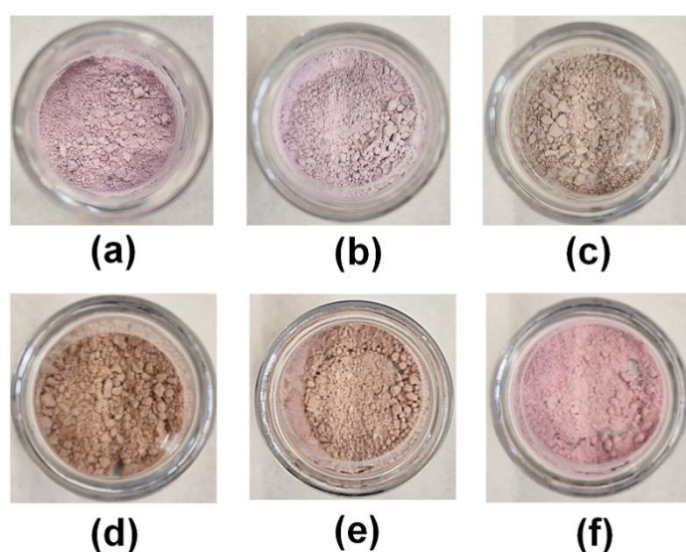


Figure 7.24. The crude precipitate obtained during the reactions using different Co^{2+} salts, (a) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; (b) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; (c) CoBr_2 ; (d) $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$; (e) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; (f) $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$.

The crude precipitate was washed several times with acetonitrile, dried in air and subsequently dissolved in DMF. For each of the precipitate, the solubilities in DMF were different. About 20 mg crude precipitate obtained from bromide and nitrate salts were completely soluble in 3 mL warm DMF (60 °C). The precipitate from acetate, chloride and perchlorate salts were partially soluble and that from sulphate salt was sparingly soluble. Their solubilities improved with dilution (Figure 7.25a). The DMF solution of the precipitate from each case were prepared and the absorption spectra were measured (Figure 7.25b). In almost all the cases, presence of the absorption bands between 500 nm and 700 nm, indicate the presence of an octahedral Co^{2+} ions.

For the solution corresponding to the chloride salt of Co^{2+} , shows an additional absorption in 575 nm-725 nm region which accounting for the blue colour of the solution. This indicates the presence of Co^{2+} ions in tetrahedral environment along with the octahedral ones (Figure 7.25b).

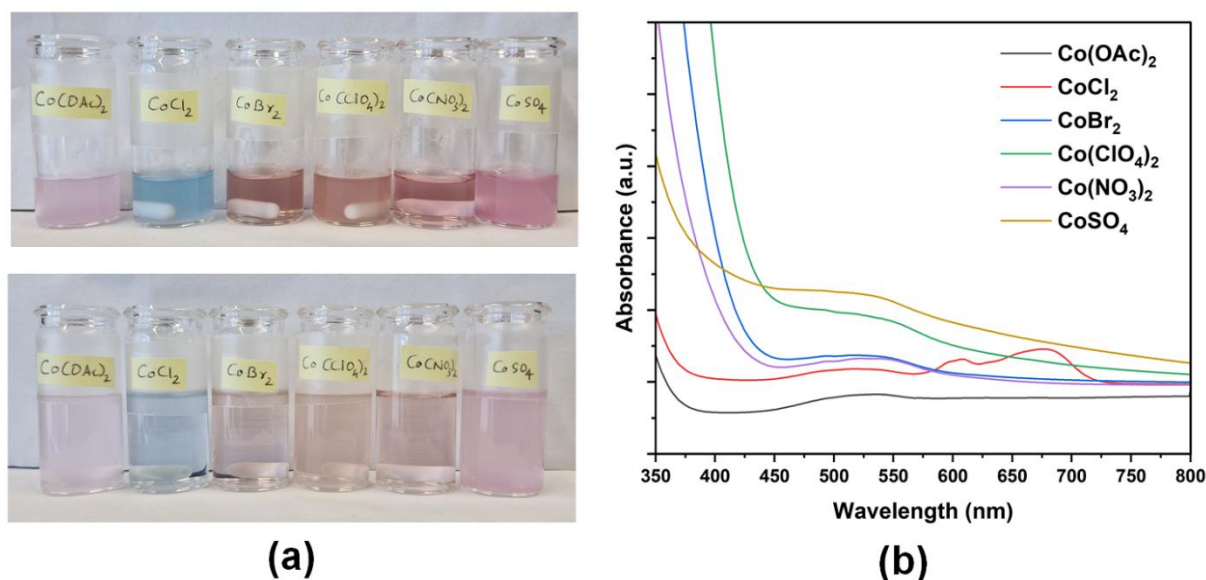


Figure 7.25. (a) The solutions obtained after dissolving the crude precipitate obtained in the reaction using different Co^{2+} salts, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, CoBr_2 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (above) in DMF and the dilutes samples for UV-Vis spectroscopy (below); (b) UV-Vis spectra of the respective diluted solutions.

The DMF solutions of the precipitates in each case were kept for evaporation. In majority of the case, pink crystals of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** of different size were obtained over a period of two weeks. Pure crystals of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** were obtained when $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and CoBr_2 were used. For $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as the source of Co^{2+} ions, the crystals of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** and TRIS ligand were obtained, indicating that the reaction progress was lower than other cases. This is also probably why the solution showed blue colour i.e., the presence of tetrahedrally coordinated Co^{2+} ions (e.g. $[\text{CoCl}_4]^{2-}$). Similarly, when $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ was used, the yield of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** crystals was very low and also the formation of crystals of unreacted salt was observed. With $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, no crystals were obtained.

Thus it was concluded that $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was the best source of Co^{2+} ions for the synthesis of **$\text{CoMo}_3(\text{TRIS})_3\text{-1}$** .

7.5.3. Variation of Divalent Acetate Salts

The crude precipitate obtained using acetate salts of Mn^{2+} , Ni^{2+} , Cu^{2+} and Pd^{2+} did not yield any crystalline products. With $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, colourless crystals of $[\text{ZnMo}_3\text{O}_7\{(\text{OCH}_2)_2\text{C}(\text{NH}_2)(\text{CH}_2\text{OH})\}_3] \cdot 5.5\text{DMF}$ (**ZnMo₃(TRIS)₃-1**) was obtained. This is an isostructural compound as **CoMo₃(TRIS)₃-1**. However, as the focus of this chapter is on $\text{Co}^{2+/3+}$ -containing POMs, further synthesis using other divalent or trivalent transition metal ions was not investigated. These were only considered to check the viability for other divalent metal ions to be incorporated into the polyoxomolybdate structure.

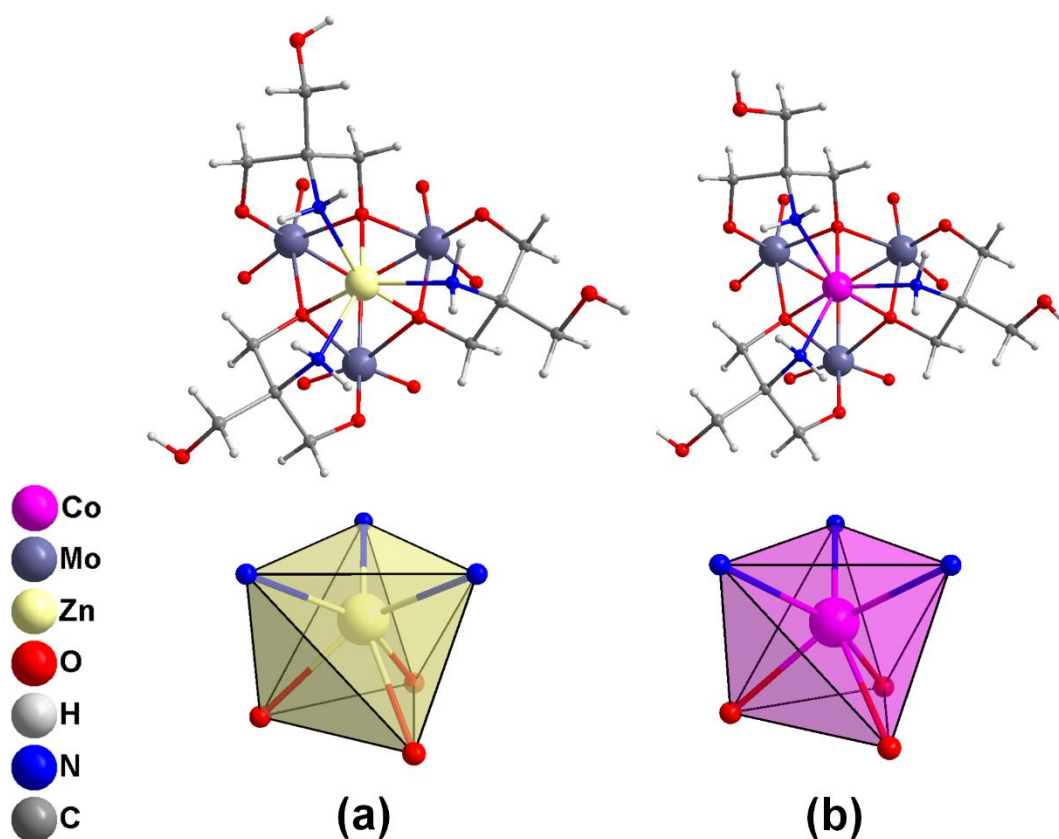


Figure 7.26. Comparison of ball-and-stick representation (top) and metal coordination polyhedra (bottom) of (a) **ZnMo₃(TRIS)₃** core and (b) **CoMo₃(TRIS)₃** core.

7.5.4. Variation of Triol Ligands

There are three hydroxymethyl ($-\text{CH}_2\text{OH}$) groups in TRIS ligand which anchor to the AE POM hybrids. In the case of **CoMo₃(TRIS)₃**, two of these groups and the amino group of the ligand is directly involved in bonding with Mo^{6+} and Co^{2+} ions to form the cluster. Different organic ligands with polyhydroxy chains listed in the Figure 7.27 were used

instead of TRIS ligand with hexamolybdate and cobalt acetate. However, no crystals of new products were obtained in any case.

Table 7.8. Reagents with variation of triol ligands.

<u>Polyoxomolybdate Salt</u>	<u>Co²⁺ Salt</u>	<u>Triol Ligands</u>
(ⁿBu₄N)₂ [Mo₆O₁₉]	Co(OAc)₂·4H₂O	- TRIS - Tricine - Pentaerythritol - Dipentaerythritol - Tripentaerythritol - Bis-tris propane - Bicine - Triethanolamine

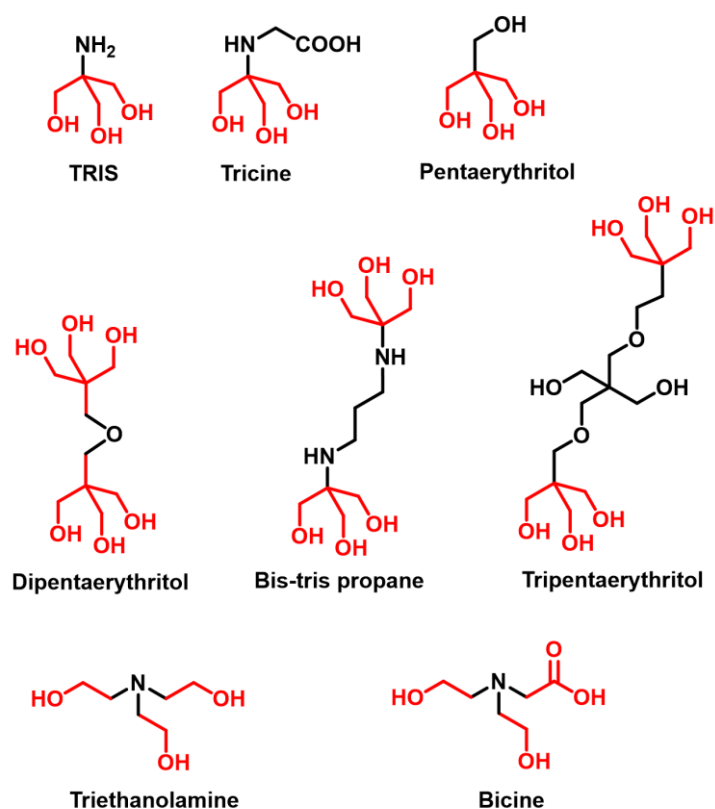


Figure 7.27. List of polyhydroxy ligands.

7.6. Optical Properties of $\text{CoMo}_3(\text{TRIS})_3$

The optical properties of $\text{CoMo}_3(\text{TRIS})_3\text{-2}$ were studied by measuring its absorption spectra in both solid-state and DMF-solution (Figure 7.28a).

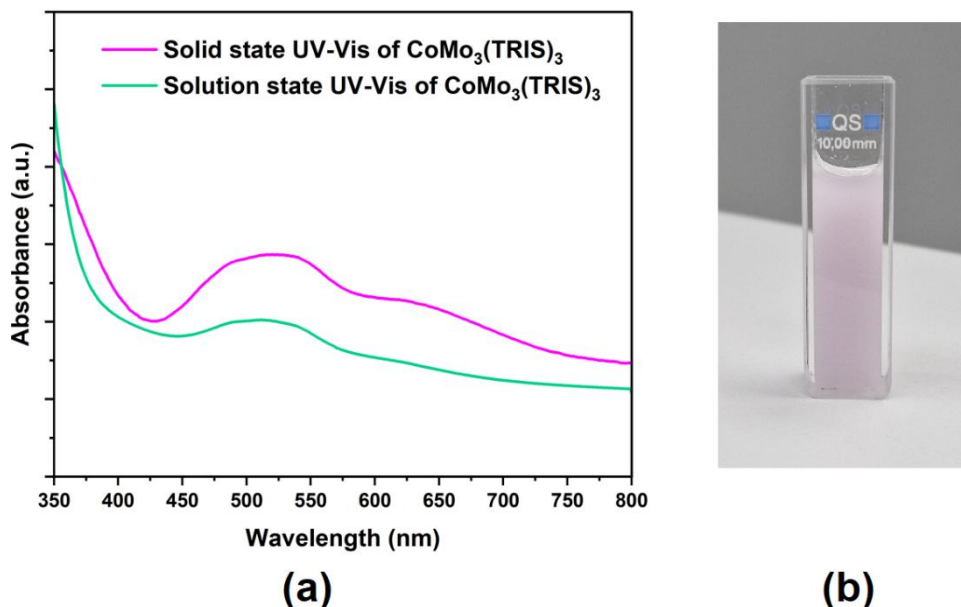


Figure 7.28. (a) UV-Vis spectra of $\text{CoMo}_3(\text{TRIS})_3\text{-2}$ in solid state and solution state (solution in DMF); (b) Colloidal suspension that is formed at higher concentration (>ca. 6.7 mM) of $\text{CoMo}_3(\text{TRIS})_3\text{-2}$ in DMF.

The ligand-to-metal charge transfer (LMCT) processes from the oxygen atoms to the vacant d- orbitals of molybdenum, which are typically high-energy transitions are seen in the UV region of the spectrum (<350 nm). In the visible region, two absorption bands are observed at 520 nm and 640 nm, which are attributed to d–d transitions of the Co^{2+} ion (d^7 configuration). These correspond to the electronic transitions ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (higher energy) and ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (lower energy), arising from the Co^{2+} ion. [171-172]

The solution state optical properties of $\text{CoMo}_3(\text{TRIS})_3\text{-2}$ were measured in DMF solution. A stock solution was prepared by dissolving 20 mg compound in 3 mL DMF (6.7 mM). At higher concentrations it forms a colloidal suspension (Figure 7.28b).

7.7. Magnetic Properties of $\text{CoMo}_3(\text{TRIS})_3$

The single ion magnetic behaviour of paramagnetic metal centres and particularly 3d transition metal ions is strongly influenced by their coordination geometry. Cobalt-based Single Molecule Magnets (SMMs) have been of particular interest because of the magnetic anisotropy of Co^{2+} ions which is a major factor contributing to slow relaxation of the magnetisation.^[157] Co^{2+} centres in various coordination environment like tetrahedral, trigonal pyramidal, octahedral, and trigonal prismatic have been investigated for their SMM behaviour. In most cases, the central coordination polyhedron exhibits slight distortions from their idealized geometries, which has a significant impact on magnetic anisotropy and relaxation dynamics.

