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Coinage Metal Bis(amidinate) Complexes as Building Blocks for Self-Assembled One-Dimensional Coordination Polymers

Cedric Uhlmann,^[a] Thomas J. Feuerstein,^[a] Michael T. Gamer,^[a] and Peter W. Roesky*^[a]

Dedicated to Professor Pierre Braunstein on the occasion of his 75th birthday

Abstract: The pyridyl functionalized amidinate $[\{\text{PyC}\equiv\text{CC}(\text{NDipp})_2\}\text{Li}(\text{thf})_2]_n$ was used to synthesize a series of bis-amidinate complexes $[\{\text{PyC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{M}_2]$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) with fully supported metallophilic interactions. These metallophilic ligands were then used as building blocks for the synthesis of one-dimensional heterobimetallic coordination polymers using $\text{Zn}(\text{hfac})_2$ ($\text{hfac} = \text{hexafluoroacetylacetonate}$) for self-assembly. Interestingly, the three coordination polymers

$[\{\text{PyC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{M}_2][\text{Zn}(\text{hfac})_2]$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$), exhibit a zig zag shape in the solid state. To achieve linear coordination geometry other connectors such as $\text{M}'(\text{acac})$ ($\text{M}' = \text{Ni}, \text{Co}$) ($\text{acac} = \text{acetylacetonate}$) were investigated. The thus obtained compounds $[\{\text{PyC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Cu}_2][\text{M}'(\text{acac})_2]$ ($\text{M}' = \text{Ni}, \text{Co}$) are indeed linear heterobimetallic coordination polymers featuring a metalloligand backbone with fully supported metallophilic interactions.

Introduction

The area of metal amidinate $[\text{RC}(\text{NR}')_2]^-$ and guanidinate $[\text{R}_2\text{NC}(\text{NR}')_2]^-$ chemistry witnessed increased growth since the late 1990s.^[1] These ligands, are considered equivalent to η^5 -cyclopentadienyl. However, they are more easily adjustable in terms of steric demand and electronic structure. Therefore, they have been and continue to be used as spectator ligands in the synthesis of a wide variety of main group, transition metal and lanthanide complexes.^[2–8] Moreover, monovalent coinage metal amidinate complexes are known to form dimeric species “ L_2M_2 ” ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$), with particularly short metal-metal distances, which are “forced by the ligand environment, and go along with metallophilic interactions.”^[8–18] Recently, we reported, that these complexes may exhibit interesting photoluminescent properties.^[19–20] Furthermore, in the solid state of many gold-containing complexes these aurophilic interactions lead to the formation of dimers, oligomers, or one-dimensional self-assembled polymers.^[21] The most important step in the synthesis of one-, two- or three-dimensional molecular networks, is the design of their building blocks, which are crucial for the formation of the desired architectural, chemical, and physical properties.^[22] Such coordination polymers are of particular

interest for creating nanometer scale spaces and for applications in separation, storage,^[23–27] and heterogeneous catalysis.^[28–32] Most coordination polymers consist of two central building blocks, connectors and linkers. Aggregation induced self-assembly in solution, or the non-condensed phase then leads to the formation of the polymer via linking of the connectors.^[33] As already mentioned, the design of those blocks is essential, since depending on the number and orientation of their binding sites different geometries and dimensionalities may be obtained. Furthermore, the choice of the inorganic counter ion, the solvent, or template molecules also has an influence on the finally obtained geometry. Linkers afford a wide variety of linking sites and different binding bond strength, directionality, and sizes.^[18,22,34] They range from simple halides to large organic moieties with neutral or anionic binding sites. One of the most used donor groups for organic linkers are bridged bidentate pyridyl ligands.^[35–41] Therefore, we aimed to synthesize a new pyridyl functionalized amidinate ligand to obtain coinage metal bis-amidinate complexes featuring fully supported metallophilic interactions as building blocks for hetero-bimetallic coordination polymers.^[42–43]

