

Charge Makes a Difference: Molecular Ionic Bismuth Compounds

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Abstract: Key challenges in modern synthetic chemistry include the design of reliable, selective, and more sustainable synthetic methods, as well as the development of promising candidates for new materials. Molecular bismuth compounds offer valuable opportunities as they show an intriguing spectrum of properties that is yet to be fully exploited: a soft character, a rich coordination chemistry, the availability of a broad variety of oxidation states (at least +V to –I) and formal charges (at least +3 to –3) at the Bi atoms, and reversible switching between multiple oxidation states. All this is paired with the status of a non-precious (semi–)metal of good availability and a tendency towards low toxicity. Recent findings show that some of these properties only come into reach, or can be substantially optimized, when *charged* compounds are specifically addressed. In this review, essential contributions to the synthesis, analyses, and utilization of ionic bismuth compounds are highlighted.

1. Introduction

1.1. Ions—a brief historical perspective

The identification of chemical species as charge carriers in electrochemical processes led to the introduction of the terms “ion” (from Greek: *ión*—to go), cation, and anion by William Whewell and Michael Faraday in the first half of the 19th century.^[1] Besides their paramount importance for electrochemical processes in solution, ions were soon identified as the source of luminescent phenomena and plasma processes, and as reactive species in electrochemical transformations. However, the broad and fundamental impact of charge on the overall properties of chemical entities is arguably best mirrored by the enhanced solubility of charged atoms and molecules in polar solvents, which affects all biochemical processes in living organisms as well as chemical synthesis on the lab scale and in industrial processes.

1.2. Ions—how charges play a role

The introduction of charge into chemical entities inevitably changes their overall physical and chemical characteristics because an electron, atom or group of atoms is removed, added or exchanged. The strength and relevance of these changes in properties depends on the type of compounds, the conditions of analysis, and sometimes even on the viewpoint of the scientific subdiscipline in which research is conducted. Thus, the changes brought about by the

introduction of charge should be viewed as modulations of properties and should be analyzed by choosing suitable reference compounds in the relevant context.

By means of their real charges (as compared to partial charges in polar covalent compounds), ionic compounds enjoy added stabilization through Coulombic interactions. This is very obvious for salts, where the lattice energy is based on the attractive Coulomb forces, but also affords high solvation energies of ions in polar solvents. From atoms to large molecules and clusters, charge is the most important means to foster solubilization in polar solvents. Furthermore, ionic species tend to exhibit a significantly enhanced Lewis acidity (cations) or Lewis basicity/nucleophilicity (anions) as compared to their underlying neutral cousins.^[2]

Regarding molecular species, the withdrawal of electrons from occupied orbitals to form cations, or the insertion of electrons into nonbonding orbitals (“lone pairs”) to form anions does not only inevitably cause charges, but in addition can cause the occurrence of additional phenomena involving these orbitals, such as π -aromaticity.^[3,4]

The formation/elimination of charges during a process will serve to switch reaction mechanisms between radical reactions (neutral species) to polar channels (ionic species). The famous $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium, which is inaccessible for $[\text{NO}_2]^-$, and the straightforward formation of $[\text{N}_2\text{OH}]^+$ and O_2 from $[\text{HNO}_2]^+$, which is hampered for HNO_2 , may serve as illustrative examples here.^[5] Furthermore, disproportionation equilibria involving neutral species can make ionic species accessible, which may (clearly or subtly) in fact be responsible for the reactivity patterns that are observed. Arguably, the most fundamental example of such a disproportionation reaction is the self-ionization of water, supplying charged species such as hydronium ions for proton transfer.^[6] Finally, the Coulomb interactions mentioned above also influence the chemical behavior of compounds through corresponding solvation and aggregation phenomena, which in turn play a major role in coordination chemical pathways.

1.3. Bismuth and bismuth-based compounds

Bismuth compounds have gained attraction during the past years as a consequence of a diversity of reasons, which have served to introduce the corresponding species into research areas ranging from fundamental chemical, physical and material sciences to fields of applied chemistry—promi-

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nently realized in the use of bismuth phosphomolybdate and related compounds as catalysts in the industrial oxidation of propene (SOHIO process).^[7-9]

The physicochemical properties of bismuth are one of the reasons that served to enhance the attention towards this element, especially in the recent past. Besides a low toxicity of this heavy metal, which allows for the application of certain Bi^{III} carboxylates even in pharmaceuticals,^[10] bismuth belongs to the more abundant and less cost-intensive heavy metals of interest compared to precious metals like palladium, platinum, rhodium, or gold, for instance.^[11] In addition, it exhibits a collection of interesting physical properties as the heaviest (widely) non-radioactive metal (half-life of $\approx 2 \times 10^{19}$ years).^[12] The metal shows an extremely strong diamagnetism, based on the still dominantly covalent bonding pattern in its grey arsenic-type crystal structure, and the strongest Hall effect of any metalloid element. In pure form, it consequently behaves as a (semi)metal with only poor conductivity. Like water (and a few other elements), liquid bismuth expands upon cooling owing to a twofold phase transition (solid to liquid and

(semi)metal to metal), which comes along with a significantly enhanced metallic conductivity in the liquid phase.^[13]

The large atomic mass of bismuth (atomic number 83, one natural isotope ²⁰⁹Bi) brings along a combination of properties (including high covalent radius, (relatively) high boiling point, and low electronegativity) which are considered to be crucial for superior thermoelectric properties of heavy chalcogenides of this element.^[14] The large nuclear charge causes bismuth compounds to exhibit distinct relativistic effects and spin-orbit coupling,^[15] and combinations of the properties mentioned above are the preconditions for bismuth (including the two-dimensional variant bismuthene)^[16] and certain bismuth compounds (such as Bi₂Te₃)^[17] to behave as topological insulators, i.e. materials that are insulating in their interior but exhibit a flow of electrons on their surface.^[18]

Last but not least, the atomic sizes, together with the peculiar location of bismuth at the border of elements that prefer covalent, directed or metallic, undirected bonding, allow for a behavior as a soft Lewis acid and a highly variable coordination chemistry.^[19,20]

All of these features explain why a constantly increasing number of research contributions is being published about bismuth and bismuth-based compounds and materials. Out of the large number of possible classes of bismuth-based compounds, this review will focus on species that exhibit a charge and this way combine the peculiarities of charged compounds with those of bismuth species.

1.4. Scope and structure of this review article

The scope of this article covers the full spectrum of molecular bismuth compounds from organometallic species through inorganic complexes to cluster compounds, thereby considering a range of oxidation states from +V to –I (taking into account that the formal concept of assigning oxidation states shows lower relevance in cluster chemistry). In the first part of this contribution, the synthesis, structure, and bonding of charged bismuth compounds are analyzed. This is sectioned by the coordination sphere of bismuth (organic, inorganic, or cluster compounds) and subsectioned by charge (cationic vs. anionic) and oxidation state (+V, +III, low-valent). These criteria are meant to provide a guideline to the reader while leaving room for overlap, underlining that research in these fields shows interdisciplinary character in many cases. In the second part of this article, physical and chemical properties of charged bismuth compounds are presented and structured according to the specific characteristics or fields of application that are addressed.

As a consequence of the high topicality of bismuth compounds, several review articles have been published in the broader field in the recent past. Thus, some specific chapters are not included in this article. Instead, we refer to corresponding literature for further reading. In this context it should be noted that—with the exception of a contribution on the narrower field of molecular monocationic bismuth(III) compounds^[20]—previous work did not focus on the special role of charge on the properties and reactivity of molecular bismuth compounds.