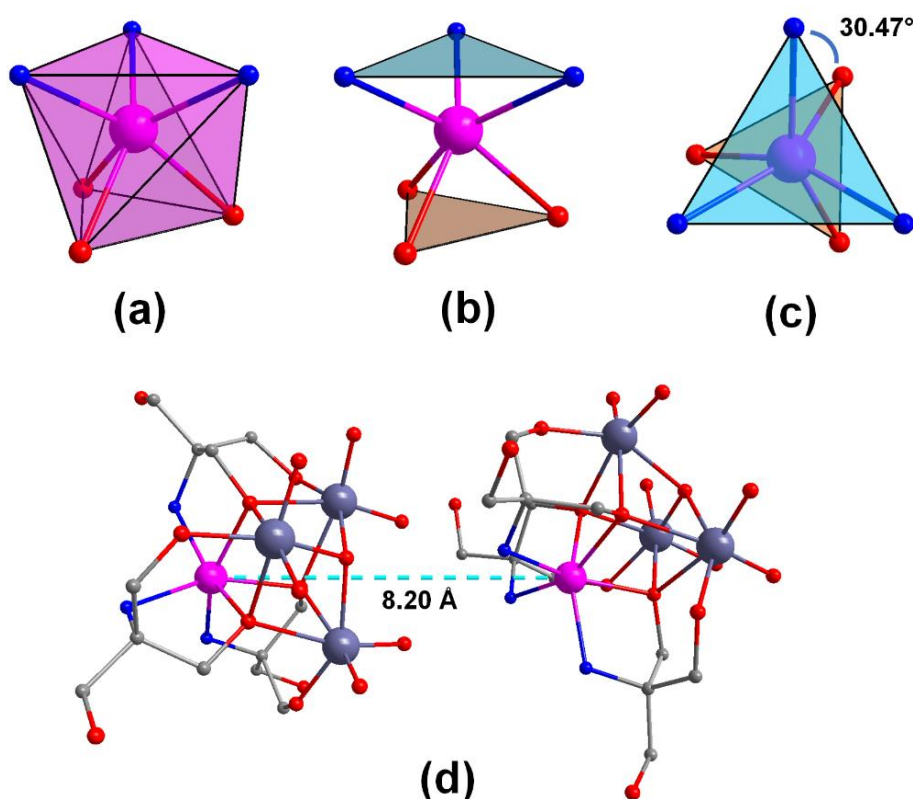


Figure 7.29. (a) 6-vertex coordination polyhedra of Co^{2+} in $\text{CoMo}_3(\text{TRIS})_3\text{-2}$; (b) Two triangular faces of the coordination polyhedra; (c) dihedral angles between the two triangular faces; (d) Distance between Co^{2+} ions from two molecular units in $\text{CoMo}_3(\text{TRIS})_3\text{-2}$.

In the compound $\text{CoMo}_3(\text{TRIS})_3\text{-2}$, the Co^{2+} centre is six coordinated with a geometry that is roughly the half-way point between an ideal octahedral and trigonal prism geometry (Figure 7.29a). This is also clear from the Continuous Shape Measurement (CShM) studies discussed in section 7.4.1 (Figure 7.29a, b). The analysis which yields

values of 4.59 and 5.64 for octahedral and trigonal prismatic geometries, respectively and thus indicates a coordination environment slightly closer to octahedral. The distortion in the coordination environment of the Co^{2+} centre thus leads to magnetic anisotropy.

A powder sample prepared from the crystals of **CoMo₃(TRIS)₃-2** was used for magnetic measurements. Variable-temperature dc magnetic susceptibility measurements (Figure 7.30) show that the Co^{2+} centre is in its high-spin state ($S = 3/2$). The $\chi_{\text{M}}T$ value for **CoMo₃(TRIS)₃-2** at 300 K is $3.37 \text{ cm}^3 \text{ K mol}^{-1}$, which is significantly higher than the spin-only value for $S = 3/2$ ($1.875 \text{ cm}^3 \text{ K mol}^{-1}$). However, it falls within the range which is typical observed for a single non-interacting high spin $d^7 \text{ Co}^{2+}$ ion with a considerable contribution of orbital angular momentum ($2.1\text{--}3.4 \text{ cm}^3 \text{ K mol}^{-1}$).^[173-174]

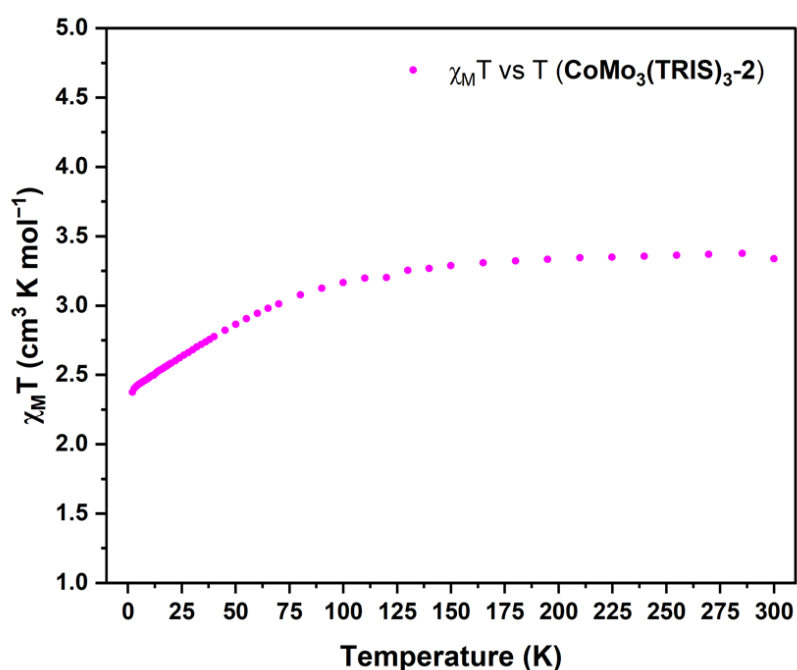


Figure 7.30. $\chi_{\text{M}}T$ vs T plot of **CoMo₃(TRIS)₃-2**.

From the crystal structure data, the Co^{2+} ions from two molecular units in **CoMo₃(TRIS)₃-2** are separated by a distance of ca. $8.20 \text{ \AA}$ (Figure 7.29c) which rules out any significant intermolecular magnetic interactions. The $\chi_{\text{M}}T$ values remain essentially constant in the high-temperature region and show a slow decrease with decreasing temperature reaching $2.37 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K (Figure 7.30). This decrease can be attributed to the intrinsic magnetic anisotropy of Co^{2+} .^[173]

The temperature and frequency dependence of the alternating current (ac) magnetic susceptibility measurements of **CoMo₃(TRIS)₃-2** were also performed (Figure 7.31). Without applied dc fields, no signal for the out-of-phase ac susceptibility (χ_M'') was observed. However, using an applied optimum field of 0.17 T, the in- and out-of-phase ac measurements of **CoMo₃(TRIS)₃-2** show slow relaxation of the magnetisation around 200 Hz at 2 K. For higher temperatures, the maxima shift towards higher frequency which implies faster relaxation. Above 5 K the relaxation is faster than the measuring window (up to 1500 Hz) as shown by the position of the maxima in the out-of-phase data. The absence of relaxation under zero applied fields could be a result of significant quantum tunnelling of the magnetization (QTM).

Relaxation times τ were extracted from the ac magnetic susceptibility data using a generalised Debye model and $\ln(\tau)$ subsequently plotted vs $1/T$ (see Figure 7.32). The resulting curve was fitted with the following multicomponent equation (equation 9) to extract the relaxation rates associated with different relaxation mechanisms.

$$\tau(T)^{-1} = AT + B + CT^n + \tau_0^{-1} \exp(-U/kBT) \quad \text{Equation 9}$$

A is the coefficient of the direct process, B is the parameter describing the zero-field quantum tunnelling of the magnetization (ZFQTM), C is the coefficient of a Raman process with the Raman exponent n, τ_0 is the pre-exponential factor of the Orbach term, U is the thermal energy barrier and k_B is the Boltzmann constant. The parameters of the fit to the equation are listed in the Table 7.9.

Table 7.9. Fitting parameters using equation 9 to fit the relaxation processes in **CoMo₃(TRIS)₃-2**.

A (s ⁻¹ K ⁻¹)	B (s ⁻¹)	C (s ⁻¹ K ⁻ⁿ)	n	τ_0 (s)	U (K)
217.59	0	3.61E-5	9	2.22E-5	8.20

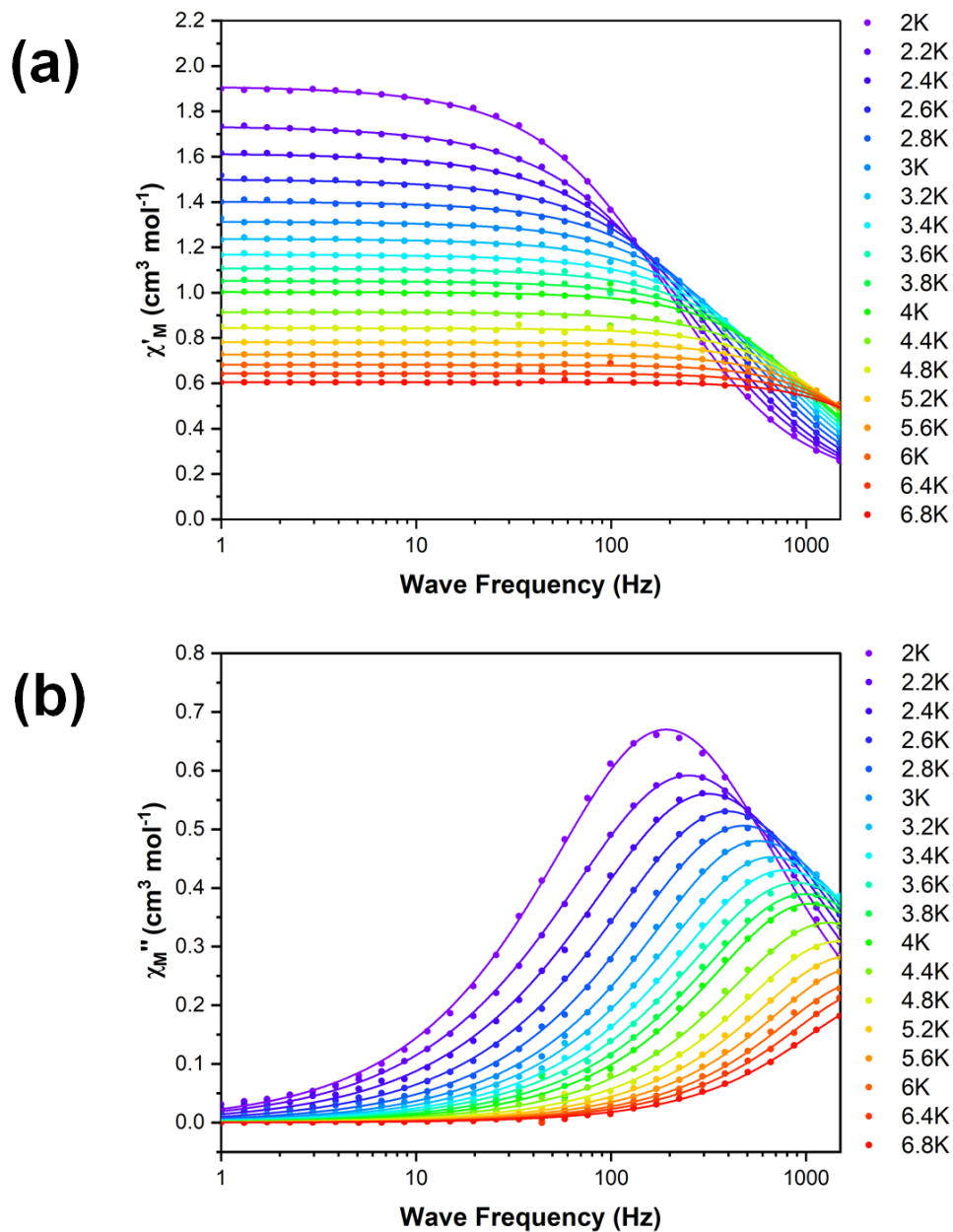


Figure 7.31. (a) In-phase and (b) out-of-phase ac susceptibility measurements of **CoMo₃(TRIS)₃-2** between 2 K and 6.8 K and 1 Hz and 1500 Hz at an applied field of 0.17 T. Lines are the best fits to the data points using the generalised Debye model.

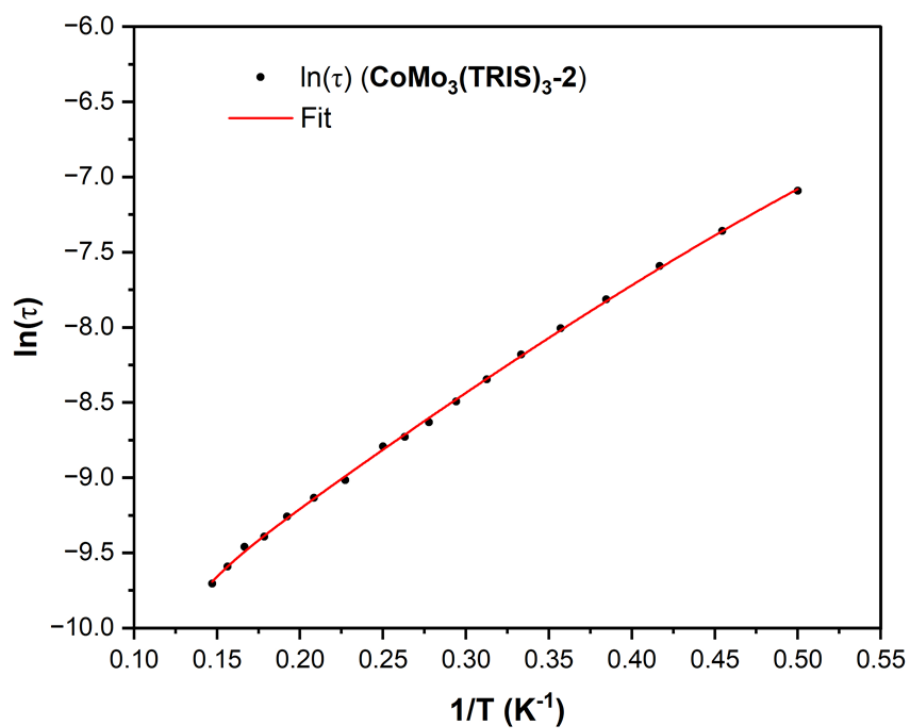


Figure 7.32. Arrhenius plot of the natural log of the relaxations time τ vs the inverse temperature, calculated from the data at dc field of 0.17 T for **CoMo₃(TRIS)₃-2**. Red lines show fit to the data using equation 9.

7.8. Photocatalytic Hydrogen Evolution Reaction Studies Using $\text{CoMo}_3(\text{TRIS})_3$

In this section, the heterogenization of the POM hybrid cluster $\text{CoMo}_3(\text{TRIS})_3$ as a co-catalyst on titania (TiO_2) for light-driven HER is discussed.

7.8.1. Heterogenization of $\text{CoMo}_3(\text{TRIS})_2$ Co-catalyst

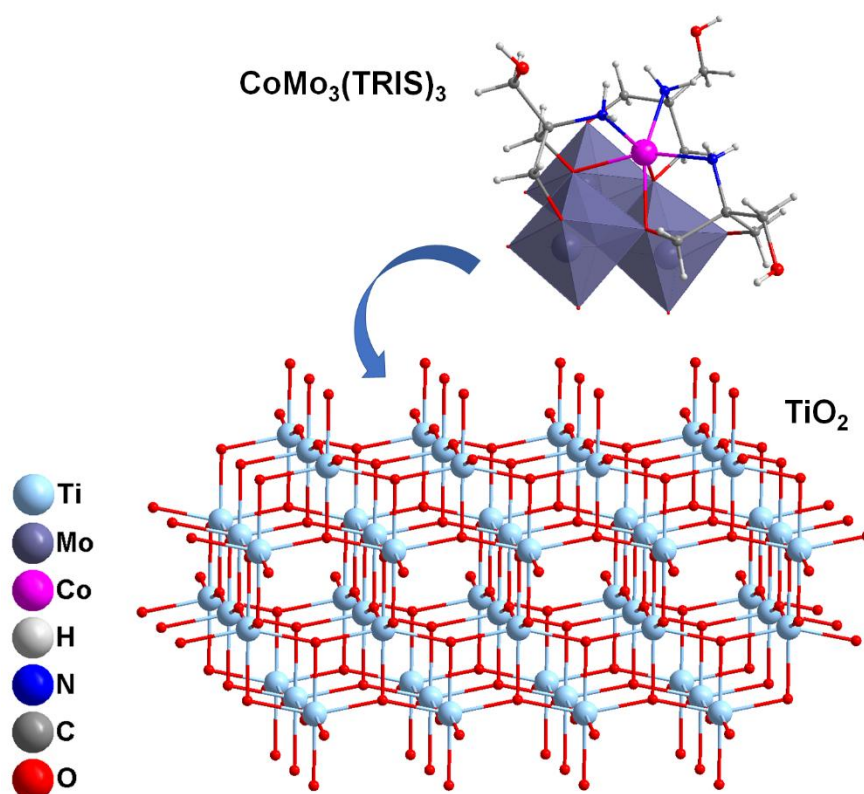


Figure 7.33. Concept of heterogenization of $\text{CoMo}_3(\text{TRIS})_3$ onto TiO_2 .