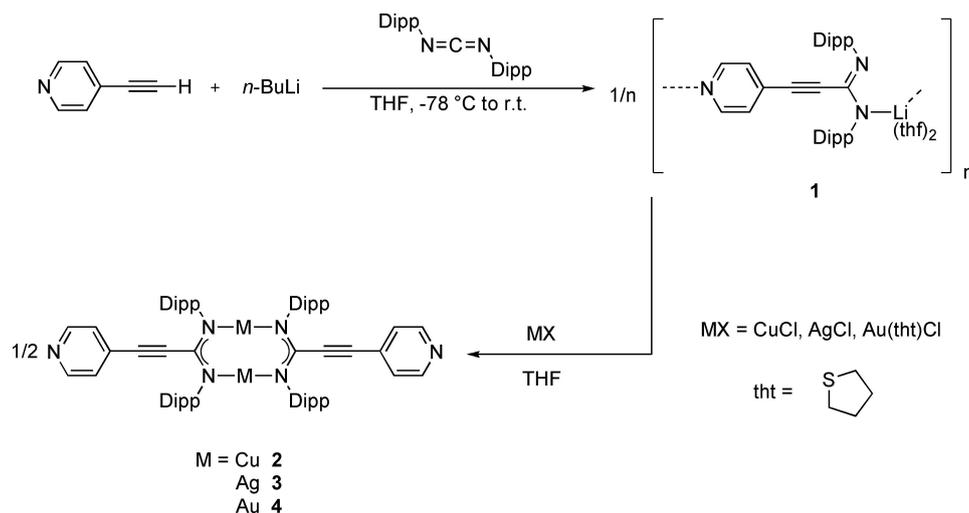
Results and Discussion

Investigations were initiated with the synthesis of the ligand $[\{\text{PyC}\equiv\text{CC}(\text{NDipp})_2\}\text{Li}(\text{thf})_2]_n$ (**1**), which was performed, by in situ lithiation of 4-ethynylpyridine followed by reaction with bis(2,6-diisopropylphenyl)carbodiimide. Thereby compound **1** was obtained in 60% yield (Scheme 1). Bis(2,6-diisopropylphenyl)carbodiimide was chosen as the starting compound because the amidinates obtained from it are known to kinetically stabilize coinage metal complexes and provide sufficient solubility in organic solvents. The ¹H NMR spectrum of

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202300289>

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Scheme 1. Synthesis of compound 1 and subsequent synthesis of the bis-amidates 2–4 via salt-metathesis reactions with coinage metal halides.

1 shows the absence of the terminal alkyne proton as well as the coordination of two tetrahydrofuran molecules per formula unit. In the ^7Li NMR spectrum a single resonance for the lithium atom is observed at $\delta = 1.25$ ppm. The product was also investigated by single crystal X-ray diffraction, revealing a polymeric structure of 1 in the solid state (see Figure S33 in the Supporting Information). However, even after several crystallization attempts, the data quality was not sufficient to discuss any structural parameters. Compound 1 has proven to be a suitable precursor for the synthesis of pyridyl functionalized multinuclear metal complexes since, via salt metathesis reactions. Thus, treatment of 1 with coinage metal halides leads to the pyridyl functionalized coinage metal bisamidate complexes 2–4 (Scheme 1). All three complexes were isolated as off-white to yellow solids in moderate yields. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compounds 2–4, the resonances of the $\text{C}\equiv\text{C}$ moiety are observed between $\delta = 85.0$ and $\delta = 98.9$ ppm, whereby the shifts in frequency correlate with the increasing electronegativity of the coinage metals from complexes 2–4. No $\text{C}\equiv\text{C}$ vibration mode was detected in the IR spectrum of compound 2. The corresponding mode for compounds 3 and 4 were observed solely in reduced intensity compared to 1. However, for all three complexes a very strong $\text{C}\equiv\text{C}$ vibration mode in the Raman spectrum as signal of the highest intensity at 2221, 2220 and 2226 cm^{-1} were observed, which are shifted by 13 to 19 cm^{-1} compared to 1.