One large and prominent class of compounds among charged bismuth complexes are bismuth oxido clusters. We direct the reader to a specialized review on this topic.^[21] Monometallic bismuth oxido clusters are of relevance both to the mechanism of hydrolysis of ionic Bi^{3+} compounds in solution^[22] and also to the action of important pharmaceuticals like bismuth subsalicylate.^[23] Heterometallic clusters with bismuth can be found in the form of polyoxometalate clusters^[24] used in catalysis^[25] and photocatalysis.^[26] Special attention is directed toward compounds featuring Mo–O–Bi-moieties,^[9,27] as they represent molecular models for $\text{Bi}_2\text{O}_3\cdot\text{MoO}_3$ catalysts used in the industrial SOHIO process, the oxidation or ammoxidation of propylene to make acrolein or acrylonitrile.^[7]

The biochemistry of bismuth complexes,^[28] and the structure and reactivity of molecular bismuth compounds with transition-metal-based ligands^[29] including ionic species, have recently been reviewed. Readers are directed to these contributions for detailed information on these topics.

Several reviews extending on intermetalloid and heterometallic Zintl clusters were published over the last decade,^[30,31] so we will focus on selected compounds, also including cationic bismuth-based clusters, for which the electron count plays a particular role with regards to structures and properties.

2. Synthesis

The targeted and efficient synthesis of charged bismuth compounds remains a challenging field, since these species may easily be susceptible to phenomena such as disproportionation reactions, ligand scrambling, aggregation equilibria, and (unwanted) redox reactions. In addition, the choice or design of suitable counter ions (with respect to aspects such as accessibility, stability, and solubility) can be difficult. The low bond dissociation energies that are generally observed for bismuth compounds may further complicate synthetic access to charged bismuth species. Thus, the toolbox of synthetic chemists that is available to tackle these challenges is presented in this chapter in order to serve as a guideline and source of inspiration for researchers in this and related fields. In the structuring of sections 2 and 3, the distinction between “organic” and “inorganic” complexes can of course not strictly be followed for examples containing mixed organic–inorganic ligand spheres and an assignment has been made based on the key role of one or the other class of ligands.

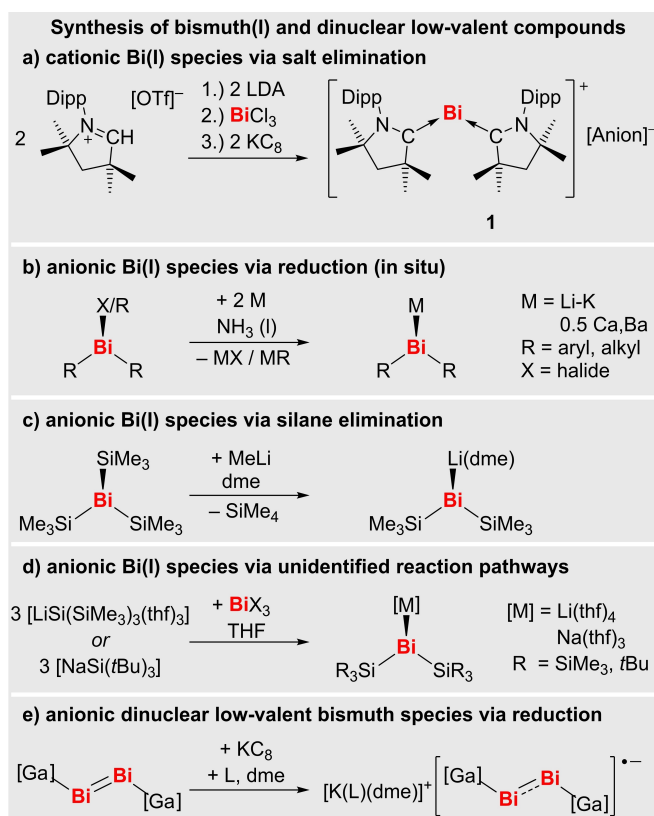
2.1. Complexes with organic ligands

The synthesis of charged bismuth compounds with organic ligands (i.e. ligands that contain CH bonds) has originally been focused on cationic bismuth(III) (and to a lesser extent bismuth(V)) compounds bearing aryl ligands. Recent developments in synthetic chemistry have granted access to compounds with other classical ligands (alkyl, allyl, silyl, aminyl),^[32–35] species with higher charges,^[36–38] and with new ligand sets such as β -diketiminato-supported gallyl moieties.^[39] In addition, first glances at well-defined low-valent bismuth compounds bearing charges have been reported.^[39,40]

2.1.1. Bismuth(I) compounds

Monocationic species. The cationic bismuth(I) compound **1** has been obtained by reduction of BiCl_3 in the presence of a cyclic alkyl(amino)carbene (cAAC), which was generated in situ by deprotonation of its triflate salt thereby releasing LiOTf (Scheme 1a).^[40] Thus, the cationization paving the way to the only isolated species of this kind has been achieved in a salt elimination approach, which has frequently been employed for bismuth(III) species.^[20]

Monoanionic species. Solutions of compounds MBiR_2 ($\text{M}=\text{Li}–\text{K}$; $\text{R}=\text{aryl, alkyl}$) or $\text{M}(\text{BiR}_2)_2$ ($\text{M}=\text{Ca, Ba}$; $\text{R}=\text{aryl}$) have been generated in situ by reduction of BiEt_3 or



Scheme 1. Synthetic routes to charged bismuth(I) compounds and related species. [Anion] = $[\text{Li}_2(\text{OTf})_3(\text{OEt}_2)]$, dme = dimethoxyethane, [Ga] = $[\text{Ga}(\text{NDippCMe}_2\text{CH}(\text{NEt}_2))_2]$, Dipp = 2,6-*i*-Pr₂-C₆H₃, L = benzo-18-crown-6.

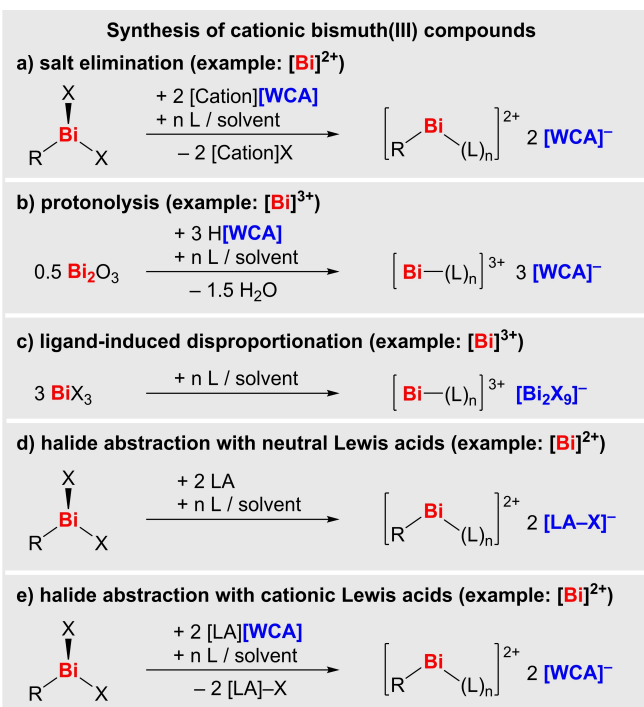
BiR_2X (R = aryl, alkyl; X = halide) with an alkali (Li–K) or alkaline earth (Ca, Ba) metal in liquid ammonia (Scheme 1b).^[41–43] The reduction of the hmpa-stabilized cationic species $\text{Bi}(\text{aryl})_2(\text{OTf})(\text{hmpa})_2$ with sodium naphthalide in THF has been reported as an alternative (hmpa = hexamethylphosphoramide).^[44] The isolation of silyl-substituted monoanionic bismuth(I) compounds $\text{M}(\text{L})_n\text{Bi}(\text{SiR}_3)_2$ has been achieved by reaction of $\text{Bi}(\text{SiMe}_3)_3$ with methyl lithium^[45] (Scheme 1c) or from side reactions of BiX_3 with three equivalents of bulky alkali metal silanides, MSiR_3 (X = Cl, Br; M = Li, Na; R = SiMe₃, *t*Bu; Scheme 1d).^[3,4] The latter route proved to be sensitive towards the choice of bismuth halide.