The $\text{CoMo}_3(\text{TRIS})_3$ cluster was heterogenized onto the anatase TiO_2 surface by following a wet-impregnation route (Figure 7.33), leading to $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composites. In particular, 10 wt % of $\text{CoMo}_3(\text{TRIS})_3$ was used in composite preparation and these are denoted as 10% $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$. TiO_2 powder was dispersed in DMF (50 mg in 50 mL) by ultrasonication for 10 min. The $\text{CoMo}_3(\text{TRIS})_3$ cluster (5 mg) were dissolved in 5 mL DMF and was added to this and sonicated for 5 minutes. The mixture was subsequently kept for stirring for 24 hours at room temperature. This was done to facilitate the adsorption of cluster on TiO_2 . The mixture was then filtered and the composite was washed with DMF to remove unattached or loosely bound clusters. The composite was divided into two portions, and then one portion was dried at 100 °C under

vacuum for 12 hours and the other at room temperature for 24 hours, which were designated as $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$ and $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-RT}$ respectively.

7.8.2. Structural Characterization of $\text{CoMo}_3(\text{TRIS})_3/\text{TiO}_2$ Composites

To evaluate the presence of $\text{CoMo}_3(\text{TRIS})_3$ cluster content within the $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composite, absorption spectra of powdered samples were measured by solid-state via diffuse-reflectance spectroscopy (DRS). Pure TiO_2 exhibit no absorption in visible region of the spectrum. In the case of $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$, minor peaks around 500-700 nm were observed, corresponding to the d-d transition from Co^{2+} (Figure 7.34a). The low intensities in spectra could be an indication of the low concentration of adsorbed cluster on the TiO_2 surface.

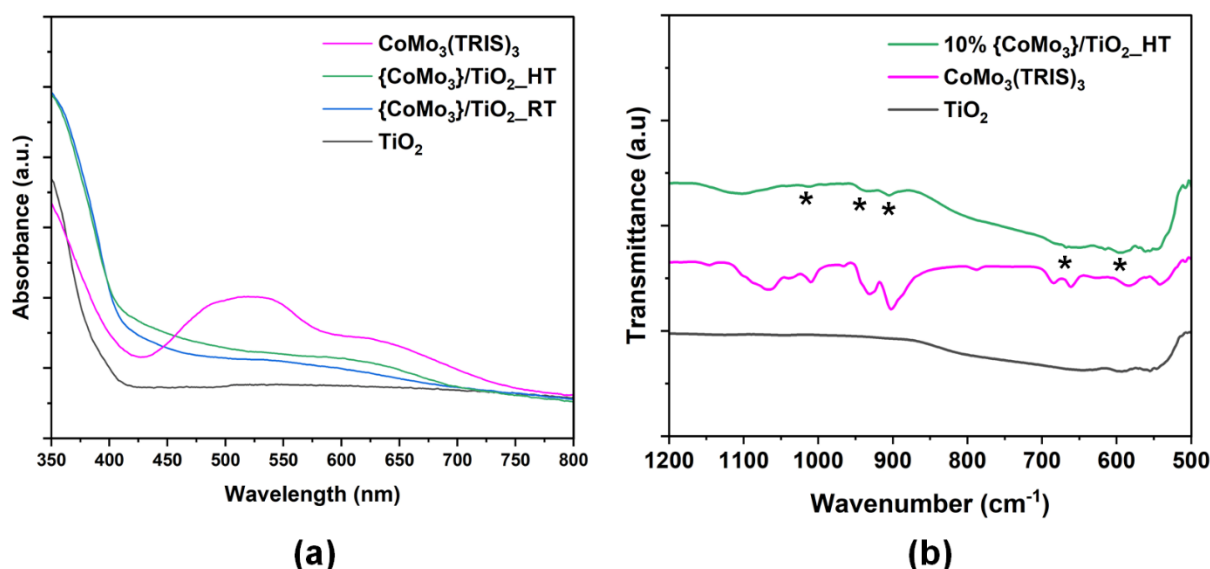


Figure 7.34. Comparison of (a) absorption spectra and (b) FT-IR spectra of composites, $\text{CoMo}_3(\text{TRIS})_3$ cluster and titania.

The FT-IR spectra of the composite show a few weak bands which might be from Mo-O stretching frequencies (Figure 7.34b). However, the low intensity signals were difficult to interpret. Furthermore, all the IR signals as in the original $\text{CoMo}_3(\text{TRIS})_3$ cluster were not visible within the composite.

To quantify the actual cluster loading, total reflection X-ray fluorescence (TXRF) spectroscopy was also performed on the composites $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$ and $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-RT}$. The obtained data indicate that the real cluster loading (based on Co) in $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$ and $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-RT}$ are 3.78 and 1.90%, respectively, which is significantly lower than the intended loading of 10%. This suggests that only a minimal fraction of the deposited cluster remains anchored to titania after the washing process.

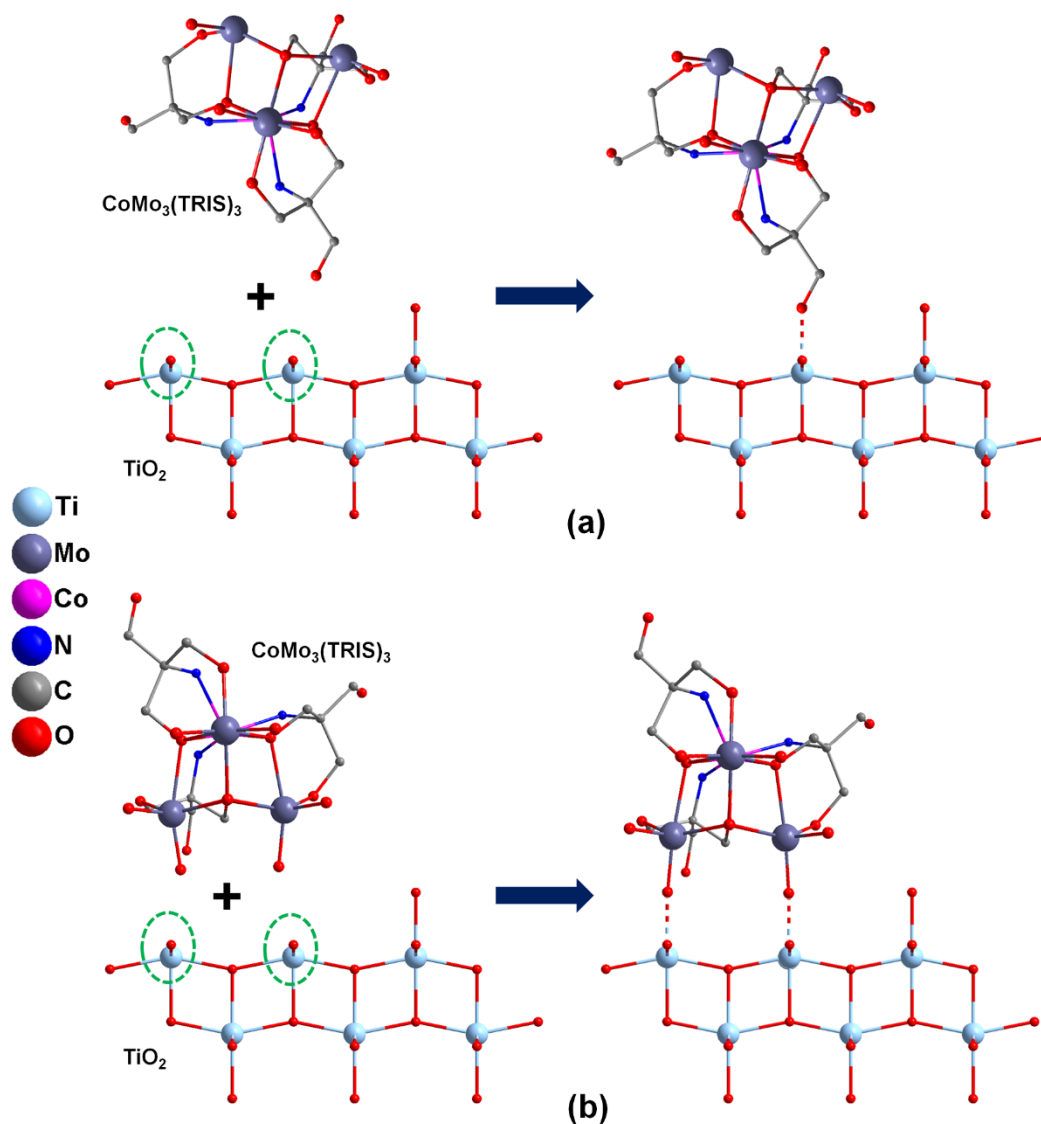


Figure 7.35. Two proposed routes of anchoring of $\text{CoMo}_3(\text{TRIS})_3$ cluster with titania. Oxygen vacancies in titania highlighted in green (All hydrogen atoms in the cluster ignored for clarity).

The heterogenization of $\text{CoMo}_3(\text{TRIS})_3$ cluster on titania^[175] is a complex process and two possible anchoring pathways are proposed below. It is presumed that the site-defects like oxygen vacancies (missing of oxygen from the lattice site) in titania would

favour the anchoring via oxygen from the cluster. In the first proposed route, the oxygen atoms from the free hydroxymethyl arm of the cluster can coordinate or have a weak interaction with the Ti^{4+} (Figure 7.35a). For the second route, the terminal $\text{Mo}=\text{O}$ oxygen from the cluster can have weak interactions with one or more Ti^{4+} (Figure 7.35b).

The characterisations so far do not comment on the actual scenario of cluster adsorption on titania in the composites. Further studies are required to confirm the structure of the cluster and examine its interaction with the TiO_2 support. Nevertheless, the composites were used for the photocatalytic hydrogen evolution reaction studies.

7.8.3 Photocatalytic Hydrogen Evolution Reaction Studies

For the photocatalytic hydrogen evolution reaction studies, 5 mg of the prepared $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composites was taken as the photocatalyst in a vial. 10 mL of $\text{MeOH-H}_2\text{O}$ (2.5 mL : 7.5 mL) mixture was added to this and sonicated for 30 seconds. The mixture was then transferred to tailor-made 30 mL reactor, closed and then kept for stirring (Figure 7.36). The reactor was flushed with argon for 10 minutes before the experiment. In a dark box, the reactor is setup with cooling water and then is subjected to UV irradiation with a 365 nm light source. After 30 minutes, 200 μL of gaseous mixture from the headspace of the reactor was injected into gas chromatography to measure the hydrogen evolved. Similar readings were taken every 30 minutes over a period of two hours for all experiments.

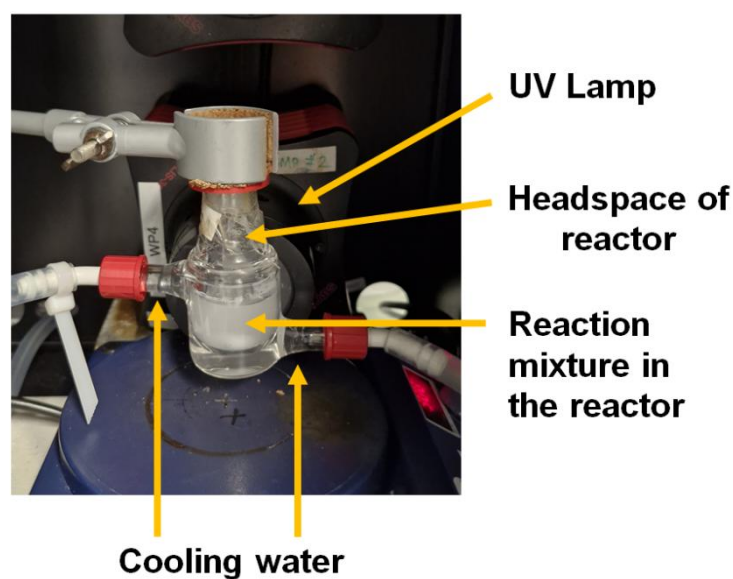


Figure 7.36. Setup for photocatalytic hydrogen evolution experiments.

The hydrogen evolution reaction (HER) performance of the catalysts $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$ and $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-RT}$ were tested multiple times. The performances (with error bars) are shown for each case in Figure 7.37a. The

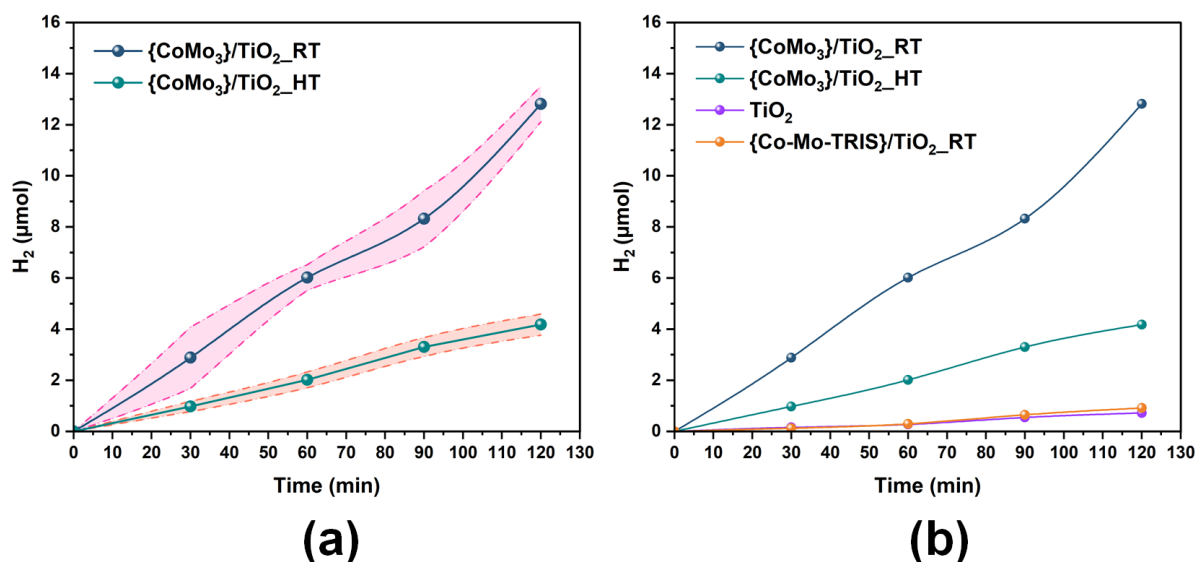


Figure 7.37. (a) Photocatalytic hydrogen evolution experiments of (a) $\text{CoMo}_3/\text{TiO}_2$ composites with 10 wt % loadings dried at room temperature (RT) and high temperature (HT) (with error bars); (b) Comparison of mean values of hydrogen evolved with $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-HT}$, $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2\text{-RT}$, $\{\text{Co-Mo-TRIS}\}/\text{TiO}_2\text{-RT}$ composites. $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composite dried at room temperature was found to be a better catalyst compared to the other and produces about 6 μmol of hydrogen in one hour. The averaged values were compared with bare TiO_2 catalyst without the addition of any cocatalyst (Figure 7.37b). Clearly, the **$\text{CoMo}_3(\text{TRIS})_3$** cluster-heterogenized composites are highly effective for hydrogen evolution compared to titania.

Another composite was prepared from the reagents used for the synthesis of **$\text{CoMo}_3(\text{TRIS})_3$** (i.e., $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ and TRIS) and TiO_2 . To prepare the $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composite, 5 mg **$\text{CoMo}_3(\text{TRIS})_3$** was used with 50 mg titania. The composition of the Co^{2+} ions, Mo^{6+} ions and TRIS in the $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ were calculated from here. Theoretically, this accounts for 1.5 mg $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 4.1 mg $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ and 2.26 mg of TRIS ligand to prepare the new composite, which is represented as $\{\text{Co-Mo-TRIS}\}/\text{TiO}_2\text{-RT}$. The performance of this composite towards HER was significantly lower than the $\{\text{CoMo}_3(\text{TRIS})_3\}/\text{TiO}_2$ composites. This might be due to the poor adsorption of these molecules onto titania. The resultant composite almost behaves as bare titania in the hydrogen evolution reaction. The number of moles

of H₂ evolved as a function of time for the catalysts discussed here is given in Table 7.10.