Single crystals suitable for X-ray analysis could be obtained for all three isostructural complexes by recrystallization from hot THF. The central structural motive is an eight membered ring containing two NCN-amidinate moieties and two coinage metal ions (Figure 1). In contrast to compound 1, which displays a monodentate binding mode, compounds 2–4 show bridging bimetallic binding with short metal-metal distances, which is typical for coinage metal bisamidates.^[7,14,19–20] The M–M' distances increase from 2 with 2.525(2) Å over 4 with 2.7095(5) Å to 3 with 2.7871(4) Å which is in line with the increasing van der Waals radii^[44] and in range of metallophilic

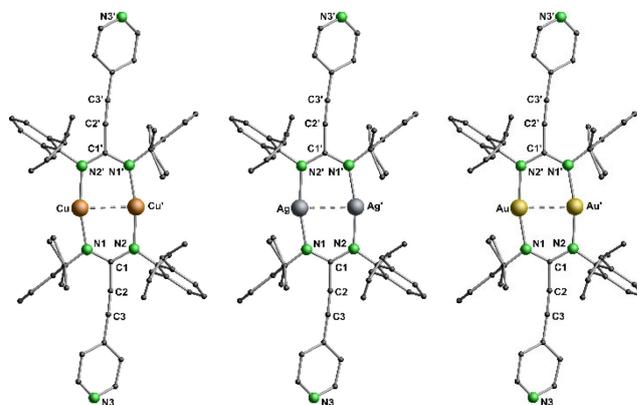
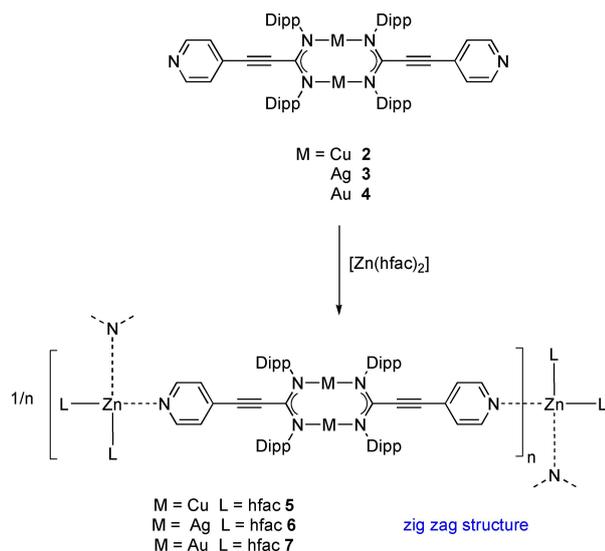


Figure 1. Molecular structure of compounds 2 (left), 3 (middle), and 4 (right) in the solid state. Hydrogen atoms are omitted for clarity. Structural parameters are given in the Supporting Information.

interactions.^[7,14,19–20] The N–C–N bite angles and the alkyne bond distances C2–C3 are with values between 123.1(3)° and 126.4(8)° and 1.183(12) Å and 1.202(5) Å in a typical range for bis-amidate bite angles and carbon triple bonds.^[6,19–20,45]

Complexes with $\text{Zn}(\text{hfac})_2$

To further utilize these pyridyl functionalized amidinate complexes as building blocks for heterobimetallic coordination polymers they were treated with $[\text{Zn}(\text{hfac})_2]$ (hfac = hexafluoroacetylacetonate). Refluxing the metalloligands 2–4 with one equivalent of $\text{Zn}(\text{hfac})_2$ in THF for several minutes and subsequent cooling to room temperature led to the formation of single crystals suitable for X-ray diffraction analysis of compounds 5–7 after several days (Scheme 2). Contrary to our expectations no linear coordination polymers were obtained, instead compounds 5–7 form one-dimensional heterobimetallic coordination polymers with metalloorganic backbones in which



Scheme 2. Synthesis of heterobimetallic coordination polymers 5–7 by reaction of compounds 2–4 with Zn(hfac)₂.

the bis-amidinate metalloligands are bridged by {Zn(hfac)₂} connectors leading to a zig zag shape in the solid state (Figures 2 and 3). The zinc atom is coordinated by two hfac[−]