2.1.2. Low-valent dinuclear bismuth compounds

Building upon previous reports,^[46,47] the isolation of a dinuclear low-valent anionic bismuth compound through reduction of a dibismuthene has recently been reported for the first time (Scheme 1e).^[3,9] The use of strong reductants such as alkali metals is necessary in this approach.

2.1.3. Bismuth(III) compounds

Cationic species. Strategies for the synthesis of bismuth(III) monocations have recently been reviewed.^[20] The most important approaches, salt elimination (a),^[37,38,48–52] protonolysis (b),^[53,54] ligand-induced disproportionation (c),^[55–62] and halide abstraction (d)^[63] are also successful for the synthesis of di- and tricationic bismuth(III) compounds (Scheme 2). In the halide abstraction approach, a neutral Lewis acid (such as AlCl_3) is commonly employed, which then becomes part of the weakly coordinating anion (WCA) in the target compound (*cf.* Scheme 2d). In a variation of this strategy, a cationic molecular Lewis acid such as a silylium ion can also be used, which offers the advantage of introducing a WCA of choice which does not inherently contain the abstracted halide atom (Scheme 2e).^[36] Early examples of dicationic bismuth(III) compounds that were accessed via salt elimination protocols faced the problem of ligand redistribution reactions ($3[\text{BiR}]^{2+} \rightleftharpoons 2[\text{Bi}]^{3+} + \text{BiR}_3$ and the like)^[48] or led to compounds with significant Bi-counteranion interactions (for anions such as carbonate, sulfate, and nitrate).^[49] These challenges have been met by the use of chelating ligands, bulky ligands with π -donating abilities, and weakly coordinating anions.^[36–38,51] Very recently, the reversible protonation of a dianionic ligand at its carbodiphosphorane functional group has been reported as a new access to cationic bismuth compounds.^[64]

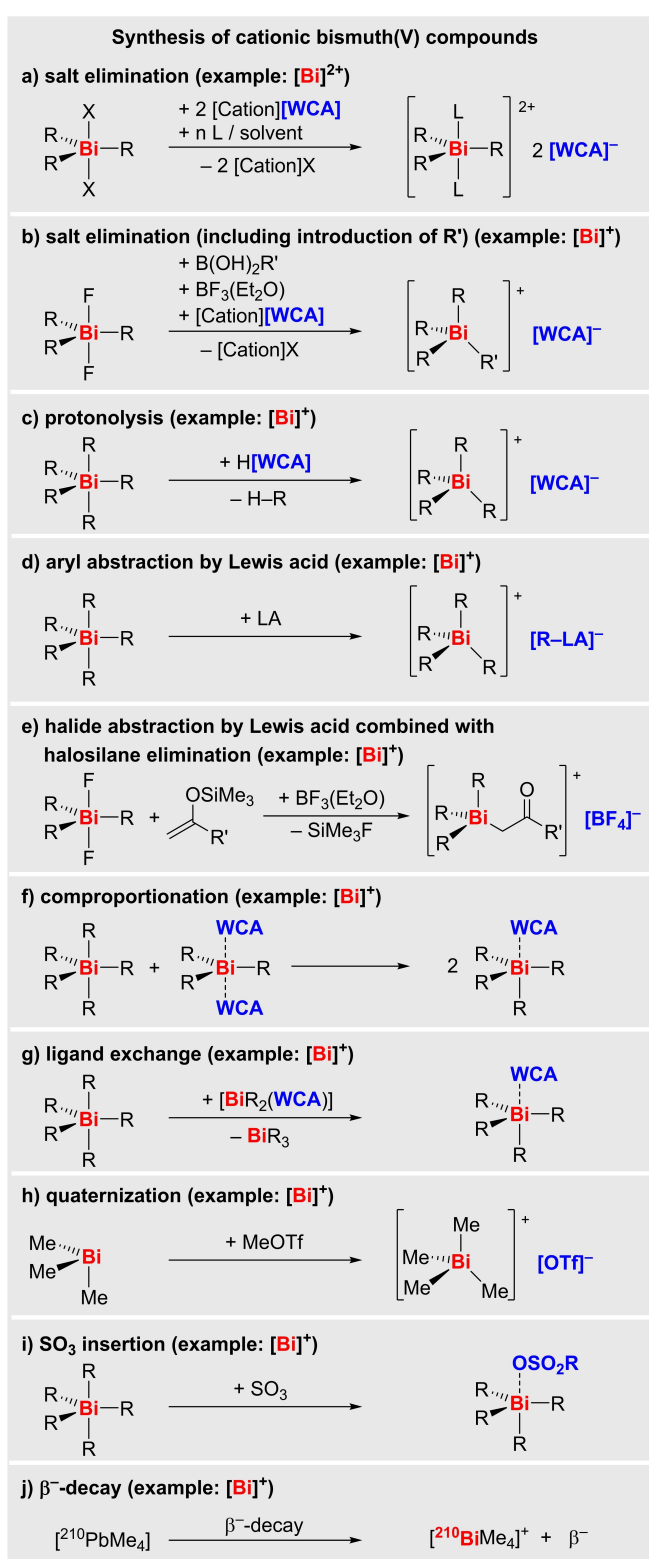


Scheme 2. Synthetic routes to (mono-, di-, and tri-) cationic bismuth(III) compounds (chemical equations show examples targeting dicationic and tricationic complexes). Additional routes are viable for the synthesis of monocationic species.^[20] X = halide, WCA = weakly coordinating anion, L = neutral ligand, LA/[LA] = neutral/cationic Lewis acid.