Table 7.10. Hydrogen evolved (μmol) from reaction mixture using various catalysts.

<u>Time (min)</u>	<u>H₂ evolved (μmol)</u>			
	{CoMo₃(TRIS)₃}/ TiO₂_RT	{CoMo₃(TRIS)₃}/ TiO₂_HT	TiO₂	{Co-Mo-TRIS}/ TiO₂_RT
0	0	0	0	0
30	2.88211	0.97521	0.15526	0.12374
60	6.01892	2.01694	0.27132	0.29284
90	8.3195	3.30241	0.54417	0.64947
120	12.81329	4.17668	0.71864	0.91387

The preliminary experiments with the titania-composite made from **CoMo₃(TRIS)₃** cluster is an efficient for hydrogen evolution compared to the one made from the mixture of individual reagents. Further experiments are planned to fully characterise the catalysts and optimise the activity of the catalyst for HER.

7.9. Conclusion and Outlook

This chapter presented a detailed investigation into TRIS-ligand decoration of cobalt-containing polyoxomolybdates. Two distinct Anderson-Evans-type POM hybrids were synthesized: the previously reported δ/δ -isomer (ⁿBu₄N)₃[Co^{III}Mo₆O₁₈{(OCH₂)₃CNH₂}₂] (**δ/δ -CoMo₆(TRIS)₂**) and the newly identified δ/χ -isomer (ⁿBu₄N)₃[Co^{II}Mo₆O₁₇(OH){(OCH₂)₃CNH₂}₂] (**δ/χ -CoMo₆(TRIS)₂**). These compounds differ in both the oxidation state of the cobalt centre (Co³⁺ or Co²⁺) and the nature of their TRIS-ligand coordination environments. The δ/χ -isomer, in particular, represents the first example of this configuration with TRIS ligands, highlighting the structural diversity accessible through subtle changes in reaction conditions.

Additionally, a charge-neutral hybrid cluster [CoMo₃O₇{(OCH₂)₂C(NH₂)(CH₂OH)}₃], (**CoMo₃(TRIS)₃**) was isolated in two crystallographically distinct forms (**CoMo₃(TRIS)₃-1** and **CoMo₃(TRIS)₃-2**), differing in lattice solvents and packing. This species is among the smallest known heteropolyoxomolybdate hybrids to date. Structural analysis revealed an unusual Co²⁺ coordination environment that lies between ideal octahedral and trigonal prismatic geometries.

The structural characteristics of **CoMo₃(TRIS)₃** were further elucidated through UV-Vis spectroscopy in both solution and solid state. Magnetic measurements confirmed that **CoMo₃(TRIS)₃** exhibits field-induced single-molecule magnet behaviour, attributed to its unique cobalt coordination geometry and electronic structure.

Preliminary catalytic evaluations indicate that **CoMo₃(TRIS)₃** is a promising co-catalyst for the hydrogen evolution reaction (HER). Future studies will focus on hydrogenizing this cluster on semiconducting supports such as TiO₂ to further explore and optimize its catalytic behaviour.

The observations gained in this study open the way for further exploration of TRIS-decorated POMs as building blocks for multifunctional materials. The synthetic approaches and structural understanding developed here can help in the rational design of new POM-based metalloligands for MOFs and hybrid catalysts. Future research will focus on tuning the reaction environment to control isomer formation, expanding the structural diversity of POM hybrids, and exploring their immobilization on semiconducting supports like TiO₂ for advanced energy applications such as photocatalysis and HER.

8. Summary and Conclusions

Each chapter has its own concluding remarks. The overall summary is discussed here.

The work described in this dissertation investigates the application of metalloligand approaches to target Heterometallic Metal-Organic Frameworks (HMOFs) and Polyoxometalate-based Coordination Polymers (POMCPs). From four projects described in chapters 4 to 7, 81 new compounds are presented. All compounds were characterised using single crystal X-ray diffraction, powder X-ray diffraction, infrared spectroscopy and CHN analysis. Structural features including unusual metal disorder are discussed in detail. In addition, solid-state and solution-state UV-Vis spectroscopy, solid-state photoluminescence spectroscopy, thermogravimetric analysis and SQUID magnetometry were performed on selected compounds.

The development of a Cu^{2+} -based metallogel using 5-nitroisophthalic acid (H_2nip) proved to be an excellent material to incorporate lanthanide ions for the synthesis of crystalline HMOFs. Crystallisation phenomena such as Ostwald ripening were investigated to probe crystallization dynamics and structural transformations both in aqueous as well as water-DMF media. Different synthetic pathways were investigated, which substantiate the importance of a step-by-step methodology for the synthesis of HMOFs.

In the final part of the thesis TRIS (tris(hydroxymethyl)aminomethane) - functionalized Anderson-Evans polyoxometalates (AE-POMs) as metalloligands for the synthesis of POMCPs are discussed. Schiff-base reactions were implemented to synthesize TRIS-functionalized AE-POMs which were characterised by SCXRD. These were then used to prepare La-based POMCPs via either ether diffusion or layering methods. Two distinct structural types were identified and their topological aspects are discussed. Furthermore, TRIS-ligand decoration in cobalt-containing polyoxomolybdates led to the discovery of a small POM cluster with an unusual coordination environment around the Co^{2+} ion. This opens a new research field for the investigation of networks combining the properties of POMs and MOFs and their potential applications in magnetism and catalysis.

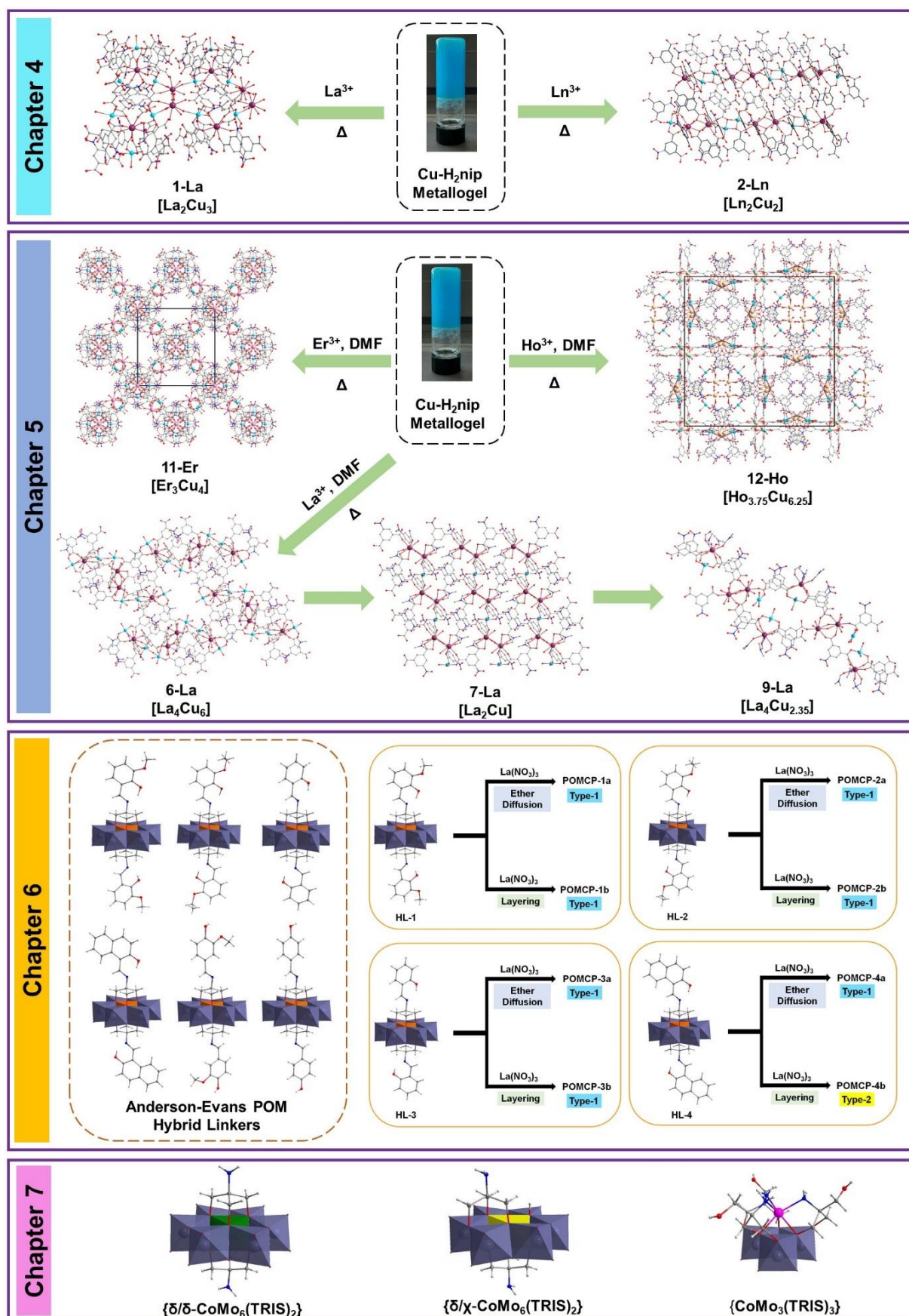


Figure 8.1. Overview of the metalloligands and related HMOFs discussed in this thesis.

9. Experimental Methods

9.1. General Procedure

All chemicals were obtained from commercial sources (Sigma Aldrich, VWR International) and used without further purification. All organic solvents were used as without drying. All syntheses, if not indicated otherwise, were performed under aerobic conditions.

Since the lanthanide nitrate salt used in this work had different the number of water molecules present per formula unit, (E.g. $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ etc.), the molar mass of anhydrous lanthanide salts were considered for calculations throughout this work.

Wheaton vials (12 mL and 20 mL capacity) with phenolic caps were used throughout the experiments for solvothermal reactions discussed in chapter 4 and 5.

9.2. Instruments and Software

9.2.1. IR spectroscopy

Attenuated total reflectance Fourier transform IR spectroscopy (ATR-FTIR) spectroscopy was performed on a Nicolet iS 50 with ATR attachment located at the Institute for Nanotechnology (INT, KIT) and Bruker Platinum Alpha ATR IR located at the Institute of Inorganic Chemistry (AOC, KIT). All FTIR spectra of TiO_2 -based photocatalysts (discussed in Chapter 7) were recorded on a Bruker Tensor 27 IR Spectrometer equipped with an ATR unit with a single reflection diamond at the Technische Universität Wien (TU Wien).

9.2.2. UV-Vis absorption spectroscopy

The solution- state UV-Vis absorption spectroscopy was performed on an Agilent Cary 5000 UV-Vis spectrometer located at the Institute for Nanotechnology (INT, KIT). The absorption spectra of powdered samples (solid-state) were measured by diffuse reflectance (DRS) UV-vis spectroscopy on a Jasco V670 UV-Vis spectrometer located at the Technische Universität Wien (TU Wien).

9.2.3. Photoluminescence (PL) spectroscopy

PL measurements were performed using PicoQuant FluoTime 300 spectrophotometer at the Technische Universität Wien (TU Wien). Xe arc lamp (300 W power) was the excitation source, coupled with a double-grating monochromator. The detection system

is comprised of a PMA Hybrid 07 detector along with a high-resolution double monochromator. The data was collected and later fitted using EasyTau2 software.

9.2.4. Powder X-ray diffraction (PXRD)

PXRD was done on a STOE STADI-P with a Cu-K α source with a characteristic wavelength of 1.5405 Å. The data was processed using WinX^{POW} package. The PXRD patterns were simulated using Mercury 2022.2.0.

9.2.5. Single crystal X-ray diffraction (SCXRD)

SCXRD was performed on area detector diffractometers: STOE IPDS II (Mo-K α , λ = 0.71073 Å, detector image plate), STOE STADIVARI ((Mo-K α , λ = 0.71073 Å, detector Pilatus300K) and STOE STADIVARI Ga-Jet (Ga K α , λ = 1.34143 Å, detector Dectris Eiger2 R 4 M (detector type HPC)) located at the Institute for Nanotechnology (INT, KIT). The crystals were attached to the goniometer head with perfluoroether oil and placed in a cold nitrogen stream (150 K or 180 K) during data collection. Data processing including unit cell determination, data integration, analytical absorption correction, data etc. were done with the X-Area single crystal diffraction software packages provided by the diffractometer manufacturers (STOE). The structures were solved and refined by full-matrix least squares using ShelXT and ShelXL in the Olex2-1.5 program.^[145, 176-177]

9.2.6. Magnetic measurements

These were performed on a Quantum Design MPMS-XL-1 SQUID magnetometer located at the Institute of Nanotechnology (INT, KIT).

9.2.7. Scanning Electron Microscopy (SEM)

SEM imaging was performed on SEM LEO-1530 (Zeiss, Germany) located at the Institute of Nanotechnology (INT, KIT). Samples were sputtered with 10 nm of gold (Cressington Sputter Coater 108auto, Germany) prior to SEM imaging. The acceleration voltages were set at 1, 2, 5 kV and working distances at 1.5-3 mm.

9.2.8. Rheological studies

The rheological experiments were performed at 25 °C using an ARES G2 rotational rheometer from TA instruments at Institute for Chemical Technology and Polymer Chemistry (ITCP, KIT).

9.2.9. Photocatalytic hydrogen evolution reaction (HER) studies

HER experiments were performed in a closed system utilizing a tailor-made 30 mL reactor, equipped with a high-intensity monochromatic UV LED light source (365 ± 6 nm, 196 mW/cm^2 , Thorlabs SOLIS). In a vial, 5 ml of powdered photocatalysts were taken with 10 ml of 25 % MeOH and water mixture and sonicated for 30 seconds, then transferred to reactor. Before the experiment, the reactor was continuously flushed with argon gas at a controlled flow rate of 15 mL min^{-1} , to remove any residual gases in the headspace of vial. The reaction mixture was stirred at 400 rpm to ensure homogeneity. The produced hydrogen gas was directly measured using gas chromatography integrated with a barrier ionization discharge (BID) detector. To maintain experimental conditions, the reactor temperature was precisely maintained at 15°C through a water-cooling system. Hydrogen detection readings were taken every 30 minutes over a period of two hours for all experiments. The experiments were performed at the Technische Universität Wien (TU Wien).

9.2.10. X-ray fluorescence spectroscopy in total reflection geometry (TXRF)

TXRF spectroscopy (ATOMIKA 8030C X-ray fluorescence analyser, Atomika Instruments GmbH, Oberschleissheim, Munich, Germany) was performed for TiO_2 -based photocatalysts (discussed in Chapter 7) at Technische Universität Wien (TU Wien).

9.2.11. Thermogravimetric Analysis (TGA)

TGA measurements were done on a Perkin Elmer Thermogravimetric Analyser, TGA 8000 at the Technische Universität Wien (TU Wien). The samples were kept in an Al_2O_3 crucible and were heated up with a ramp rate of 5°C/min under air ranging from 30°C to 700°C .

9.2.12. Elemental (CHN) analysis

These analyses were performed on an Elementar Vario MicroCube located at the Institute for Nanotechnology (INT, KIT).

9.2.13. Software

Spectroscopic and magnetic data was analysed and all graphs were plotted and fits performed using Origin 2023.

Diamond 4.0 was used for the visualization and graphic representation of crystal structures all the compounds.

Continuous Shape Measures (CShM) calculations were performed using SHAPE program. The analyses compare the experimental coordination polyhedra of atoms (transition metal/lanthanide ions etc.) with the ideal shapes of the regular polyhedral. The CShM number indicates how distorted the structure, and the lower value is the one which describe the ideal shape.^[105-106]

9.3. Synthesis from Chapter 4

Cu-H₂nip-Ln HMOFs from Aqueous Medium

Cu-H₂nip metallogel

Cu(OAc)₂·H₂O (100 mg, 0.5 mmol, 1 eq.) was dissolved in 10 mL water taken in a 12 mL Wheaton glass vial. To the pale blue clear solution, 5-nitroisophthalic acid (H₂nip) (106 mg, 0.5 mmol, 1 eq.) was added and it was magnetically stirred vigorously for 15 minutes at room temperature until a uniform blue gel is formed.