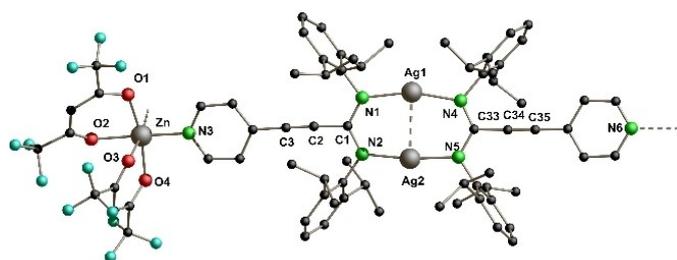


Figure 2. Molecular structure of compound 6 in the solid state. Hydrogen atoms are omitted for clarity. Structural parameters are given in the Supporting Information.

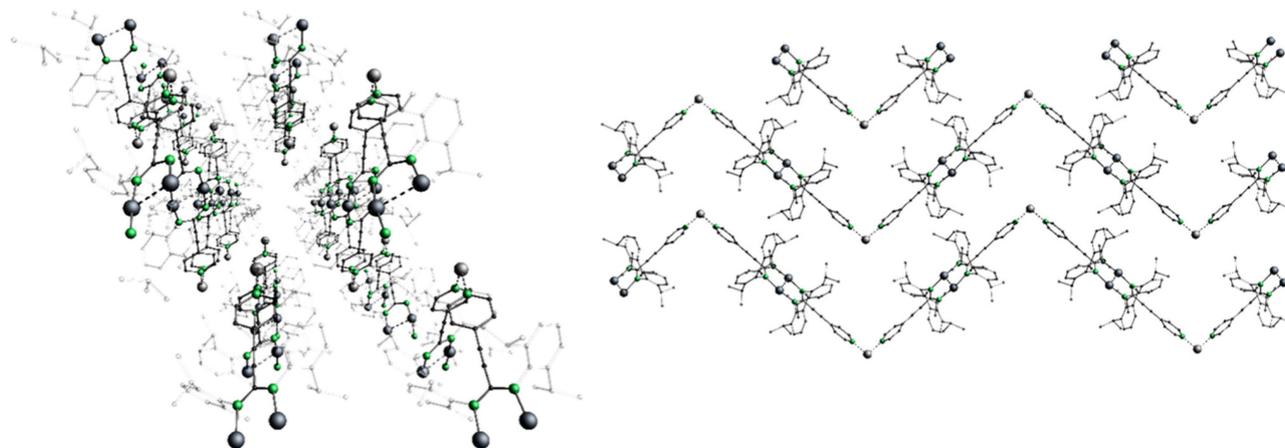
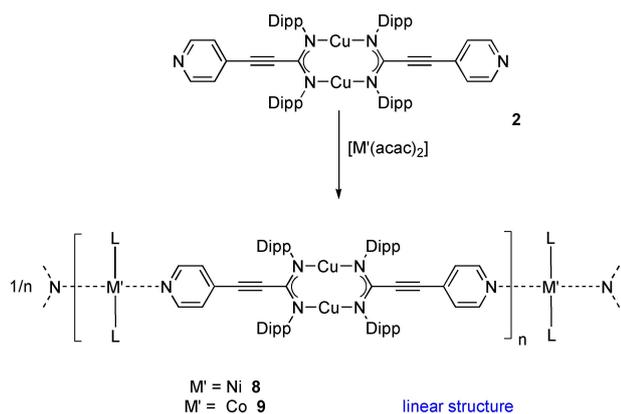


Figure 3. Polymeric structure of compound 6 in the solid state. Hydrogen atoms, solvent molecules as well as hfac[−] ligands are omitted for clarity. Dipp (2,6-diisopropylphenyl)-groups are displayed with 60% transparency. Colour code: Ag: dark grey, Zn: light grey, C: black, N: green.