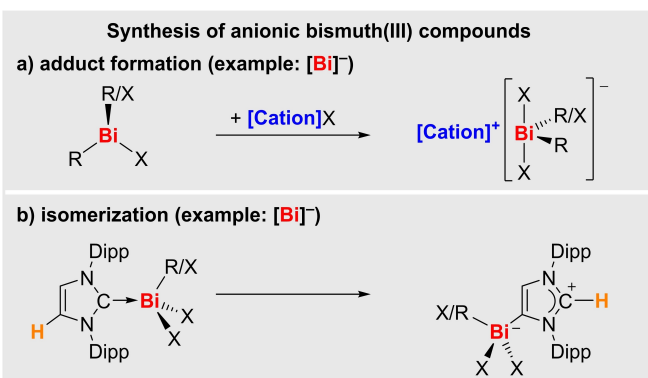
Anionic species. A straightforward, and at the same time the most common, route to mono- and dianionic bismuth(III) compounds is the adduct formation between a sufficiently Lewis acidic bismuth compound (typically BiRX_2 , BiR_2X , or Bi(OR)_3 ; R = alkyl, aryl; X = halide) and a nucleophile X^- or $(\text{OR})^-$ (Scheme 3a).^[65–73] Adduct formations of this type have also been observed as a result of more complex, unforeseen ligand redistribution reactions^[74,75] and degradation reactions due to over-reduction of bismuth(III) precursors.^[76] An unexpected route to anionic bismuth(III) compounds has been observed for carbene adducts of bismuth halides. These isolable compounds isomerize in solution (presumably through proton shuttling involving free carbenes) to give the mesoionic compounds featuring abnormal carbene ligands (Scheme 3b).^[77,72] Oligonuclear anionic bismuth compounds with bridging halide ligands can also be accessed by ligand-induced disproportionation (Scheme 2c).^[55–61]

2.1.4. Bismuth(V) compounds

Cationic species. Various synthetic routes to mono- and dicationic bismuth(V) compounds are accessible (Scheme 4). With easily accessible precursors $[\text{Bi(aryl)}_3(\text{halide})_2]$, salt elimination reactions afford the target compounds in good yields (Scheme 4a).^[78] Over the course of such transformations, ligand exchange reactions to give compounds of the type $[\text{Bi(aryl)}_4][\text{WCA}]$ have also been reported.^[79–82] Analogous to the salt elimination shown in Scheme 4a, the transformation of metastable $[\text{Bi(aryl)}_4(\text{halide})]$ into $[\text{Bi(aryl)}_4][\text{WCA}]$ is also possible.^[79,80] The transformation of $[\text{Bi(aryl)}_3\text{F}_2]$ into a cationic species via salt elimination may also be combined with the introduction of a fourth organic substituent using an alkyl-, aryl-, vinyl-, or alkynylboronic acid (Scheme 4b) or a tin species as a transfer reagent.^[83–87] The abstraction of anionic substituents from bismuth(V) precursors with Brønsted acids such as HOTf ^[88–91] or Lewis acids such as BPh_3 ^[79] offers an alternative route to monocationic bismuth(V) compounds (Scheme 4c,d). In a variation of the Lewis acid approach, triaryl(alkyl)bismuth(V)



Scheme 4. Synthetic routes to (mono-, and di-) cationic bismuth(III) compounds. X = halide, WCA = weakly coordinating anion, L = neutral ligand, LA = Lewis acid; $[\text{OTf}]^- = [\text{O}_3\text{SCF}_3]^-$.



Scheme 3. Synthetic routes to (mono-, di-) anionic bismuth(III) compounds (chemical equations show examples targeting monoanionic complexes). X = halide; Dipp = 2,6- $i\text{-Pr}_2\text{-C}_6\text{H}_3$.

cations can be accessed by addition of silyl-protected enolates (Scheme 4e).^[92,93] With dicationic bismuth(V) compounds in hand, monocationic derivatives can be obtained

by comproportionation with neutral bismuth(V) species (Scheme 4f). Ligand exchange between BiR_5 and BiR_2^- (WCA) also gives monocationic bismuth(V) compounds, with the formation of the stable triarylbismuth compound BiR_3 as a driving force (Scheme 4g). While the quaternization of pnictanes is a typical reaction for the lighter congeners, especially amines and phosphanes, it is very unusual for the heaviest derivatives, BiR_3 . As a rare example, the reaction of BiMe_3 with methyltriflate has been reported to produce $[\text{BiMe}_4][\text{OTf}]$ (Scheme 4h).^[94] When cationic bismuth(V) species with organosulfonate counteranions are targeted, the insertion of SO_3 into a Bi–C bond offers an unusual alternative (Scheme 4i).^[95] In an exotic approach (from the preparative chemist's point of view), $^{210}\text{BiMe}_4^+$ has been generated in the gas phase through β^- -decay of $^{210}\text{PbMe}_4$, but rapidly deposited a film of Bi^0 on the wall of the reaction vessel under the conditions chosen in these studies (Scheme 4j).^[96]

Anionic species. Anionic bismuth(V) compounds with organic ligands are rare, and have only been accessed by reaction of a BiR_5 compound with an excess of the respective organolithium species LiR , which act as a strong alkylating/aryllating agent ($\text{R} = \text{Me}, \text{Ph}$).^[94,97,98] However, the resultant complexes are subject to equilibrium reactions, $\text{Li}[\text{BiR}_6] \rightleftharpoons \text{LiR} + \text{BiR}_5$, rendering their isolation a challenging task and hampering detailed analysis in solution (*cf.* section 3.1.4.2).

2.2. Complexes with inorganic ligands

Bismuth complexes featuring inorganic ligands such as oxides or halides are among the earliest investigated bismuth compounds, since they are easily accessible and show a great variability.^[99] While some of the approaches outlined in section 2.1 can readily be applied for the synthesis of charged bismuth compounds with inorganic ligands, additional strategies include solid state syntheses and mechanochemical approaches.

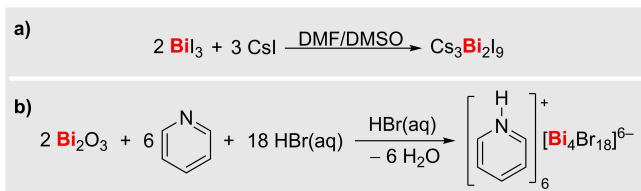
2.2.1. Bismuth(III) compounds

Cationic species. Cationic, mononuclear bismuth complexes featuring exclusively inorganic ligands are extremely rare.^[20,53] However, a small number of compounds containing formal “ BiX_2^+ ” fragments have been reported, including $[\text{BiCl}_2(18\text{-crown-6})]_2[\text{Bi}_2\text{Cl}_8]$,^[100] $[\text{BiBr}_2(18\text{-crown-6})]_2[\text{BiBr}_4]$,^[101] $[\text{BiBr}_2(\text{NC}_5\text{H}_5)_5][\text{B}((\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$,^[62] and $[\text{BiBr}_2(\text{IPr})(\text{AlBr}_4)]$ ^[77] ($\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{-imidazol-2-ylidene}$). These species have been accessed either by ligand-induced disproportionation or by halide abstraction with a neutral Lewis base, respectively. Synthetic approaches that have been outlined for compounds featuring organic ligands are reported in section 2.1.3 (Scheme 2c,d) and in the literature.^[20]