[Cu₅(OH)₂(nip)₄(H₂O)₆]·4.25H₂O or Cu₅-cluster MOF (Cu-nip)

The vial that contains Cu-H₂nip metallogel was placed in an oven and heated to 95 °C for about 12-24 hours. **Cu-nip** was isolated as blue crystals.^[16]

[La₂Cu₃(nip)₆(H₂O)₉]·8H₂O (1-La)

La(NO₃)₃·xH₂O (162 mg, 0.5 mmol, 1 eq.) was added to the Cu-H₂nip gel, and stirred vigorously using a magnetic pellet for 20 minutes. The blue colour of gel faded slowly and the gel collapsed into pale blue colloidal mixture. The uniformity of the mixture was ensured by occasionally agitating the magnetic stir bar inside the vial with an external magnet. The vial was placed in an oven at room temperature and then gradually heated to 95 °C. Dark blue crystals started forming within 24 hours and crystallization was complete over 64 hours (Yield =180 mg).

[La₂Cu(nip)₄(H₂O)₆] (A-La) and Ln₂Cu(nip)₄(H₂O)₄]·6H₂O (4-Ln) (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y)

This is a modified procedure from reference ^[103].

$\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (325 mg, 1 mmol, 2 eq.) was added to the Cu-H₂nip gel, and stirred vigorously using a magnetic pellet for 20 minutes. A pale blue colloidal mixture was obtained and the reaction vial was placed in an oven at room temperature and then gradually heated to 95 °C. Blue crystals started forming within 24 hours.

4-Ln was obtained instead of **A-La** along with crystals of **Cu-nip** and $[\text{Ln}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$ (**3-Ln**) when $\text{La}(\text{NO}_3)_3$ was replaced with $\text{Ln}(\text{NO}_3)_3$.

$[\text{LaCu}(\text{nip})_2(\text{Hnip})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]$ (B-La)

$\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (162 mg, 0.5 mmol, 1 eq.) was added to the Cu-H₂nip gel, and stirred vigorously for 10 minutes. 5-nitroisophthalic acid (H₂nip) (106 mg, 0.5 mmol, 1 eq.) was added and again stirred for 15 minutes. The pale blue colloidal mixture was then placed in an oven and heated to 95 °C under autogenous pressure. Dark blue crystals were formed within 48 hours.

This is a modified procedure from reference ^[102].

$[\text{La}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (2-La) and $[\text{La}_4\text{Cu}_{1.25}(\text{nip})_{4.5}(\text{Hnip})_{5.5}(\text{H}_2\text{O})_{8.5}] \cdot 12.5 \text{H}_2\text{O}$ (2-La-meta)

$\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.5 mmol) was added directly to the Cu-H₂nip gel, followed by 5-nitroisophthalic acid (H₂nip) (317 mg, 1.5 mmol) and entire mixture was stirred vigorously for 20 minutes. The blue colour of gel faded slowly and the gel collapsed into pale blue colloidal mixture. The vial was kept in oven at room temperature and then gradually heated to 95 °C. Pale blue crystals of **2-meta** started forming within a few hours and could be isolated within 17-24 hours, along with some blue crystals of **2-La**. All crystals of **2-meta** is converted to **2-La** within 48 hours. Once the crystallization is complete, the hot contents in the vial was immediately filtered and the blue crystals were separated and stored in distilled water. This is done because the excess H₂nip recrystallize in the solution once the reaction vial cools down to room temperature and sticks over the blue crystals. (Yield of **2-La** = 240 mg).

$[\text{Ln}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (2-Ln) (Ln = Ce, Pr, Nd)

The procedure is same as for **2-La**. Different lanthanide salts were used instead of $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.5 mmol). No metastable compounds were obtained here and blue

crystals of **2-Ln** were obtained within 17 hours. (Yield = 210 to 220 mg depending on the Ln- analogues).

[Ln₂Cu₂(nip)₂(Hnip)₆(H₂O)₄]·4H₂O (2-Ln) and [Ln₂(nip)₂(Hnip)₂(H₂O)₄] (5-Ln)
(Ln = Sm, Eu, Gd)

The procedure is same as for **2-La**. Different lanthanide salts were used instead of La(NO₃)₃·xH₂O (0.5 mmol). Metastable compounds of **5-Ln** were obtained here as colourless crystals within 12-24 hours along with blue crystals of **2-Ln**. Over period of two to four weeks, the colourless crystals completely dissolved into the solution, and the amount of crystals of **2-Ln** increased. (Yield = 220 to 240 mg depending on the Ln- analogues).

[M(nip)(H₂O)₅] (M-nip) (for M=Co and Ni), [Zn(nip)(H₂O)] (Zn-nip)

M(OAc)₂·xH₂O (0.5 mmol, 1 eq. (125 mg for M²⁺ = Co, Ni (x = 4) and 110 mg for M²⁺ = Zn (x = 2)) was dissolved in 10 mL water taken in a 20 mL Wheaton glass vial. To the clear solution, 5-nitroisophthalic acid (H₂nip) (106 mg, 0.5 mmol, 1 eq.) was added and the mixture was magnetically stirred vigorously for 15 minutes at room temperature. Clear solutions in water with the characteristic colours of the metal ions are obtained: Co²⁺ (pink), Ni²⁺ (green), Zn²⁺ (colourless). The vial was then kept in an oven and gradually heated to 95 °C. After 24 hours the reaction vials were kept outside the oven. The clear solutions in the three vials were filtered hot and was kept for evaporation. The crystals of [Co(nip)(H₂O)₅] (**Co-nip**), [Ni(nip)(H₂O)₅] (**Ni-nip**) starts to form over a period of about 1 month and [Zn(nip)(H₂O)] (**Zn-nip**) within 1 day. (Yield = 150 to 180 mg).

[Cu(Hbtc)(H₂O)₃] (Cu-Hbtc)

Cu(OAc)₂·H₂O (100 mg, 0.5 mmol, 1 eq.) was dissolved in 10 mL water taken in a 20 mL Wheaton glass vial. 1,3,5-benzene tricarboxylic acid (H₃btc) (106 mg, 0.5 mmol, 1 eq.) was added to the resultant pale blue clear solution and the mixture was magnetically stirred vigorously for 15 minutes at room temperature. The resultant mixture was heated in an oven to 95 °C. Greenish blue coloured, needle shaped crystals of **Cu-Hbtc** were obtained within 24 hours. (Yield = 90 mg).

[Cu(dnb)(OH)] (Cu-dnb)

Cu(OAc)₂·H₂O (100 mg, 0.5 mmol, 1 eq.) was dissolved in 10 mL water taken in a 20 mL Wheaton glass vial. 3,5-dinitrobenzoic acid. (H₃btc) (106 mg, 0.5 mmol, 1 eq.) was added to the resultant pale blue clear solution and the mixture was magnetically stirred vigorously for 15 minutes at room temperature. The resultant mixture was heated in an oven to 95 °C. Blue coloured, joint block crystals of **Cu-dnb** were obtained within 24 hours. (Yield = 105 mg)

9.4. Synthesis from Chapter 5

Cu-H₂nip-Ln HMOFs from Water-DMF Media

[Ln₂Cu(nip)₄(DMF)₂(H₂O)₂] (7-Ln) Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y

Ln(NO₃)₃·xH₂O (0.5 mmol, 1.5 eq.) was added to the Cu-H₂nip gel and stirred vigorously using a magnetic pellet for 20 minutes. The blue colour of gel faded slowly and the gel collapsed into pale blue colloidal mixture. The uniformity of the mixture was ensured by occasionally agitating the magnetic stir bar inside the vial with an external magnet. 2 mL DMF added and stirring continued for 15 minutes. The vial was placed in an oven at room temperature and then gradually heated to 95 °C. Dark blue crystals of **7-Ln** started forming within 24 hours and crystallization was complete over 2-5 days. (Yield = 180 mg, for **7-La**).

Alternate route with higher yield:

Ln(NO₃)₃·xH₂O (0.5 mmol, 1.5 eq.) was added to the Cu-H₂nip gel and stirred vigorously using a magnetic pellet for 15 minutes. The blue colour of gel faded slowly and the gel collapsed into pale blue colloidal mixture. The uniformity of the mixture was ensured by occasionally agitating the magnetic stir bar inside the vial with an external magnet. H₂nip (1 mmol, 2 eq.) was added and stirred for 10 minutes. 2 mL DMF added and stirring continued for 15 minutes. The vial was placed in an oven at room temperature and then gradually heated to 95 °C. Dark blue crystals of **7-Ln** started forming within 24 hours and crystallization was complete over 2-5 days. (Yield = 205 mg, for **7-La**).

As described in Chapter 5, different crystalline phases are formed during reaction. in the case of heavier lanthanides. E.g., mixture of crystals (e.g., **10-Er**, **11-Er**, **12-Er**) were obtained as side products during initial 2-3 days of heating during the

synthesis of **7-Er**. However, the thermodynamic product **7-Ln** is always left behind after 2-5 days for all cases.

[La₄Cu₆(nip)₁₂(H₂O)₁₀(DMF)₂] (6-La)

During the synthesis of **7-La**, the crystals of **6-La** are also formed during initially over about 12 hours. As the heating is continued, these crystals completely dissolve and lead to further crystallization of **7-La**.

[La₂(nip)₂(HCOO)₂(H₂O)₄] (8-La)

When the reaction mixture obtained when the crystallization of **7-La** is heated further at 95 °C in oven for about 10 days, the crystals undergo structural transformation and result in the formation of **8-La**.

[La₄Cu_{2.35}(nip)_{6.7}(Hnip)_{1.3}(HCOO)_{0.5}(HCOOH)_{0.5}(DMF)₆(H₂O)_{16.7}]⁺·8.3H₂O (9-La)

When the dark blue crystals of **7-La** are stored with the mother liquor at room temperature for about two months, these crystals slowly dissolve into the solution and the crystals of **9-La** are obtained.

[Er₃Cu₄(nip)₈(DMF)₄(H₂O)₈]⁺·11DMF (11-Er) and [Er₂(nip)₂(Hnip)₂(H₂O)₄] (10-Er)

Er(NO₃)₃·xH₂O (0.5 mmol, 1.5 eq.) was added to the Cu-H₂nip gel and stirred vigorously using a magnetic pellet for 20 minutes. To the blue gelatinous mixture, 2 mL DMF added and stirring continued for 15 minutes. The vial was placed in an oven at room temperature and then gradually heated to 75 °C. Blue crystals of **11-Er** are formed along with the dark blue crystals of **7-Er** and a few colourless crystals of **10-Er** over a period of about 12-24 hours. When heating is continued, the crystals of **11-Er** and **10-Er** dissolve and more crystals of **7-Er** form.

[Ho_{3.75}Cu_{6.25}(nip)₁₂ (H₂O)_{13.25}]^{(0.25)-}·9DMF (12-Ho) and [Ho₂(nip)₂(Hnip)₂(H₂O)₄] (10-Ho)

Ho(NO₃)₃·xH₂O (0.5 mmol, 1.5 eq.) was added to the Cu-H₂nip gel and stirred vigorously using a magnetic pellet for 20 minutes. To the blue gelatinous mixture, 2 mL DMF added and stirring continued for 15 minutes. The vial was placed in an oven at room temperature and then gradually heated to 75 °C. Blue crystals of **12-Ho** and colourless crystals of **10-Ho** are formed along with the dark blue crystals of **7-Ho**

over a period of about 12-24 hours. When heating is continued, the crystals of **12-Ho** and **10-Ho** dissolve, yielding more crystals of **7-Ho**.

9.5. Synthesis of Previously Reported Precursors and Polyoxometalate Hybrids

- **(ⁿBu₄N)₄[α -Mo₈O₂₆]**

(ⁿBu₄N)₄[α -Mo₈O₂₆] was synthesized according to the literature method.^[178] A solution of Na₂MoO₄·2H₂O (5.00 g, 20.70 mmol) dissolved in 12 mL H₂O was acidified with 5.17 mL of 6 N aqueous HCl (31.00 mmol) with vigorous stirring over a period of 2 min at room temperature. A solution of tetrabutylammonium bromide (3.34 g, 10.40 mmol) dissolved in 10 mL H₂O was added and the resulting suspension stirred for 10 min. The resulting white precipitate was isolated by filtration and was washed with 20 mL of H₂O, 20 mL of ethanol, 50 mL acetone and 20 mL diethyl ether. This crude product is dissolved in 35 mL of acetonitrile and stored for 24 hours at -10 °C. The clear, colourless, block-shaped crystals are collected by suction filtration and dried.

- **(Me₄N)₂Na₂[β -Mo₈O₂₆]**

(Me₄N)₂Na₂[β -Mo₈O₂₆] was synthesized according to the procedure in reference^[179]. Na₂MoO₄·2H₂O (5.0 g, 20.7 mmol) was dissolved in H₂O (12 mL) before being acidified with 6 M HCl (5.05 mL). The reaction mixture was stirred vigorously for 1–2 min before a solution of tetramethylammonium bromide (1.6 g, 10.4 mmol) in H₂O (10 mL) was added. The reaction mixture was stirred vigorously for 10 min before the resulting white precipitate was collected. It was successively washed with H₂O (20 mL), EtOH (20 mL), acetone (20 mL) and diethyl ether (20 mL). The compound, (Me₄N)₂Na₂[β -Mo₈O₂₆], was obtained as a white powder.

- **(ⁿBu₄N)₂[Mo₆O₁₉]**

(ⁿBu₄N)₂[Mo₆O₁₉] was synthesized according to the literature method.^[178] A solution of 2.50 g (10.3 mmol) of commercial, ACS reagent grade, sodium molybdate dihydrate (Na₂MoO₄·2H₂O) in 10 mL of water is acidified with 2.9 mL of 6 N aqueous HCl (17.4 mmol) in a 50-mL Erlenmeyer flask with vigorous stirring over a 1-min period at ambient temperature. A solution of 1.21 g (3.75 mmol) of commercial, 99% pure tetrabutylammonium bromide in 2 mL of water is then added with vigorous stirring to cause immediate formation of a white precipitate. The resulting slurry is then heated to 75 to 80 °C with stirring for about 45 minutes. During this period, the white solid slowly

changes to yellow. This crude product is collected on a medium-porosity filter with suction and washed with three 20-mL portions of water. Crystallization is accomplished by dissolving the air-dried crude product in 80 mL of hot acetone (60 °C) and cooling the solution to -20 °C. After 24 hours, the yellow crystalline product is collected on a filter with suction, washed twice with 20-mL portions of diethyl ether, and dried for 12 hours in *vacuo*.

- (**ⁿBu₄N**)₄[**MnMo₆O₁₈{(OCH₂)₃CNH₂}₂**] (**MnMo₆(TRIS)₂**)

The Anderson-Evans hybrid **MnMo₆(TRIS)₂** was synthesized according to the literature method^[57] with some modifications. A mixture (ⁿBu₄N)₄[α-Mo₈O₂₆] (8.00 g, 3.70 mmol), Mn(OAc)₃·2H₂O (1.49 g, 5.60 mmol) and tris(hydroxymethyl)aminomethane (1.56 g, 12.80 mmol) in 150 mL acetonitrile was refluxed for 20 hours. Then the orange suspension was cooled to room temperature centrifuged and the brown precipitate was discarded. The filtrate was kept aside for about 2 hours and the resulting white precipitate was filtered off and discarded. Then the filtrate was exposed to diethyl ether vapour. After one day, orange crystals had formed. For a higher yield, the diethyl ether diffusion was continued for about 1 week. The crystals were collected by filtration and air dried.

- (**ⁿBu₄N**)₄[**CoMo₆O₁₈{(OCH₂)₃CNH₂}₂**] (**CoMo₆(TRIS)₂**)

CoMo₆(TRIS)₂ was synthesized according to the literature method.^[156] (ⁿBu₄N)₄[Mo₈O₂₆] (0.538 g, 0.25 mmol, 1 eq.), Co(OAc)₂·4H₂O (0.094 g, 0.377 mmol, 1.5 eq.) and TRIS (0.091g, 0.75 mmol, 3 eq.) are taken in a 50 mL round bottom flask. 20 mL acetonitrile is added and the reaction mixture is refluxed at 95 °C for 2 days. The pale grey coloured turbid solution is cooled to room temperature and centrifuged. Pale greenish-grey solution was kept in an atmosphere of diethyl ether for diffusion. Green crystals of **CoMo₆(TRIS)₂** were obtained over a period of 2-5 days.