ligands as well as two nitrogen atoms from consecutive pyridyl moieties in a distorted octahedral coordination geometry. Both nitrogen atoms occupy *cis*-positions of the coordination polyhedron, with a N–Zn–N angle of 98.6(2)° for compound 6, which is in agreement with is in accordance with [Zn(hfac)₂(py)₂]^[46] and leads to the overall observed zig zag arrangement. These chains are stacked along the crystallographic *a*- and *c*-axis. The calculated packing coefficients with solvent molecules of compounds 6 is 62.6%, and a hypothetical packing density, in which only the polymeric backbones and not the intercalated solvent molecules are considered in the calculation, is 42.6%.^[47] Due to the bad crystal quality of compound 5 and 7 no packing coefficient could be calculated. The NMR spectra of all coordination polymers were recorded in pyridine-d₅, because in other solvents no sufficient solubility was observed. ¹H NMR spectroscopic analysis shows not only the amidinate ligand protons but also the resonances of the two protons of the hexafluoroacetylacetonate ligands at 6.25 (5), 6.28 (6) and 6.28 ppm (7), respectively. In ¹³C{¹H} NMR spectra, the resonances of the CO and CF₃ carbon atoms were detected at 178.4 and 118.8 ppm (6), and 178.7 and 118.8 ppm (7) respectively. Resonances of the fluorine atoms were observed at −75.6 (5), −75.7 (6) and −75.3 ppm (7) in the respective ¹⁹F NMR spectra. In the ¹³C{¹H} NMR spectrum of compound 5 no resonance of the hfac ligand was detected. Nevertheless, ¹H and ¹⁹F NMR spectra clearly indicates its presence. Furthermore, another important aspect was to assess whether coordination polymers 5–7 are also present in solution or if the addition of pyridine led to the breakup of the polymer into metalloligand and [Zn(hfac)₂(py)₂]. Therefore, diffusion ordered NMR spectroscopy (DOSY) was applied, leading to the distinguishing of molecules according to their diffusion coefficient (*D*), which also correlates with their hydrodynamic radius.^[48–50] Only compound 5 was examined as a representative example. For 5, two distinguished species with a diffusion coefficient of 3.12–3.24·10^{−9} and 4.71·10^{−9} were determined (Supporting Information, Figure S14). This confirms the assumption that compound 5 decomposes in solution in two distinct



Scheme 3. Synthesis of heterobimetallic coordination polymers **8** and **9** by reaction of compound **2** with $[M'(\text{acac})_2]$ ($M' = \text{Ni, Co}$).

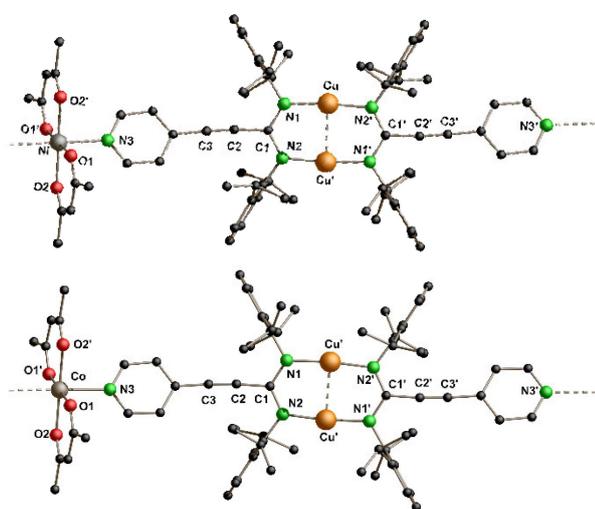


Figure 4. Structures of asymmetric units of compounds **8** (top) and **9** (bottom) in the solid state. Hydrogen atoms are omitted for clarity. Structural parameters are given in the Supporting Information.