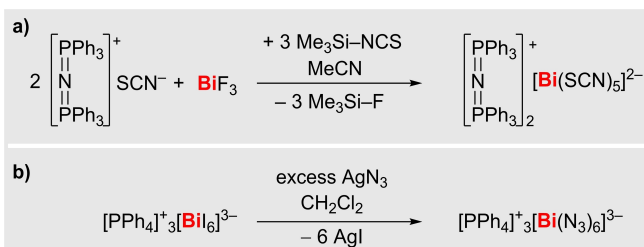
Anionic species. Common starting materials for the synthesis of anionic bismuth complexes with inorganic ligands include binary salts BiX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$,

acetate), Bi_2O_3 or $(\text{BiO})_2\text{CO}_3$ when working in acidic media. Reactions are typically conducted in dilute or concentrated aqueous solutions of acids HX , polar organic solvents like acetonitrile or mixtures of both. Often, reactions proceed in a simple manner using BiX_3 and the salt of the desired cation^[102] (Scheme 5a), and show analogies with the approach outlined in Scheme 3 (section 2.1.3). Both, the bismuth halide and the counteranion in the product of such reactions can also be generated in situ, for example when using Bi_2O_3 , $\text{HX}(\text{aq})$ and amines as starting materials (Scheme 5b).^[103] If desired, additional neutral ligands can be coordinated to the bismuth atoms of the -ate complex.^[104] Often, the organic or inorganic cation acts as a template and only one compound will be obtained, even when different stoichiometries or reaction conditions are applied. In some instances, however, several compounds with the same cation, but different overall compositions are accessible. In these cases, the stoichiometry of the reaction can play a decisive role. This has been demonstrated, for example, for compounds featuring 2,6-diisopropylanilinium cations and bromido bismuthate anions, where four different compounds with different Bi:Br ratios were obtained.^[105]

Due to the facile ligand exchange in solution, bismuth halides and halogenido bismuthates can also be used as starting materials for ligand exchange reactions towards pseudohalide compounds as shown in Scheme 6 for the synthesis of $[\text{PNP}]_2[\text{Bi}(\text{SCN})_5]$ ($\text{PNP} = \text{bis}(\text{triphenylphosphoranylidene})\text{ammonium}$)^[106] and $[\text{PPh}_4]_3[\text{Bi}(\text{N}_3)_6]$ ^[107] utilizing the volatility of trimethylsilyl fluoride or the low solubility of AgI , respectively, to drive the reaction toward the products.



Scheme 5. a) Direct synthesis of $\text{Cs}_3\text{Bi}_2\text{I}_9$ from the binary starting materials in solution.^[102] b) Synthesis of a bromido bismuthate by in situ generation of BiBr_3 and pyridinium cations in hydrobromic acid solution.^[103]



Scheme 6. a) Synthesis of a thiocyanato bismuthate from BiF_3 through the generation of volatile Me_3SiF .^[106] b) Synthesis of an azido bismuthate from a iodido bismuthate using the low solubility of AgI .^[107]

While the most common synthetic methods target reactions in solution, other methods have been employed for specific compounds. $\text{Cs}_3\text{Bi}_2\text{I}_9$ is well-investigated in this regard: It has been prepared in solution,^[102] from solid state reactions,^[108] using mechanochemistry,^[109] and as nanoparticles.^[110] Solvothermal reactions can be employed to promote single crystal growth. They are especially suitable for the controlled in situ generation of specific cations including viologen derivatives such as *N,N'*-dimethyl-4,4'-bipyridinium. Here, the reaction can be conducted according to Scheme 7, where the alkylation reaction takes place at elevated temperatures and with prolonged reaction times.^[111] When preparing oxido bismuthates, concentrated KOH solutions can also be used as a reaction medium, for example in the reaction between Ag_2O and Bi_2O_3 to obtain Ag_3BiO_4 .^[112,113]

2.2.2. Bismuth(III/V) and bismuth(V) compounds

Similar to observations in neutral binary bismuth compounds, mixed-valence $\text{Bi}^{\text{III/V}}$ or Bi^{V} complexes with purely inorganic ligands are only available with fluoro and oxido ligands.

For example, a solid state reaction using KO_2 and elemental Bi yields the mixed-valence $\text{K}_9\text{Bi}_5\text{O}_{13}$.^[114]

Similar to halogenido bismuthates(III), fluoro bismuthates(V) can be prepared by combining BiF_5 with the fluoride of the desired cation either in a solid state reaction or at low temperatures in solution yielding, for example, A_2BiF_7 ($\text{A} = \text{Na}-\text{Cs}, \text{NMe}_4, \text{NO}_2$).^[115]

A number of challenges are associated with the synthesis of new bismuth complexes with inorganic ligands such as halides. The solution behavior of bismuthate compounds is assumed to be governed by the fast interconversion of species with varying nuclearity in equilibrium reactions, although this is difficult to study in detail.^[116] As a consequence, the crystallization of compounds with specific anion motifs can be dependent on a number of different factors, including the templating effect of the cation, the reaction stoichiometry, solvent, and crystallization kinetics. Additionally, the existence of several metastable compounds^[117] can make it necessary to grow crystals of specific compounds under non-stoichiometric conditions,^[118] precluding subsequent solution processing to prepare thin films. Thus, the design of anionic bismuth compounds with

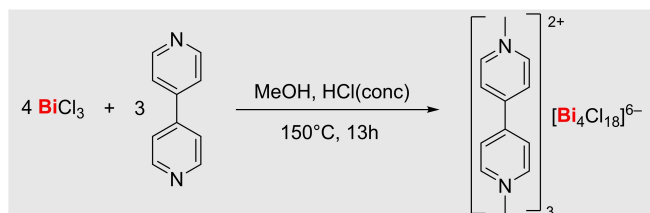
inorganic ligands in the strict sense^[119] is not possible to date. But naturally, the choice of templating cations, ligands and prior knowledge of similar reaction systems allow for well-founded estimations with regard to possible reaction products and their characteristics, even if the specifics cannot be predicted.

2.3. Low-valent bismuth-based cluster compounds

A continuation of the systematic consideration of oxidation states inevitably leads to compounds in which the bismuth atoms have only small positive or even negative oxidation states. This is the case in cluster compounds, which exhibit covalent bonding between bismuth atoms or between bismuth and other (semi)metal atoms. The resulting compounds show characteristics of (semi)metals themselves, with colors ranging between deep-red and black, and in some cases even exhibiting metallic luster. We will categorize the family of bismuth-based cluster compounds in clusters that possess an overall positive charge (polycations) and clusters with an overall negative charge (polyanions, Zintl clusters). While the total charges do not automatically define the oxidation state of the involved bismuth atoms, which can still be formally zero, none of these compounds show large deviations from formally neutral bismuth atoms and can therefore be considered as low-valent species.

2.3.1. Compounds with polycationic cluster molecules

Polycationic bismuth-based clusters were first realized during investigations of the BiCl system typically prepared by dissolution of bismuth metal in BiCl_3 at elevated temperatures over the course of several days.^[120] Upon using ionic melts such as NaAlCl_4 as solvent, or addition of the pure metal halides AlCl_3 and HfCl_4 , the polybismuth cations Bi_5^{3+} , Bi_8^{2+} and Bi_9^{5+} were identified and in some cases structurally characterized.^[121,122–124] However, syntheses specifically targeting such compounds by these methods were shown to depend crucially on the acidity of the medium controlled by the metal halide additive. Moving away from these melts, another route was devised by taking inspiration from cationic chalcogenide cluster synthesis. The use of pnictogen(V) halides as oxidants with bismuth metal in SO_2 solution led to the isolation of Bi_5^{3+} with AsF_5 being the most successful in this vein, ultimately yielding $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$.^[125] En route to this compound, the octanuclear dication Bi_8^{2+} was presumed as an intermediate by extension of observations from the reaction with PF_5 ; however, it was not isolable as the arsenate or stibate salt. More recently, an alternative method was reported using GaCl_3 as either an oxidant towards bismuth metal or as a reductant in cooperation with Ga metal to BiCl_3 . The main advantage of these routes was the use of typical organic solvents, such as benzene or dichloromethane, or ionic liquids at ambient temperature.^[126–129] Incorporating other metals into the framework of polycationic bismuth clusters has had limited success, which may be ascribed to their