9.6. Synthesis from Chapter 6

Synthesis of Hybrid Linkers

All hybrid linkers were synthesized by the Schiff-base reaction of **MnMo₆(TRIS)₂** (1 g 0.53 mmol, 1 eq.) with different aldehydes (1 mmol, 2 eq.). Both reagents are taken in a vial and stirred (at 80 °C) with 20 mL DMF for 30 minutes. Clear orange solutions obtained are cooled to room temperature and then kept in ether atmosphere. Orange

crystals of hybrid linkers are obtained over a period of 2 weeks. Aldehydes considered for the hybrid linkers are given below:

- **HL-1:** o-vanillin (2-hydroxy-3-methoxybenzaldehyde).
- **HL-2:** 3-ethoxysalicylaldehyde (3-ethoxy-2-hydroxybenzaldehyde).
- **HL-3:** 2-hydroxybenzaldehyde.
- **HL-4:** 2-hydroxy-1-naphthaldehyde.
- **HL-5:** vanillin (4-hydroxy-3-methoxybenzaldehyde)
- **HL-6:** 4-hydroxybenzaldehyde

Yields: **HL-1** = 970 mg; **HL-2** = 960 mg; **HL-3** = 1020 mg; **HL-4** = 977 mg; **HL-5** = 850 mg, **HL-6** = 980 mg.

Synthesis of POMCPs by Ether-Diffusion Method

The hybrid linker **HL-x**, for x = 1 to 4 (0.0465 mmol, 1 eq.) was first dissolved in 2 mL DMF in a narrow vial (GC vial) and to this La(NO₃)₃ (98.2 mg, 0.302 mmol, 6.5 eq.) dissolved in 1 mL DMF was added. The entire mixture was stirred with heating (75 °C-80 °C) for 30 minutes. Afterwards, the vial was cooled to room temperature and then kept in diethyl ether atmosphere. Over several days, ether in the outer container diffuses into the inner vial as vapours. This decreases the solubility of the product in the solution and forces it out. Orange crystals of the **POMCP-xa** (x = 1 to 4) are obtained over a period of 1 week.

Amount of hybrid linkers used: **HL-1** = 100 mg, **HL-2** = 102 mg, **HL-3** = 97.2 mg, **HL-4** = 102 mg.

Yields: **POMCP-1a** = 121 mg; **POMCP-2a** = 118 mg; **POMCP-3a** = 109 mg; **POMCP-4a** = 105 mg.

Synthesis of POMCPs by Layering Method

In a narrow vial, the hybrid linker **HL-x**, for x = 1 to 4 (0.025 mmol, 1 eq.) was first dissolved in 1 mL DMF which forms the bottom layer. A boundary layer of a mixture of DMF/MeOH (1:1/v:v, 2 mL) was slowly pipetted over this. Over this, 1 mL of methanolic solution of La(NO₃)₃ (53 mg, 0.162 mmol, 6.5 eq.) is layered. The slow diffusion of reactants resulted in the formation of **POMCP-xb** (x = 1 to 4) as orange block crystals over a period of two weeks.

Amount of hybrid linkers used: **HL-1** = 54 mg, **HL-2** = 55 mg, **HL-3** = 53 mg, **HL-4** = 55 mg

Yields: **POMCP-1b** = 60 mg; **POMCP-2b** = 62 mg; **POMCP-3b** = 57 mg; **POMCP-4b** = 48 mg.

9.7. Synthesis from Chapter 7

- δ/χ -**CoMo₆(TRIS)₂**, δ/χ -**CoMo₆(TRIS)₂** and **CoMo₃(TRIS)₃**
(ⁿBu₄N)₂[Mo₆O₁₉] (1.364 g, 1 mmol, 1 eq.), Co(OAc)₂·4H₂O (500 mg, 2 mmol, 2 eq.) and TRIS (728 mg, 6 mmol, 6 eq.) are taken in a 100 mL round bottom flask. 60 mL acetonitrile is added and then kept reflux at 95 °C for 6 hr. As the reaction progress, the reaction mixture become turbid and later to pink coloured turbid mixture. After the course of the reaction, the pink coloured turbid suspension is centrifuged. The supernatant is kept in ether diffusion from which the crystals of δ/δ -**CoMo₆(TRIS)₂** and δ/χ -**CoMo₆(TRIS)₂** were obtained in about 5-7 days. Since it is a crystalline mixture, the estimation of absolute yield of individual compound was not possible.

The crude pink precipitate obtained after the centrifugation (ca. 1.33 g) is dried overnight in air. The air-dried precipitate is dissolved in 50 mL DMF by stirring with heating (70-80 °C) for 15 minutes. The clear pink solution is cooled to room temperature and is then kept for ether diffusion. Pink crystals of **CoMo₃(TRIS)₃** are obtained over a period of 3-5 days (Yield = 1.1 g).

- **Co(TRIS)₃**
Co(OAc)₂·4H₂O (150 mg, 1 mmol, 1 eq.) is dissolved in 5 mL DMF taken in a vial. TRIS (364 mg, 4 mmol, 4 eq.) is added and then stirred with heating at 80 °C for 30 minutes. Clear, dark purple solution thus obtained is transferred to a beaker and kept for evaporation. Hexagonal shaped block crystals of **Co(TRIS)₃** forms after about 3-4 weeks as the contents in the beaker is close to dryness (Yield = 130 mg).

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11. Appendix

11.1. Table of Compounds

<u>Compound</u>	<u>Molecular Formula</u>
Cu-nip	$[\text{Cu}_5(\text{OH})_2(\text{nip})_4(\text{H}_2\text{O})_6] \cdot 4.25\text{H}_2\text{O}$
Co-nip	$[\text{Co}(\text{nip})(\text{H}_2\text{O})_5]$
Ni-nip	$[\text{Ni}(\text{nip})(\text{H}_2\text{O})_5]$
Zn-nip	$[\text{Zn}(\text{nip})(\text{H}_2\text{O})]$
Cu-dnb	$[\text{Cu}(\text{dnb})_6(\text{OH})]$
Cu-Hbtc	$[\text{Cu}(\text{Hbtc})(\text{H}_2\text{O})_5]$
1-La	$[\text{La}_2\text{Cu}_3(\text{nip})_6(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$
2-Ln	$[\text{Ln}_2\text{Cu}_2(\text{nip})_2(\text{Hnip})_6(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$; $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$
2-La-meta	$[\text{La}_4\text{Cu}_{1.25}(\text{nip})_{4.5}(\text{Hnip})_{5.5}(\text{H}_2\text{O})_{8.5}] \cdot 12.5\text{H}_2\text{O}$
3-Ln	$[\text{Ln}_2(\text{nip})_2(\text{OAc})_2(\text{H}_2\text{O})_4] \cdot x\text{H}_2\text{O}$; $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$
4-Ln	$[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$; $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}, \text{Y}^{3+}$
5-Ln	$[\text{Ln}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$; $\text{Ln}^{3+} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}$
A-La	$[\text{La}_2\text{Cu}(\text{nip})_4(\text{H}_2\text{O})_6]$
B-La	$[\text{LaCu}(\text{nip})_2(\text{Hnip})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
6-La	$[\text{La}_4\text{Cu}_6(\text{nip})_{12}(\text{DMF})_2(\text{H}_2\text{O})_6] \cdot 6\text{H}_2\text{O}$
7-Ln	$[\text{Ln}_2\text{Cu}(\text{nip})_4(\text{DMF})_2(\text{H}_2\text{O})_2]$; $\text{Ln}^{3+} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Y}^{3+}$
8-La	$[\text{La}(\text{nip})(\text{HCOO})(\text{H}_2\text{O})_2]$
9-La	$[\text{La}_4\text{Cu}_{2.35}(\text{nip})_{6.7}(\text{Hnip})_{1.3}(\text{HCOO})_{0.5}(\text{HCOOH})_{0.5}(\text{DMF})_6(\text{H}_2\text{O})_{16.7}]^+ \cdot 8.3\text{H}_2\text{O}$
10-Ln	$[\text{Ln}_2(\text{nip})_2(\text{Hnip})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$; $\text{Ln}^{3+} = \text{Ho}^{3+}, \text{Er}^{3+}$
11-Er	$[\text{Er}_3\text{Cu}_4(\text{nip})_8(\text{DMF})_4(\text{H}_2\text{O})_8]^+ \cdot 11\text{DMF}$
12-Ho	$[\text{Ho}_{0.75}\text{Cu}_{6.25}(\text{nip})_{12}(\text{H}_2\text{O})_{13.25}]^{(0.25)-} \cdot 9\text{DMF}$

MnMo₆(TRIS)₂	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CNH}_2\}_2]$
HL-1a	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot 2\text{DMF}$
HL-1b	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot \text{DMF}$
HL-1c	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot 0.3\text{DMF}\cdot 1.3\text{H}_2\text{O}\cdot 0.3\text{Et}_2\text{O}$
HL-2	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}_2\}]\cdot \text{DMF}$
HL-3	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})\}]\cdot 2\text{DMF}$
HL-4	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}_2\}]\cdot 0.5\text{DMF}$
HL-5	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(3\text{-OCH}_3)(4\text{-OH})\}]\cdot \text{DMF}\cdot \text{CH}_3\text{CN}$
HL-6	$(^n\text{Bu}_4\text{N})_3[(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(4\text{-OH})\}]\cdot 2\text{DMF}$
POMCP-1a	$[\text{La}(\text{DMF})_7][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot 2\text{DMF}$
POMCP-1b	$[\text{La}(\text{DMF})_4(\text{MeOH})_2][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot 2\text{DMF}$
POMCP-2a	$[\text{La}(\text{X})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}_2\}]\cdot y\text{DMF}$
POMCP-2b	$[\text{La}(\text{DMF})_6(\text{MeOH})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OCH}_3)\}_2\}]\cdot 2\text{DMF}$
POMCP-3a	$[\text{La}(\text{DMF})_6(\text{H}_2\text{O})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}_2\}]\cdot 2\text{DMF}$
POMCP-3b	$[\text{La}(\text{X})][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_6\text{H}_3)(2\text{-OH})(3\text{-OC}_2\text{H}_5)\}_2\}]\cdot y\text{DMF}$
POMCP-4a	$[\text{La}(\text{DMF})_6][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}_2\}]\cdot 2\text{DMF}$
POMCP-4b	$[\text{La}(\text{DMF})_6(\text{MeOH})_2][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CN}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-OH})\}_2\}][(\text{MnMo}_6\text{O}_{18})\{(\text{OCH}_2)_3\text{CNH}=\text{CH}\{(\text{C}_{10}\text{H}_5)(2\text{-O})\}_2\}]\cdot 2\text{DMF}\cdot 2\text{MeOH}$

CoMo₃(TRIS)₃ -1	[Co ^{II} Mo ₃ O ₇ {(OCH ₂) ₂ C(NH ₂)(CH ₂ OH)} ₃]·4.5DMF
CoMo₃(TRIS)₃ -2	[Co ^{II} Mo ₃ O ₇ {(OCH ₂) ₂ C(NH ₂)(CH ₂ OH)} ₃]·2DMF·2H ₂ O
δ/δ- CoMo₆(TRIS)₂	[(ⁿ Bu ₄ N) ₃ [Co ^{III} Mo ₆ O ₁₈ {(OCH ₂) ₃ CNH ₂ } ₂]·H ₂ O
δ/χ- CoMo₆(TRIS)₂	[(ⁿ Bu ₄ N) ₃ [Co ^{II} Mo ₆ O ₁₇ (OH){(OCH ₂) ₃ CNH ₂ } ₂]·MeCN·H ₂ O
Co(TRIS)₃	[Co ₂ {(NH ₂)C(CH ₂ O) ₃ }{(NH ₂)C(CH ₂ OH) ₃ }] [(NH ₃)C(CH ₂ OH)] ₂ Cl ₄

11.2. Crystallographic Data

Compound	1-La
Formula	C ₄₈ H ₅₀ Cu ₃ La ₂ N ₆ O ₅₂
Formula Weight / g mol ⁻¹	2011.38
Crystal System	monoclinic
Space Group	Cc
<i>a</i> / Å	14.6041(3)
<i>b</i> / Å	30.3996(4)
<i>c</i> / Å	15.3477(3)
α / °	90
β / °	98.217(2)
γ / °	90
<i>V</i> / Å ³	6743.8(2)
<i>Z</i>	4
<i>T</i> / K	180
<i>F</i> (000)	3988
<i>D_c</i> / Mg m ⁻³	1.981
μ / mm ⁻¹	12.360
Crystal description	block
Crystal colour	dark blue
Wavelength	1.34143 (Ga K α)
Data Measured	38642
Unique Data	13146
<i>R_{int}</i>	0.0183
Unique Data with $I \geq 2\sigma(I)$	0.0183
Parameters/Restraints	1050/45
<i>wR</i> ₂ , (all data)	0.0791
<i>S</i> (all data)	1.018
<i>R</i> ₁ [$I \geq 2\sigma(I)$]	0.0297
Flack χ parameter	0.281(4)
Biggest diff. peak/hole	1.725/-0.743

Compound	2-La	2-Ce
Formula	C64 H46 Cu2 La2 N8 O56	C64 H46 Ce2 Cu2 N8 O56
Formula Weight / g mol ⁻¹	2227.99	2230.41
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	11.3433(3)	11.3327(3)
$b / \text{\AA}$	14.3193(4)	14.2785(4)
$c / \text{\AA}$	14.4875(4)	14.4934(4)
$\alpha / ^\circ$	61.314(2)	61.544(2)
$\beta / ^\circ$	68.147(2)	67.958(2)
$\gamma / ^\circ$	87.458(2)	87.538(2)
$V / \text{\AA}^3$	1889.77(10)	1884.44(10)
Z	1	1
T / K	150	180
$F(000)$	1106	1108
$D_c / \text{Mg m}^{-3}$	1.958	1.965
μ / mm^{-1}	9.643	10.078
Crystal description	block	block
Crystal colour	blue	blue
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	22653	24815
Unique Data	8223	8949
R_{int}	0.0257	0.0187
Unique Data with $I \geq 2\sigma(I)$	7375	8752
Parameters/Restraints	629/13	628/13
wR_2 , (all data)	0.0950	0.0710
S (all data)	1.066	1.051
$R_1 [I \geq 2\sigma(I)]$	0.0923	0.0274
Flack χ parameter		
Biggest diff. peak/hole	0.820/-1.093	1.398/-1.832

Compound	2-Pr	2-Nd
Formula	C ₆₄ H ₄₆ Cu ₂ N ₈ O ₅₆ Pr ₂	C ₆₄ H ₄₆ Cu ₂ N ₈ Nd ₂ O ₅₆
Formula Weight / g mol ⁻¹	2231.99	2238.65
Crystal System	triclinic	triclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a / Å	11.3051(2)	11.2927(2)
b / Å	14.3085(3)	14.2863(3)
c / Å	14.4706(3)	14.4481(3)
α / °	61.5210(10)	61.6750(10)
β / °	67.9070(10)	67.837(2)
γ / °	87.705(2)	87.744(2)
V / Å ³	1878.34(7)	1872.16(7)
Z	1	1
T / K	180	180
F(000)	1110	1112
D _c / Mg m ⁻³	1.973	1.986
μ / mm ⁻¹	10.527	10.994
Crystal description	block	block
Crystal colour	Greenish blue	blue
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	22850	26541
Unique Data	8860	8903
R _{int}	0.0199	0.0162
Unique Data with I $\geq$ 2 σ (I)	8606	8679
Parameters/Restraints	628/13	628/13
wR ₂ , (all data)	0.0901	0.0693
S (all data)	1.029	1.024
R ₁ [I $\geq$ 2 σ (I)]	0.0336	0.0267
Flack χ parameter		
Biggest diff. peak/hole	1.838/ -2.196	0.823/-1.589

Compound	2-Eu	2-Gd
Formula	C64 H46 Cu2 Eu2 N8 O56	C64 H46 Cu2 Gd2 N8 O56
Formula Weight / g mol ⁻¹	2254.09	2264.67
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	11.2541(3)	11.2412(3)
$b / \text{\AA}$	14.1730(4)	14.1379(4)
$c / \text{\AA}$	14.4444(4)	14.4402(3)
$\alpha / ^\circ$	62.465(2)	62.689(2)
$\beta / ^\circ$	67.431(2)	67.365(2)
$\gamma / ^\circ$	87.871(2)	87.926(2)
$V / \text{\AA}^3$	1858.63(10)	1854.27(9)
Z	1	1
T / K	180	180
$F(000)$	1118	1120
$D_c / \text{Mg m}^{-3}$	2.014	2.028
μ / mm^{-1}	12.497	13.041
Crystal description	tiny plate	tiny plate
Crystal colour	blue	blue
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	27359	27342
Unique Data	8855	8858
R_{int}	0.0329	0.0294
Unique Data with $I \geq 2\sigma(I)$	8171	8219
Parameters/Restraints	628/13	628/14
wR_2 , (all data)	0.1427	0.1121
S (all data)	1.089	1.062
$R_1 [I \geq 2\sigma(I)]$	0.0512	0.0414
Flack χ parameter		
Biggest diff. peak/hole	1.983/-3.100	1.947/-1.978