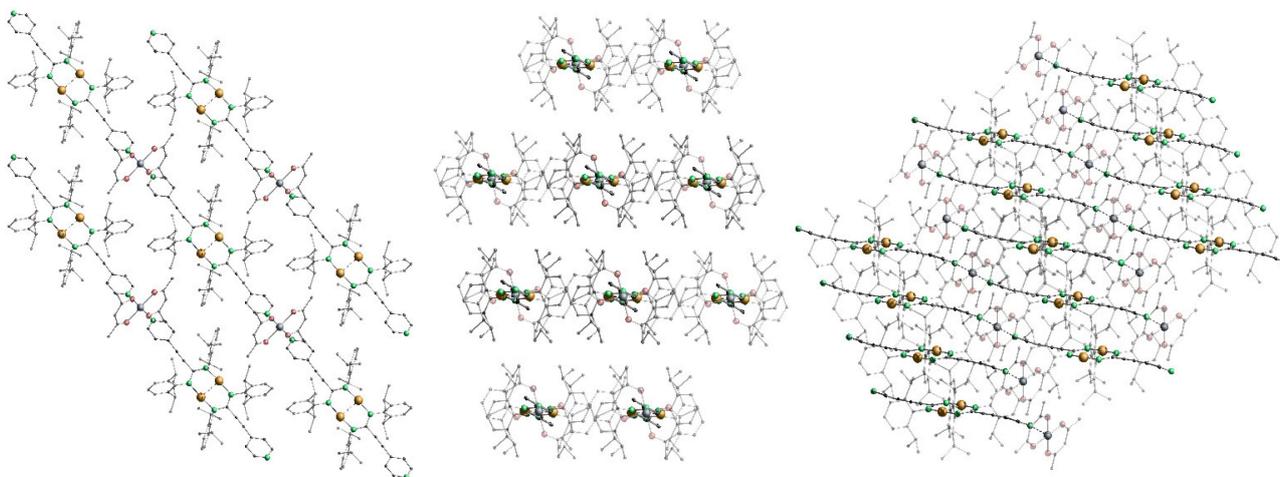


Figure 5. Polymeric structure of compound **8** in the solid state. Hydrogen atoms as well as solvent molecules are omitted for clarity. Dipp-groups and acac-ligands are displayed with 60% transparency.

species, which we suggest are compound **2** and $[\text{Zn}(\text{hfac})_2(\text{py})_2]$. The formation of compounds **5–7** can thus be seen as “solid-state-effect”. The coordination of the metalloligand to the $\{\text{Zn}(\text{hfac})_2\}$ unit in the solid state could also be observed by Raman spectroscopy based on the characteristic $\text{C}\equiv\text{C}$ valence vibration. Compared to the metalloligands **2–4**, the vibrations are shifted towards higher wavenumbers by 4 cm^{-1} (**5**), 10 cm^{-1} (**6**), and 6 cm^{-1} (**7**).

Complexes with $[M'(\text{acac})_2]$ ($M' = \text{Ni, Co}$) (acac = acetylacetonate)

Compounds **8** and **9** were obtained by dissolving compound **2** in DCM and layering with a toluene solution of $[\text{Co}(\text{acac})_2]$ or $[\text{Ni}(\text{acac})_2]$, respectively as crystalline material (Scheme 3). Analogous to the coordination polymers described above, the cobalt or nickel atom is coordinated by two acetylacetonate ligands as well as two nitrogen atoms of consecutive pyridyl groups. In contrast to compounds **5–7**, the two nitrogen atoms occupy *trans*-position within the coordination polyhedral formed by the Co and Ni atoms. Therefore, compounds **8** and **9** form a one-dimensional heterobimetallic coordination polymer with a linear shape in the solid state (Figures 4 and 5). Compared to the copper bis-amidinate **2**, the Cu–Cu' (2.5122(5) (**8**), 2.5102(3) (**9**) vs. 2.525(2) Å) distance and C2–C3 (1.193(3) (**8**), 1.197(2) (**9**) vs. 1.202(5) Å) distances are slightly decreased. The Ni–O (2.022(2), 2.0262(14)) and Ni–N (2.146(2)) as well as Co–O (2.038(1), 2.0441(10)) and Co–N (2.2060(12)) distances are in the expected range for complexes of the type $[M(\text{acac})_2(\text{py})_2]$ with $M = \text{Ni, Co}$ and $\text{py} = \text{pyridine}$.^[51–52] In the IR spectra the CO stretching frequencies were detected as signals with high intensity at 1590 cm^{-1} and 1591 cm^{-1} , respectively. For the nickel complex no shift was observed compared to $[\text{Ni}(\text{acac})_2]$, while for the Co complex the signal is shifted by 18 cm^{-1} towards higher wavenumbers. In the solid state these one-dimensional coordination polymers are stacked along the