Scheme 7. Solvothermal synthesis of a chlorido bismuthate with a *N,N'*-dimethyl-4,4'-bipyridinium cation generated through in situ alkylation.^[111]

tendency to form infinite higher-dimensional structures. From what is known of these relatively elusive species, the synthetic methodologies to date are similar to those aiming at the homoatomic clusters. Either melting elemental metals with bismuth(III) halides, melting metal halides with bismuth(III) halides, or dissolution of elemental metals and bismuth(III) halides in ionic liquids, followed by controlled annealing and crystallization has afforded a few structures.^[130–134] The subbromide $\text{Bi}_{34}\text{Ir}_3\text{Br}_{37}$ was shown to be a complicated mixture of four different cluster molecules with the homonuclear Bi_5^+ and Bi_6^{2+} clusters as the cationic components. Actual incorporation of transition metals into polycationic bismuth clusters has only been observed on a few occasions, as part of the structures of metal-rich halogenido networks as $[\text{Au}@\text{Bi}_{10}]^{5+}$ and $[\text{Pd}@\text{Bi}_{10}]^{4+}$ clusters, or the intermetalloid cluster $[\text{Pt}@\text{Bi}_{10}]^{4+}$ with Al^{III} bromides as counterions for example. Compounds of this type have been reviewed elsewhere.^[30] It is worthy to note that neutral clusters are known in the examples of $[\{\text{RhBi}_7\}\text{Br}_8]$ and $[\text{Bi}_{10}\{\text{Au}(\text{SbBi}_3\text{Br}_9)_2\}]$.

2.3.2. Compounds with polyanionic cluster molecules

Polyanionic bismuth-based clusters, also known as polybismuthide clusters or Zintl clusters, can be easily correlated with the lighter congeners of the pnictogens, especially phosphorus. As early as the pioneering work of Zintl, evidence of polybismuthides had been observed through potentiometric titration of BiI_3 and sodium in liquid ammonia.^[135] Synthetic accessibility was not achieved until significantly later, when the now ubiquitous method of extraction of intermetallic solids and phases with ethane-1,2-diamine and 222-crypt was applied to intermetallics of potassium and bismuth.^[136] The first synthetically observed member of the Bi_x^{q-} series was the square-planar $[\text{K}(222\text{-crypt})]_2\text{Bi}_4$ by extraction of K_5Bi_4 or K_3Bi_2 . On changing the extraction time and crystallization conditions, $[\text{K}(222\text{-crypt})]_2\text{Bi}_2$ can also be obtained from the K_5Bi_4 intermetallic solid.^[137] Though neither of these two are strictly cluster molecules, they are often postulated as important species involved in the formation of larger homoatomic and heteroatomic polyanionic bismuth clusters. Access to Bi_7^{3-} was achieved by switching the extraction solvent to pyridine and the use of an additive, $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in this case.^[138] The final example of this series, Bi_{11}^{3-} , was obtained by treatment of the *pseudo*-tetrahedral $(\text{GaBi}_3)^{2-}$ with pyridine (Scheme 8).^[139] It is believed that the pyridine plays a vital

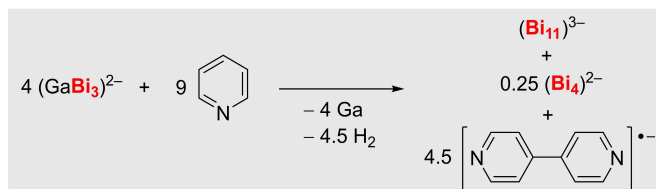
role in these reactions as the redox partner to the necessary oxidative coupling reactions required to form these larger clusters. In addition, due to the overall negative charge of the $(\text{GaBi}_3)^{2-}$ cluster, the Ga can be eliminated via an oxidative process to elemental Ga.

As just introduced, the $(\text{GaBi}_3)^{2-}$ anion represents a member of a family of binary, pseudo tetrahedral $(\text{E}_x\text{Bi}_y)^{2-}$ clusters containing group 13 or group 14 elements, which are isoelectronic to the archetypal P_4 . To date, only $(\text{GaBi}_3)^{2-}$, $(\text{InBi}_3)^{2-}$, $(\text{TlBi}_3)^{2-}$, $(\text{Sn}_2\text{Bi}_2)^{2-}$ and $(\text{Pb}_2\text{Bi}_2)^{2-}$ are known for bismuth, each isolable from extraction of appropriate intermetallic solids.^[140–143] The stability of such species, and in turn the reason for the difficulty in the isolation of the missing combinations, is dependent on a combination of the relative sizes of, and charge distribution over, the atoms in the cluster, described in more detail in section 3.3.2.^[144] This has a marked effect on their reactivity and use as starting materials for the synthesis of polyanionic Bi clusters, in particular those containing d- and f- block metals either as part of the cluster framework or encapsulated inside the cluster. Large anionic heteroatomic Bi clusters are typically prepared in the same way, by reaction of either an intermetallic solid in the presence of 222-crypt or the isolated pseudo tetrahedron salt and an organometallic reagent in ethane-1,2-diamine. The plethora and diverse range of products obtained by these approaches have been recently reviewed elsewhere.^[30] All these complex polybismuth frameworks require charge to stabilize the “naked” metal atoms in the molecule. Other neutral polybismuth compounds have been synthesized that contain $[\text{Bi}_4]$ and $[\text{Bi}_8]$ fragments, however these all contain bonding interactions with metal-based ligands, for example $(^{\text{Dipp}}\text{NacnacGa}(\text{Cl}))_2\text{Bi}_4$ and $(^{\text{Dipp}}\text{NacnacMg})_4\text{Bi}_8$ ($^{\text{Dipp}}\text{Nacnac} = \text{HC}(\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3))_2$).^[145]

3. Structure and bonding

Neutral compounds featuring only strongly covalent bismuth-element bonds of low polarity commonly show predictable coordination geometries with little room for variations. Typical examples are triaryl- or trialkylbismuth complexes with trigonal pyramidal coordination geometries. The introduction of ligands that bind to the bismuth center through bonds of higher polarity usually increases the structural diversity, because the corresponding antibonding σ^* -orbitals become energetically accessible, leading to the coordination of additional neutral ligands or to aggregation and thus to a larger variety of coordination numbers and coordination geometries. This trend is further increased in ionic bismuth compounds: in addition to vacant atomic orbitals in cationic bismuth species, increased Coulomb interactions, and subtle anion-cation bonding draws an even more complex scenario of coordination chemistry, which is highlighted in this section.