Compound	2-La meta	5-Gd
Formula	C80 H77.5 Cu1.25 La4 N10 O81	C32 H32 Gd2 N4 O33
Formula Weight / g mol ⁻¹	3110.08	1315.11
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	11.0039(4)	9.6203(3)
$b / \text{\AA}$	13.9560(6)	10.4685(3)
$c / \text{\AA}$	18.9981(6)	13.4671(4)
$\alpha / ^\circ$	103.721(3)	68.181(2)
$\beta / ^\circ$	90.970(3)	70.411(2)
$\gamma / ^\circ$	107.863(3)	65.262(2)
$V / \text{\AA}^3$	2684.93(18)	1117.28(6)
Z	1	1
T / K	180	180
$F(000)$	1540	644
$D_c / \text{Mg m}^{-3}$	1.923	1.955
μ / mm^{-1}	10.429	16.019
Crystal description	needle	block
Crystal colour	pale blue	colourless
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	42526	15205
Unique Data	11693	5281
R_{int}	0.0612	0.0244
Unique Data with $I \geq 2\sigma(I)$	7545	5218
Parameters/Restraints	816/136	345/12
wR_2 , (all data)	0.1279	0.0980
S (all data)	0.970	1.103
$R_1 [I \geq 2\sigma(I)]$	0.0483	0.0363
Flack χ parameter		
Biggest diff. peak/hole	1.211/-1.613	1.412/-1.883

Compound	3-La	3-Eu
Formula	C10 H11.12 La N O10.56	C10 H10.52 Eu N O10.26
Formula Weight / g mol ⁻¹	453.19	460.83
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	6.9756(3)	6.8115(6)
$b / \text{\AA}$	10.6567(4)	10.5876(11)
$c / \text{\AA}$	10.7538(5)	10.8261(11)
$\alpha / ^\circ$	69.792(3)	68.823(7)
$\beta / ^\circ$	74.197(3)	72.985(7)
$\gamma / ^\circ$	76.348(3)	72.557(7)
$V / \text{\AA}^3$	712.87(6)	679.47(12)
Z	2	2
T / K	180	180
$F(000)$	439	445
$D_c / \text{Mg m}^{-3}$	2.111	2.252
μ / mm^{-1}	16.460	24.596
Crystal description	tiny plate	Block
Crystal colour	colourless	colourless
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	10654	9680
Unique Data	2990	3205
R_{int}	0.0447	0.0148
Unique Data with $I \geq 2\sigma(I)$	2626	3147
Parameters/Restraints	216/5	229/4
wR_2 , (all data)	0.1508	0.0428
S (all data)	1.111	1.066
$R_1 [I \geq 2\sigma(I)]$	0.1470	0.0164
Flack χ parameter		
Biggest diff. peak/hole	3.430/-1.629	0.564/-0.844

Compound	3-Gd	3-Tm
Formula	C10 H10.48 Gd N O10.24	C10 H10.30 N O10.15 Tm
Formula Weight / g mol ⁻¹	465.76	475.82
Crystal System	triclinic	triclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	6.8058(2)	6.7094(4)
<i>b</i> / Å	10.5736(4)	10.4784(6)
<i>c</i> / Å	10.8391(4)	10.7676(7)
α / °	68.591(3)	68.832(5)
β / °	72.522(3)	72.357(5)
γ / °	72.235(3)	72.974(5)
<i>V</i> / Å ³	675.66(5)	658.24(8)
<i>Z</i>	2	2
<i>T</i> / K	200	180
<i>F</i> (000)	447	455
<i>D_c</i> / Mg m ⁻³	2.289	2.401
μ / mm ⁻¹	26.158	6.797
Crystal description	plate	block
Crystal colour	colourless	Colourless
Wavelength	1.34143 (Ga K α)	0.71073 (Mo K α)
Data Measured	7512	9861
Unique Data	3171	5059
<i>R_{int}</i>	0.0396	0.0318
Unique Data with $I \geq 2\sigma(I)$	3127	4388
Parameters/Restraints	217/6	220/5
<i>wR</i> ₂ , (all data)	0.1284	0.1191
<i>S</i> (all data)	1.081	1.060
<i>R</i> ₁ [$I \geq 2\sigma(I)$]	0.0496	0.0445
Flack χ parameter		
Biggest diff. peak/hole	5.653/-3.853	7.953/-1.824

Compound	6-La	7-La
Formula	C108 H144 Cu6 La4 N16 O116	C38 H30 Cu La2 N6 O28
Formula Weight / g mol ⁻¹	4459.26	1360.04
Crystal System	monoclinic	triclinic
Space Group	<i>P2₁/c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	10.7961(2)	10.3405(3)
<i>b</i> / Å	22.5925(6)	10.7952(3)
<i>c</i> / Å	34.0268(7)	11.7774(4)
α / °	90	72.113(2)
β / °	94.558(2)	75.992(2)
γ / °	90	72.281(2)
<i>V</i> / Å ³	8273.3(3)	1175.67(7)
<i>Z</i>	2	1
<i>T</i> / K	180	180
<i>F</i> (000)	4468	667
<i>D_c</i> / Mg m ⁻³	1.790	1.921
μ / mm ⁻¹	10.159	12.507
Crystal description	needle	Plate
Crystal colour	blue	dark blue
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	67882	13351
Unique Data	18442	5212
<i>R_{int}</i>	0.0371	0.0207
Unique Data with $I \geq 2\sigma(I)$	15373	5104
Parameters/Restraints	1067/62	349/2
<i>wR₂</i> , (all data)	0.1242	0.0894
<i>S</i> (all data)	1.041	1.076
<i>R₁</i> [$I \geq 2\sigma(I)$]	0.0450	0.0326
Flack χ parameter		
Biggest diff. peak/hole	1.426/-1.493	1.358/-2.009

Compound	7-Ce	7-Gd
Formula	C38 H30 Ce2 Cu N6 O28	C38 H30 Cu Gd2 N6 O28
Formula Weight / g mol ⁻¹	1362.46	1396.72
Crystal System	triclinic	triclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	10.3386(4)	10.3513(9)
<i>b</i> / Å	10.7175(4)	10.5312(9)
<i>c</i> / Å	11.7160(4)	11.5858(11)
α / °	72.424(3)	73.255(7)
β / °	75.377(3)	76.670(7)
γ / °	72.098(3)	71.691(7)
<i>V</i> / Å ³	1159.28(8)	1134.50(19)
<i>Z</i>	1	1
<i>T</i> / K	150	150
<i>F</i> (000)	669	681
<i>D</i> _c / Mg m ⁻³	1.952	2.044
μ / mm ⁻¹	2.490	3.461
Crystal description	block	block
Crystal colour	dark blue	dark blue
Wavelength	0.71073 (Mo K α)	0.71073 (Mo K α)
Data Measured	14928	10735
Unique Data	7905	5401
<i>R</i> _{int}	0.0274	0.0647
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	6883	3700
Parameters/Restraints	348/2	348/3
<i>wR</i> ₂ , (all data)	0.1197	0.1271
<i>S</i> (all data)	1.079	1.024
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0421	0.0567
Flack χ parameter		
Biggest diff. peak/hole	3.545/-1.159	1.511/-0.943

Compound	7-Tb	7-Er
Formula	C38 H30 Cu N6 O28 Tb2	C38 H30 Cu Er2 N6 O28
Formula Weight / g mol ⁻¹	1400.06	1416.74
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	10.3237(6)	10.3545(7)
$b / \text{\AA}$	10.4981(5)	10.4463(7)
$c / \text{\AA}$	11.5891(6)	11.5267(8)
$\alpha / ^\circ$	73.134(4)	73.523(6)
$\beta / ^\circ$	76.370(4)	77.144(6)
$\gamma / ^\circ$	71.820(4)	71.571(5)
$V / \text{\AA}^3$	1127.35(11)	1122.13(14)
Z	1	1
T / K	180	150.15
$F(000)$	683	689
$D_c / \text{Mg m}^{-3}$	2.062	2.097
μ / mm^{-1}	3.678	4.283
Crystal description	block	block
Crystal colour	dark blue	Dark blue
Wavelength	0.71073 (Mo K α)	0.71073 (Mo K α)
Data Measured	10068	10108
Unique Data	5378	5344
R_{int}	0.0637	0.0687
Unique Data with $I \geq 2\sigma(I)$	4883	4441
Parameters/Restraints	348/3	348/3
wR_2 , (all data)	0.2182	0.2484
S (all data)	1.046	1.097
$R_1 [I \geq 2\sigma(I)]$	0.0851	0.0877
Flack χ parameter		
Biggest diff. peak/hole	9.810/-4.743	9.191/-2.456

Compound	8-La
Formula	C ₉ H ₈ La N O ₁₀
Formula Weight / g mol ⁻¹	429.07
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	14.2183(2)
<i>b</i> / Å	9.8094(2)
<i>c</i> / Å	8.6234(3)
α / °	90
β / °	97.885(2)
γ / °	90
<i>V</i> / Å ³	1191.36(5)
<i>Z</i>	4
<i>T</i> / K	180
<i>F</i> (000)	824
<i>D_c</i> / Mg m ⁻³	2.392
μ / mm ⁻¹	19.448
Crystal description	needle
Crystal colour	colourless
Wavelength	1.34143 (Ga K α)
Data Measured	22655
Unique Data	2645
<i>R_{int}</i>	0.1227
Unique Data with $I \geq 2\sigma(I)$	2145
Parameters/Restraints	208/4
<i>wR₂</i> , (all data)	0.0738
<i>S</i> (all data)	0.954
<i>R_I</i> [$I \geq 2\sigma(I)$]	0.0278
Flack χ parameter	
Biggest diff. peak/hole	1.141/-1.287

Compound	9-La-A	9-La-B
Formula	C84 H69.23 Cu2.39 La4 N14 O85	C84 H70.31 Cu2.34 La4 N14 O84
Formula Weight / g mol ⁻¹	3342.26	3324.17
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	12.0669(3)	12.1019(2)
$b / \text{\AA}$	12.6882(3)	12.6726(2)
$c / \text{\AA}$	22.0699(5)	21.9730(4)
$\alpha / ^\circ$	87.840(2)	86.461(2)
$\beta / ^\circ$	90.135(2)	89.383(2)
$\gamma / ^\circ$	66.413(2)	66.300(2)
$V / \text{\AA}^3$	3093.99(13)	3079.39(10)
Z	1	1
T / K	273.15	180
$F(000)$	1649	1640
$D_c / \text{Mg m}^{-3}$	1.794	1.793
μ / mm^{-1}	1.875	10.058
Crystal description	block	block
Crystal colour	blue	green
Wavelength	0.71073 (Mo K α)	1.34143 (Ga K α)
Data Measured	39147	51751
Unique Data	14516	14632
R_{int}	0.0509	0.0299
Unique Data with $I \geq 2\sigma(I)$	10393	12457
Parameters/Restraints	899/76	965/156
wR_2 , (all data)	0.1483	0.1395
S (all data)	0.957	1.049
$R_1 [I \geq 2\sigma(I)]$	0.0532	0.0534
Flack χ parameter		
Biggest diff. peak/hole	2.012/-1.873	1.677/-1.987

Compound	10-Ho	10-Er
Formula	C32 H34 Ho2 N4 O34	C32 H34 Er2 N4 O34
Formula Weight / g mol ⁻¹	1348.49	1353.15
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
$a / \text{\AA}$	9.7049(3)	9.6949(5)
$b / \text{\AA}$	10.5939(4)	10.5867(5)
$c / \text{\AA}$	13.3119(4)	13.2937(7)
$\alpha / ^\circ$	105.131(3)	104.381(4)
$\beta / ^\circ$	96.942(2)	97.732(4)
$\gamma / ^\circ$	116.199(2)	116.207(3)
$V / \text{\AA}^3$	1140.56(7)	1138.03(11)
Z	1	1
T / K	273.15	150
$F(000)$	660	662
$D_c / \text{Mg m}^{-3}$	1.963	1.974
μ / mm^{-1}	3.557	3.776
Crystal description	block	block
Crystal colour	colourless	Colourless
Wavelength	0.71073 (Mo K α)	0.71073 (Mo K α)
Data Measured	12426	13600
Unique Data	5352	6861
R_{int}	0.0253	0.0375
Unique Data with $I \geq 2\sigma(I)$	5034	5587
Parameters/Restraints	343/9	351/11
wR_2 , (all data)	0.1163	0.1317
S (all data)	1.102	1.061
$R_1 [I \geq 2\sigma(I)]$	0.0410	0.0475
Flack χ parameter		
Biggest diff. peak/hole	2.051/-1.747	3.252/-1.243

Compound	11-Er	12-Ho
Formula	C109 H145 Cu4 Er3 N23 O71	C96 H62.50 Cu6.25 Ho3.75 N12 O85.25
Formula Weight / g mol ⁻¹	3669.41	3763.69
Crystal System	tetragonal	tetragonal
Space Group	<i>P</i> $\bar{4}$ <i>n</i> 2	<i>P</i> 4 ₂ / <i>ncm</i>
<i>a</i> / Å	22.9638(4)	39.7218(4)
<i>b</i> / Å	22.9638(4)	39.7218(4)
<i>c</i> / Å	26.9104(6)	22.8785(2)
α / °	90	90
β / °	90	90
γ / °	90	90
<i>V</i> / Å ³	14190.8(6)	36098.2(8)
<i>Z</i>	4	8
<i>T</i> / K	200	180
<i>F</i> (000)	7392	14696
<i>D</i> _c / Mg m ⁻³	1.718	1.385
μ / mm ⁻¹	9.498	11.698
Crystal description	tiny block	block
Crystal colour	green-blue	blue
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	45742	84151
Unique Data	13293	17344
<i>R</i> _{int}	0.0789	0.0934
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	8362	12576
Parameters/Restraints	714/57	896/66
<i>wR</i> ₂ , (all data)	0.1434	0.2549
<i>S</i> (all data)	0.927	1.044
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0554	0.0927
Flack χ parameter	0.006(7)	
Biggest diff. peak/hole	0.952/-0.796	1.573/-2.158

Compound	HL-1a	HL-1b
Formula	C78 H150 Mn Mo6 N7 O30	C75 H143 Mn Mo6 N6 O29
Formula Weight / g mol ⁻¹	2296.62	2223.53
Crystal System	monoclinic	triclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	23.4458(8)	16.4624(2)
<i>b</i> / Å	15.0720(3)	23.6007(3)
<i>c</i> / Å	27.8115(8)	24.9252(3)
α / °	90	87.6160(10)
β / °	94.075(3)	87.7170(10)
γ / °	90	85.3690(10)
<i>V</i> / Å ³	9803.0(5)	9637.6(2)
<i>Z</i>	4	4
<i>T</i> / K	180	180
<i>F</i> (000)	4736	4576
<i>D</i> _c / Mg m ⁻³	1.556	1.532
μ / mm ⁻¹	5.225	5.201
Crystal description	block	Block
Crystal colour	orange	orange
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	113076	103722
Unique Data	23443	41707
<i>R</i> _{int}	0.0562	0.0148
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	14430	38746
Parameters/Restraints	1096/34	2173/18
<i>wR</i> ₂ , (all data)	0.0999	0.0786
<i>S</i> (all data)	0.882	1.037
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0414	0.0279
Flack χ parameter		
Biggest diff. peak/hole	1.259/-0.754	1.355/-0.846

Compound	HL-1c	HL-2
Formula	C77.33 H151.33 Mn Mo6 N6.33 O31	C82.5 H160.5 Mn Mo6 N6.5 O30.5
Formula Weight / g mol ⁻¹	2296.62	2362.24
Crystal System	orthorhombic	monoclinic
Space Group	<i>Pna2₁</i>	<i>C2/c</i>
<i>a</i> / Å	28.6588(2)	28.0283(6)
<i>b</i> / Å	45.5828(3)	28.9899(6)
<i>c</i> / Å	23.1199(2)	27.5278(5)
α / °	90	90
β / °	90	111.607(1)
γ / °	90	90
<i>V</i> / Å ³	30202.6(4)	20795.6(7)
<i>Z</i>	12	8
<i>T</i> / K	293	180
<i>F</i> (000)	14216	9776
<i>D_c</i> / Mg m ⁻³	1.515	1.509
μ / mm ⁻¹	5.160	0.892
Crystal description	block	block
Crystal colour	orange	orange
Wavelength	1.34143 (Ga K α)	0.71073 (Mo K α)
Data Measured	174662	94760
Unique Data	52009	24701
<i>R_{int}</i>	0.0315	0.0333
Unique Data with $I \geq 2\sigma(I)$	46812	16552
Parameters/Restraints	3143/405	1168/82
<i>wR₂</i> , (all data)	0.0996	0.0709
<i>S</i> (all data)	1.079	0.923
<i>R₁</i> [$I \geq 2\sigma(I)$]	0.0344	0.0322
Flack χ parameter		
Biggest diff. peak/hole	0.841/-1.153	0.620/-0.603