Cu–Cu' and O1–M–O1' (M=Ni, Co) axis to form a layered structure (Figure 5). In adjacent chains, along the Cu–Cu' axis, metalloligand and {M(acac)₂} units alternate, as this presumably minimizes the steric repulsion of the Dipp groups (Dipp=2,6-diisopropylphenyl) and thus the packing density is increased. The calculated packing coefficients with solvent molecules of compounds **8** and **9** are 66.3% and 60%,^[47] respectively, and are thus slightly increased compared to compound **6**. A hypothetical packing density, in which only the polymeric backbones and not the intercalated solvent molecules are considered in the calculation, is 54.6% and 54.9%.^[47] This suggests far less solvent accessible voids compared to zig zag compounds **5–7**. NMR spectroscopic analysis was not possible due to the paramagnetism of compounds **8** and **9** as expected for Ni^{II}L₆ and Co^{II}L₆ type complexes.

Conclusion

Starting from new pyridyl functionalized amidinate ligand complexes **2–4** were obtained. These compounds feature fully supported metallophilic interactions and were used as connectors to obtain different heterobimetallic coordination polymers. More precisely, compounds **2–4** were treated with [Zn(hfac)₂] to yield compounds **5–7**, which form one-dimensional heterobimetallic zig zag shaped chains in the solid state. In these chains, the bis-amidinate metalloligands are bridged in a cis-configuration via the {Zn(hfac)₂} connectors leading to the observed zig zag structural motif. To achieve a linear coordination geometry [M'(acac)₂] (M'=Co, Ni) were used as linker whereupon compounds **8** and **9** were obtained. Both compounds form one-dimensional heterobimetallic coordination polymers with a linear scaffold in the solid state. The two pyridyl moieties occupy trans-position within the coordination polyhedral formed by the Co and Ni atoms.

Experimental Section

Experimental details are given in the Supporting Information is available free of charge via the internet. The Supporting Information includes materials, characterization methods, experimental procedures, full spectroscopic data for all new compounds, copies of ¹H, ¹³C{¹H}, ⁷Li{¹H}, ¹⁹F NMR, IR and Raman spectra, elemental analyses, and crystallographic data.

Deposition Numbers 2238218 (**2**), 2238219 (**3**), 2238220 (**4**), 2238221 (**5**), 2238222 (**6**), 2238223 (**7**), 2238224 (**8**), and 2238225 (**9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

Financial support by the DFG funded transregional collaborative research centre SFB/TRR 88 “Cooperative Effects in Homo and Heterometallic Complexes (3MET)” (project C3) is gratefully

acknowledged. CU thanks the Fonds der Chemischen Industrie for the generous fellowship (No. 108320). Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: amidinate · coinage metals · coordination polymer · metalloligand · self-assembly

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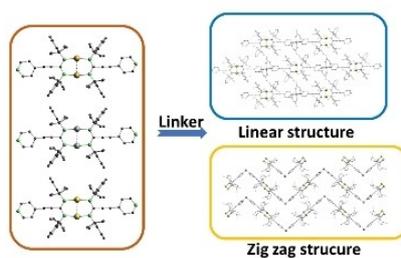
Manuscript received: January 27, 2023

Accepted manuscript online: February 10, 2023

Version of record online: ■■, ■■

RESEARCH ARTICLE

Two different self-assembled one-dimensional heterobimetallic coordination polymer types were synthesized by combining newly designed metal-ligands with $[\text{Zn}(\text{hfac})_2]$ or $[\text{M}(\text{acac})_2]$ ($\text{M} = \text{Ni}/\text{Co}$) as linker. These polymers show either a linear or zig zag structure in the solid state.



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**Coinage Metal Bis(amidinate)
Complexes as Building Blocks for
Self-Assembled One-Dimensional Co-
ordination Polymers**