Stereoactive or -inactive lone pairs in Bi^{III} -compounds. Whether a lone pair in Bi^{III} complexes is stereoactive remains difficult to predict and correctly identify without dedicated quantum chemical investigations. The VSEPR

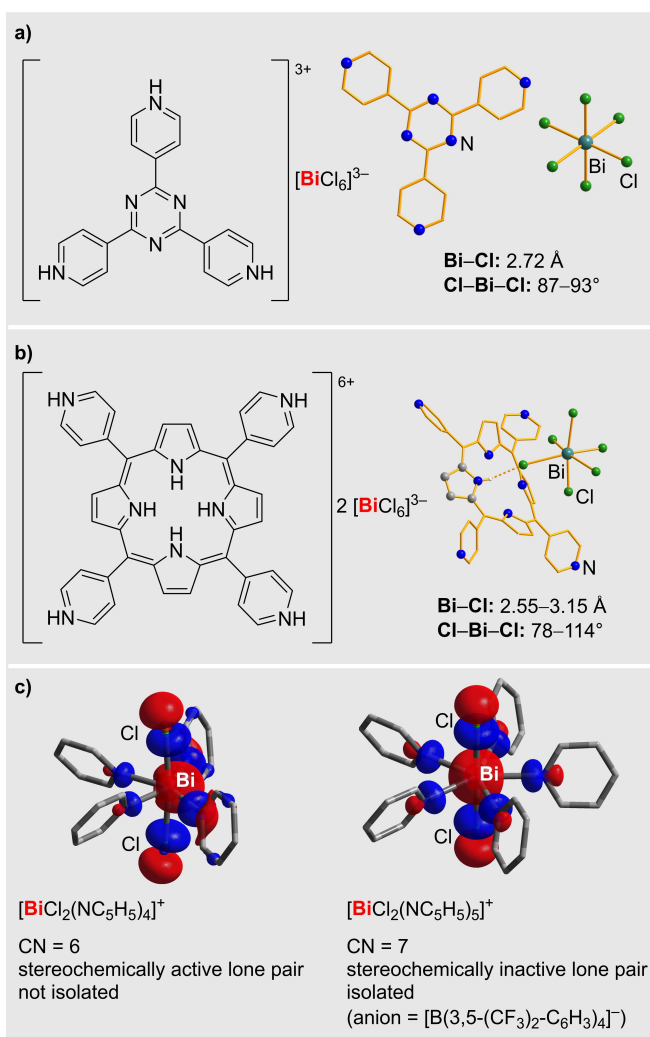


Scheme 8. Proposed reaction equation for the formation of the Bi_{11}^{3-} anion by oxidation of $(\text{GaBi}_3)^{2-}$ with pyridine.^[139]

model and its extensions can provide a basic expectation^[146] of the shape of the complex. A modern approach using DFT calculations, and considering vibronic coupling,^[147] may give more detailed predictions. According to these analyses, the tendency of a Bi^{III} complex to undergo distortion from the highest possible symmetry due to a stereoactive lone pair increases with increasing chemical hardness of the species under consideration. For example, the X-type ligands O²⁻ and F⁻ and small coordination numbers result in [BiX_n]^{q-} species with greater hardness, leading to distortion. However, charged complexes make the identification of a potentially stereoactive lone pair difficult due to the inevitable presence of counterions. As a simple example, [BiCl₆]³⁻ ions can be considered. They can be found nearly perfectly octahedral (enforced by the crystal symmetry)^[148] or strongly distorted,^[149] depending on their specific environment in the crystal (see Scheme 9a,b). The presence of stereochemically active lone pairs has also been discussed in cationic and dicationic species such as [BiCl₂(18-c-6)]₂, [Bi₂Cl₈] and [BiPh(hmpa)₄][PF₆]₂ based on structural parameters.^[48,100,101] A recent contribution centered around cations of type [BiBr₂(NC₅H₅)_n]⁺ demonstrates by a combination of DFT calculations and X-ray diffraction studies that high coordination numbers of up to seven disfavor the stereochemical activity of the lone pair in these compounds (Scheme 9c).^[62] The complexity of these analyses is further supported by extended X-ray absorption fine structure (EXAFS) spectroscopy combined with DFT calculations, which reveal that the stereochemical activity of the lone pair at bismuth in solutions of Bi³⁺ in water only comes into play when the second coordination sphere of water molecules is taken into account.^[150]

Notably, considerations about lone pairs become more complex when moving on to cluster compounds. As reported for the two related ternary anionic cluster structures [Ln@Tt₇Bi₇]⁴⁻ and [Ln@Tt₄Bi₉]⁴⁻ (Ln=La, Ce, Nd, Gd, Sm, Tb; Tt=Sn, Pb), and related compounds,^[151] the bismuth atoms can be considered as possessing a ±0 charge (one lone pair), a positive charge of ≈1 (two lone pairs plus four bonds being highly polarized towards neighboring atoms), or a corresponding negative charge (one lone pair plus three bond(s) being highly polarized towards this atom). This is illustrated in Scheme 10 for [La@Sn₇Bi₇]⁴⁻ and [La@Sn₄Bi₉]⁴⁻ as examples.

Structural *trans*-effect in halogenido bismuthates. Bismuth complexes can show considerable structural *trans*-effects. This can be seen especially well in halogenido bismuthates,^[152] with the [Bi₂Cl₁₁]⁵⁻ anion of the compound (C₄H₁₀N)₈[Bi₂Cl₁₁][BiCl₆]·2H₂O shown in Scheme 11 as an example.^[153] Here, typical variations in bond length can be observed in the single-crystal structure: Bridging Bi–Cl bonds are longest, terminal Bi–Cl bonds *trans* to other terminal bonds are in between and terminal Bi–Cl bonds *trans* to bridging bonds are shortest. In mono- and dicationic bismuth complexes stabilized by a monoanionic tridentate tris(pyrazolyl)borate ligand scaffold, a thermodynamic *trans*-effect also becomes apparent as the donor strength of the remaining substituents at bismuth is varied.^[50] It should be noted that a structural *trans*-effect has also been discussed in

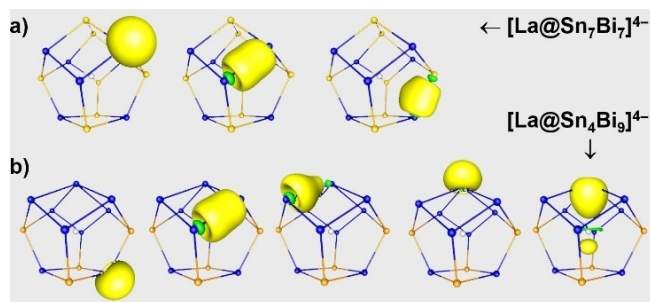


Scheme 9. a) Example of a nearly perfectly octahedral [BiCl₆]³⁻ anion in [1,3,5-tris(4-pyridinium)-2,4,6-triazine][BiCl₆].^[148] b) Example of a strongly distorted [BiCl₆]³⁻ anion in [H₆TPyP][BiCl₆]₂ (TPyP = tetra(4-pyridyl)porphyrin).^[149] c) HOMOs of [BiBr₂(NC₅H₅)_n]⁺ cations as determined by DFT calculations revealing the accessibility of structures with a stereochemically active lone (*n* = 4, left) and a stereochemically inactive lone pair (*n* = 5, right).^[62]

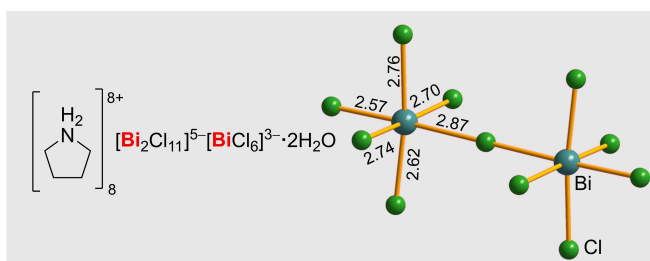
cationic bismuth halides and in cationic bismuth carbene compounds.^[64,154]

3.1. Complexes with organic ligands

A profound understanding of the complex coordination chemistry and bonding situations in charged bismuth compounds featuring organic ligands is extraordinarily valuable not only from a fundamental point of view, but also because of the high potential of these compounds for applications in fields such as organic synthesis and polymerization catalysis. Important scientific questions center around the availability of (in some cases multiple energetically close-lying) coordination geometries, unusual modes of stabilization (such as ligand-bismuth multiple bonding), the accessibility of coor-