Compound	HL-3	HL-4
Formula	C72 H136.67 Mn Mo6 N5.67 O26.67	C79.5 H139.5 Mn Mo6 N5.5 O26.5
Formula Weight / g mol ⁻¹	2139.11	2227.04
Crystal System	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	22.7378(5)	15.2662(3)
<i>b</i> / Å	43.0112(5)	24.8667(6)
<i>c</i> / Å	27.9863(6)	24.2678(5)
α / °	90	90
β / °	96.677(2)	94.074(2)
γ / °	90	90
<i>V</i> / Å ³	27184.4(9)	9189.3(3)
<i>Z</i>	12	4
<i>T</i> / K	180	180
<i>F</i> (000)	13184	4576
<i>D</i> _c / Mg m ⁻³	1.568	1.610
μ / mm ⁻¹	5.602	5.540
Crystal description	block	Block
Crystal colour	yellow	yellow
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	198664	53125
Unique Data	41467	21447
<i>R</i> _{int}	0.0468	0.0346
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	41467	17949
Parameters/Restraints	3009/235	1070/94
<i>wR</i> ₂ , (all data)	0.1182	0.1282
<i>S</i> (all data)	0.956	1.043
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0409	0.0450
Flack χ parameter		
Biggest diff. peak/hole	1.569/-1.109	0.972/-0.791

Compound	HL-5	HL-6
Formula	C77 H148 Mn Mo6 N7 O30	C76 H146 Mn Mo6 N7 O28
Formula Weight / g mol ⁻¹	2282.60	2236.57
Crystal System	monoclinic	monoclinic
Space Group	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> / Å	25.1452(12)	14.4009(2)
<i>b</i> / Å	17.0521(6)	28.8848(5)
<i>c</i> / Å	22.5390(9)	23.1983(3)
α / °	90	90
β / °	97.326(4)	93.938(1)
γ / °	90	90
<i>V</i> / Å ³	9585.3(7)	9626.9(2)
<i>Z</i>	4	4
<i>T</i> / K	150	180
<i>F</i> (000)	4704	4608
<i>D_c</i> / Mg m ⁻³	1.582	1.543
μ / mm ⁻¹	0.964	5.299
Crystal description	Block	block
Crystal colour	Orange	yellow
Wavelength	0.71073 (Mo K α)	1.34143 (Ga K α)
Data Measured	33359	70016
Unique Data	10012	22199
<i>R_{int}</i>	0.1109	0.0399
Unique Data with $I \geq 2\sigma(I)$	5536	18653
Parameters/Restraints	1084/225	1086/73
<i>wR₂</i> , (all data)	0.1964	0.0943
<i>S</i> (all data)	1.022	1.035
<i>R₁</i> [$I \geq 2\sigma(I)$]	0.0771	0.0338
Flack χ parameter		
Biggest diff. peak/hole	0.892/-0.654	0.921/-1.304

Compound	POMCP-1a	POMCP-3a
Formula	C51 H91 La Mn Mo6 N11 O37	C44 H78 La Mn Mo6 N8 O34
Formula Weight / g mol ⁻¹	2219.83	2032.63
Crystal System	triclinic	monoclinic
Space Group	<i>P</i> 1	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	12.1092(4)	25.719(2)
<i>b</i> / Å	14.2123(5)	13.5705(10)
<i>c</i> / Å	14.2371(5)	22.8196(14)
α / °	101.437(3)	90
β / °	109.596(3)	119.270(5)
γ / °	113.225(2)	90
<i>V</i> / Å ³	1960.52(13)	6947.6(9)
<i>Z</i>	1	4
<i>T</i> / K	180	180
<i>F</i> (000)	1104	4016
<i>D_c</i> / Mg m ⁻³	1.880	1.943
μ / mm ⁻¹	1.708	1.914
Crystal description	block	block
Crystal colour	orange	orange
Wavelength	0.71073 (Mo K α)	0.71073 (Mo K α)
Data Measured	17304	26266
Unique Data	14614	7099
<i>R_{int}</i>	0.0291	0.0818
Unique Data with $I \geq 2\sigma(I)$	12808	4257
Parameters/Restraints	977/3	392/26
<i>wR</i> ₂ , (all data)	0.1367	0.1357
<i>S</i> (all data)	1.044	1.014
<i>R</i> ₁ [$I \geq 2\sigma(I)$]	0.0488	0.0483
Flack χ parameter	0.284(18)	
Biggest diff. peak/hole	1.994/-0.621	1.412/-0.505

Compound	POMCP-4a	POMCP-1b
Formula	C108 H168 La2 Mn2 Mo12 N20 O68	C38 H66 La Mn Mo6 N6 O35
Formula Weight / g mol ⁻¹	4373.59	1936.45
Crystal System	triclinic	monoclinic
Space Group	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> / Å	12.7459(13)	22.0004(4)
<i>b</i> / Å	16.1566(15)	14.7409(3)
<i>c</i> / Å	20.795(2)	18.9884(4)
α / °	86.343(8)	90
β / °	74.139(8)	96.300(2)
γ / °	69.734(8)	90
<i>V</i> / Å ³	3862.0(7)	6120.9(2)
<i>Z</i>	1	4
<i>T</i> / K	180	200
<i>F</i> (000)	2168	3800
<i>D_c</i> / Mg m ⁻³	1.881	2.101
μ / mm ⁻¹	1.729	12.029
Crystal description	block	block
Crystal colour	orange	orange
Wavelength	0.71073 (Mo K α)	1.34143 (Ga K α)
Data Measured	21369	27914
Unique Data	11038	8172
<i>R_{int}</i>	0.1029	0.0194
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	6242	7502
Parameters/Restraints	976/0	800/295
<i>wR</i> ₂ , (all data)	0.1681	0.0755
<i>S</i> (all data)	1.124	1.040
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0843	0.0297
Flack χ parameter		0.164(13)
Biggest diff. peak/hole	0.857/-0.784	1.324/-2.699

Compound	POMCP-2b	POMCP-4b
Formula	C51 H92 La Mn Mo6 N10 O37	C110 H186 La2 Mn2 Mo12 N18 O74
Formula Weight / g mol ⁻¹	2206.83	4483.74
Crystal System	monoclinic	triclinic
Space Group	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	17.4339(4)	12.7592(2)
<i>b</i> / Å	21.7523(5)	14.3962(3)
<i>c</i> / Å	20.6125(5)	23.8288(5)
α / °	90	92.207(2)
β / °	97.969(2)	90.435(2)
γ / °	90	115.1670(10)
<i>V</i> / Å ³	7741.3(3)	3957.14(14)
<i>Z</i>	4	1
<i>T</i> / K	200	200
<i>F</i> (000)	4392	2232
<i>D_c</i> / Mg m ⁻³	1.893	1.882
μ / mm ⁻¹	9.482	9.281
Crystal description	block	block
Crystal colour	orange	orange
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	70805	69721
Unique Data	17279	18821
<i>R_{int}</i>	0.0581	0.0276
Unique Data with $I \geq 2\sigma(I)$	10720	15041
Parameters/Restraints	926/13	1027/60
<i>wR₂</i> , (all data)	0.1279	0.0923
<i>S</i> (all data)	0.933	0.996
<i>R₁</i> [$I \geq 2\sigma(I)$]	0.0481	0.0329
Flack χ parameter		
Biggest diff. peak/hole	1.042/-0.839	1.601/-0.784

Compound	CoMo₃(TRIS)₃-1	CoMo₃(TRIS)₃-2
Formula	C28.5 H58.5 Co Mo3 N8.5 O21.5	C18 H39 Co Mo3 N5 O20
Formula Weight / g mol ⁻¹	1211.08	992.29
Crystal System	monoclinic	triclinic
Space Group	P 1 21/c 1	<i>P</i> $\bar{1}$
<i>a</i> / Å	13.9822(3)	11.9990(4)
<i>b</i> / Å	14.9610(3)	15.0259(6)
<i>c</i> / Å	21.9247(6)	18.6165(6)
α / °	90	83.126(3)
β / °	94.498(2)	89.198(3)
γ / °	90	78.944(3)
<i>V</i> / Å ³	4572.25(18)	3270.4(2)
<i>Z</i>	4	4
<i>T</i> / K	180	180
<i>F</i> (000)	2456	1980
<i>D_c</i> / Mg m ⁻³	1.759	2.015
μ / mm ⁻¹	6.896	9.484
Crystal description	Needle	plates
Crystal colour	pink	pink
Wavelength	1.34143 (Ga K α)	1.34143 (Ga K α)
Data Measured	90226	47954
Unique Data	10980	15302
<i>R_{int}</i>	0.0259	0.0344
Unique Data with <i>I</i> $\geq$ 2 σ (<i>I</i>)	9612	12453
Parameters/Restraints	635/77	885/8
<i>wR</i> ₂ , (all data)	0.0794	0.1109
<i>S</i> (all data)	1.058	0.993
<i>R</i> ₁ [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	0.0277	0.0398
Flack χ parameter		
Biggest diff. peak/hole	0.889/-0.933	1.292/-1.782

Compound	δ/χ -CoMo ₃ (TRIS) ₂	Co(TRIS) ₃
Formula	C57 H128.50 Co Mo6 N5.50 O25	C28 H75 Cl4 Co2 N7 O21
Formula Weight / g mol ⁻¹	1925.72	1105.61
Crystal System	tetragonal	trigonal
Space Group	<i>I</i> 4 ₁ <i>cd</i>	<i>R</i> 32
<i>a</i> / Å	25.2317(3)	10.3009(4)
<i>b</i> / Å	25.2317(3)	10.3009(4)
<i>c</i> / Å	50.0412(8)	37.5939(18)
α / °	90	90
β / °	90	90
γ / °	90	120
<i>V</i> / Å ³	31858.2(9)	3454.6(3)
<i>Z</i>	16	3
<i>T</i> / K	180	150
<i>F</i> (000)	15808	1746
<i>D_c</i> / Mg m ⁻³	1.606	1.594
μ / mm ⁻¹	6.649	1.035
Crystal description	block	block
Crystal colour	light yellow	purple
Wavelength	1.34143 (Ga K α)	0.71073 (Mo K α)
Data Measured	229301	8483
Unique Data	19195	1643
<i>R_{int}</i>	0.0341	0.0486
Unique Data with $I \geq 2\sigma(I)$	18170	1428
Parameters/Restraints	862/296	122/24
<i>wR₂</i> , (all data)	0.1025	0.2015
<i>S</i> (all data)	1.080	1.105
<i>R₁</i> [$I \geq 2\sigma(I)$]	0.0392	0.0710
Flack χ parameter	0.039(9)	0.46 (8)
Biggest diff. peak/hole	0.757/-0.432	1.054/-0.823

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13. Curriculum Vitae

13.1. Educational Qualification

Doctoral Candidate , under the supervision of Prof. Annie K. Powell, Karlsruhe Institute of Technology, Karlsruhe, Germany, funded by DAAD Doctoral Scholarship.	2021- present
Integrated M.Sc. in Chemistry Amrita School of Arts and Science, Amrita Vishwa Vidyapeetham, Kollam, Kerala, India, CGPA: 9.61/10. (First Class with Distinction) First Rank Holder and Gold Medal winner)	2012-2017
Masters Project (as IRCC Research Internship) at IIT Bombay, Mumbai, India	January-May 2017

13.2. Previous Work and Research Experiences

- Junior Research Fellow (JRF) for DST- SERB Sponsored Project, at NIT Calicut, India (March 2019– August 2020).
- Guest Lecturer (Chemistry) at Government Polytechnic College, Kozhikode, Kerala, India (December 2017– January 2019).

13.3. Scholarship and Grants

- **DAAD Doctoral Scholarship:** Research Grants - Doctoral Programmes in Germany: January 2021-June 2025.
- **KHYS Networking Grant** (2023). Funding for doctoral researchers at KIT to generate new international contacts.
- **KHYS Aspirant Grant** (2019). Funding to support one month research stay at KIT to meet potential supervisors, to get to know each other and to discuss the possibility of doing a doctorate at KIT.

13.4. Conferences, Summer Schools and Meetings

GDCh Conference at Munich (Germany), poster presentation.	September 2024
NANOMAT Conference at Vienna (Austria), poster presentation.	August 2024
CS2fE Summer School at Aussois (France), poster presentation.	June 2024
MSE Day at Geesthacht (Germany), poster presentation.	November 2023
International Conference on f Elements (ICFE-11) at Strasbourg (France), poster presentation.	August 2023
KIT GradCHEMBIO Retreat at Trifels (Germany), oral presentation.	November 2022
SchaulnsLand Meeting at Wildberg (Germany), oral contribution.	September 2022
POM-BASICS Summer School at La Rochelle (France)	June 2022

13.5. Stays Abroad

- Two-week research stay at Technische Universität Wien, Austria as the part of the **KHYS Networking Grant** (March 2024).
- One-month research Stay at Technische Universität Wien, Austria (November 2024).

13.6. Workshops

- Discover Hidden Champions: Navigating the Hidden Job Market for Scientists (March 2025).
- KHYS Networking Grant Kick-off Workshop: Strategies for Establishing International Contact (December 2023).
- Olex2 workshop at KIT (December 2023).

13.7. Master Thesis Supervision and Teaching Assistant

- Supervision of the Master Thesis of Sören Lischewski (Powell Group): March-September 2023.
- Assistant at Anorganisch-chemisches Praktikum für Fortgeschrittene (ACF): SS2022, WS 2022/2023, SS 2023, WS 2023/2024.

14. Collaborations

- Dr. Christopher Klein (Prof. Manfred Wilhelm group) - Rheological analysis.
Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT).
- Dr. Sören Schlittenhardt, Dr. Barbora Brachnakova and Dr. Senthil Kumar Kuppusamy, (Prof. Mario Ruben group) - Magnetic studies.
Institute for Nanotechnology (INT), Karlsruhe Institute of Technology (KIT).
- Asst. Prof. Alexey Cherevan and Univ. Prof. Dominik Eder – Photoluminescence and photocatalytic hydrogen evolution reactions.
Molecular Materials Chemistry division, Vienna University of Technology, Getreidemarkt 9/165, 1060 Wien, Austria.

15. List of Publications

- A. Raveendranathan, C. O. Klein, C. E. Anson, P. de Oliveira, M. Ibrahim, A. K. Powell. "A Metallogel-Mediated Crystal Growth of Cu^{II}-La^{III} Heterometallic Metal-Organic Frameworks and Coordination Polymers", **in preparation**.
- V.A. Njayappallil, A. Raveendranathan, S.K. Kuppusamy, P. Chakraborty, T. Bergfeldt, N.Malinová, M. M. Kappes, M. Ruben, C. E. Anson, M. Ibrahim, A. K. Powell. "Chiral Networks Assembled from Hexalanthanide Polyoxometalate Sandwich Building Units showing Solid State Temperature-Dependent Photoluminescence", **submitted**.
- A. Raveendranathan, J. Chauhan, S. N. Myakala, Z. Huang, M. Weisweiler, M. H. Berchtel, A. Ertl, S. Wöhrer, G. Ramer, B. Lendl, M. Ibrahim, C. E. Anson, J. Lu, P. O. Å. Persson, D. Eder¹, A. K. Powell and A. Cherevan. "Charge-neutral Co-Mo polyoxometalate hybrid enables H₂ evolution at the molecular/semiconductor interface", **in preparation**.
- A. Raveendranathan, V.A. Njayappallil, M. Ibrahim, G. Mathew, C. E. Anson, A. K. Powell. "Solvent-Mediated Structural Transformations in a Cu^{II}-La^{III} Heterometallic Coordination Polymers Under Solvothermal & Ambient Conditions", **in preparation**.
- A. Raveendranathan, V.A. Njayappallil, N.Malinová, S.K. Kuppusamy, M. Ibrahim, C. E. Anson, M. Ruben, A. K. Powell. "Crystal Growth of Lanthanide- based Heterometallic and Homometallic Coordination Polymers & Metal-Organic Frameworks and their Solid-State Photoluminescence Studies", **in preparation**.
- A. Raveendranathan, M. Ibrahim, C. E. Anson, A. K. Powell. "Synthesis and Topological considerations in La^{III}- based-Coordination Polymers from Anderson-Evans type Polyoxometalate Hybrid Linkers", **in preparation**.