Scheme 10. Calculated molecular structures of clusters $[\text{La}@\text{Sn}_7\text{Bi}_7]^{4-}$ (a) and $[\text{La}@\text{Sn}_4\text{Bi}_9]^{4-}$ (b) upon geometry optimization using DFT methods, and illustration of representative localized molecular orbitals (LMOs). These indicate (from left to right): A lone pair on a formally Bi^0 atom, a homoatomic homopolar Bi^0-Bi^0 bond and a heteroatomic (essentially) homopolar Sn^--Bi^0 bond in $[\text{La}@(\text{Sn}^-)_7(\text{Bi}^0)_7]^{4-}$ (top), and a lone pair on a formally Bi^0 atom, a homoatomic homopolar Bi^0-Bi^0 bond, a homoatomic highly heteropolar Bi^--Bi^+ bond, and two lone pairs (outwards and inwards) on a formally Bi^+ atom in $[\text{La}@(\text{Sn}^-)_4(\text{Bi}^0)_4(\text{Bi}^-)_4(\text{Bi}^+)_4]^{4-}$ (bottom).



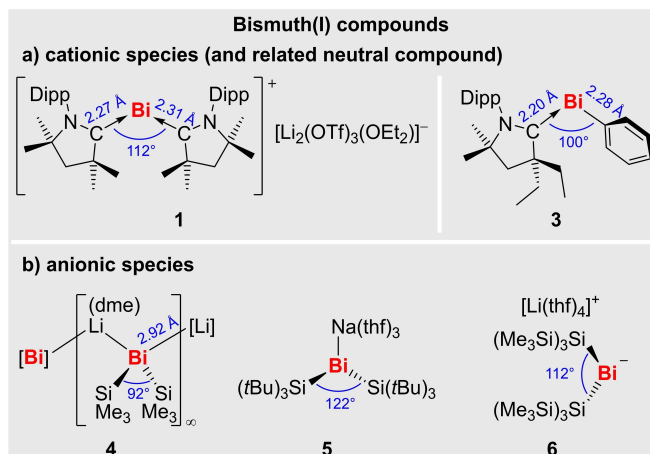
Scheme 11. Bond lengths in the $[\text{Bi}_2\text{Cl}_{11}]^{5-}$ anion of $(\text{C}_4\text{H}_9\text{N})_8[\text{Bi}_2\text{Cl}_{11}]\cdot[\text{BiCl}_6]\cdot 2\text{H}_2\text{O}$ highlighting the structural *trans*-effect in halogenido bismuthates.^[153]

dination sites, and the mechanism and reversibility of bond activation in bismuth compounds. The important cornerstones and recent highlights of research in this topical field of research are summarized in this section.

3.1.1. Bismuth(I) compounds

3.1.1.1. Cationic bismuth(I) species

Monocationic species. Insights into the properties of neutral organometallic bismuth(I) compounds^[155a-c,156] have recently been exploited to present the first example of an organometallic bismuth(I) cation, $[\text{Bi}(\text{cAAC}^{\text{Me/Dipp}})_2][\text{Li}_2(\text{OTf})_3(\text{OEt}_2)]$ (**1**, Scheme 12).^[40] A bent geometry was observed with a $\text{C}-\text{Bi}-\text{C}$ angle of 112° , which is smaller than that in the related pseudo-two-coordinate bismuth(III) cation $[\text{Bi}(\text{2,6-(Mes)}_2\text{-C}_6\text{H}_3)_2][\text{B}(\text{3,5-(CE)}_3\text{-C}_6\text{H}_3)_4]$ (**2**, $\text{C}-\text{Bi}-\text{C}$: 117° , $\text{Mes}=\text{2,4,6-Me}_3\text{-C}_6\text{H}_2$),^[157] but larger than that in $\text{BiPh}(\text{cAAC}^{\text{Et/Dipp}})$ **3** (Scheme 12, $\text{C}-\text{Bi}-\text{C}$: 100°) or bismuth(III) compounds with bulky aryl ligands such as $[\text{Bi}(\text{2,4,6-Ph}_3\text{-C}_6\text{H}_2)_3]$ ($\text{C}-\text{Bi}-\text{C}$: $104\text{--}109^\circ$).^[156,158] The $\text{Bi}-\text{C}^{\text{AAC}}$ bond lengths in **1** ($2.27\text{--}2.31\text{ \AA}$) are larger than that in the related



Scheme 12. a) Cationic (left) and neutral (right) organometallic bismuth(I) compounds featuring cAAC ligands. b) anionic bismuth(I) compounds. Bond lengths and angles as determined by single-crystal X-ray diffraction analysis are shown in blue. Dipp = 2,6-*i*Pr₂-C₆H₃; dme = dimethoxyethane.

neutral bismuth(I) compound **3** (2.20 \AA), suggesting the relevance of steric repulsion and π -type $\text{Bi}-\text{C}^{\text{AAC}}$ backbonding.^[156] Theoretical calculations based on energy decomposition analysis and the natural orbitals for chemical valence (NOCV) method suggest that bonding in **1** is best described by σ -donation of the cAAC ligands into vacant p_x and p_y atomic orbitals (AOs) of a Bi^+ ion and π -back-donation from the occupied $p_z(\text{Bi}^+)$ AO into ligand-centered molecular orbitals of appropriate symmetry.^[40] While “ Bi^+ ions” in molten BiCl_3 (or in eutectic mixtures of BiCl_3 and other salts) have been reported to occur only under conditions of high dilution,^[120,124,159] **1** has been reported to be stable in THF and diethyl ether solution only at high concentrations.^[40]

3.1.1.2. Anionic bismuth(I) species

Monoanionic species. Monoanionic bismuth(I) compounds remain rare to date. In the contact ion pairs $[\text{Li}(\text{dme})\text{Bi}(\text{SiMe}_3)_2]_\infty$ (**4**) and $[\text{Na}(\text{thf})_3\text{Bi}(\text{Si}t\text{Bu}_3)_2]$ (**5**), the bismuth atoms adopt a strongly distorted tetrahedral and a pyramidal coordination geometry, respectively (Scheme 12b).^[34,160] In the solvent-separated ion pair $[\text{Li}(\text{thf})_4][\text{Bi}(\text{Si}(\text{SiMe}_3)_3)_2]$ (**6**), the two-coordinate bismuth ion adopts a bent coordination geometry (Scheme 12b).^[34] The $\text{Si}-\text{Bi}-\text{Si}$ angles amount to 92° (**4**), 122° (**5**), and 112° (**6**), the larger bond angles in **5** and **6** being a result of steric repulsion between the bulky $\text{Si}(t\text{Bu})_3/\text{Si}(\text{SiMe}_3)_3$ groups according to MP2 calculations.^[34] The $\text{Li}-\text{Bi}$ distances in **4** are identical to the $\text{Li}-\text{Sb}$ distances in the lighter homolog, suggesting relatively strong $\text{Li}\cdots\text{Bi}$ interactions in this complex.^[160] The compound $[\text{K}(\text{crypt})][\text{BiPh}_2]$ (crypt = 2.2.2-cryptand) has been obtained serendipitously in single-crystalline form and shows a two-coordinate bismuth atom.^[161]

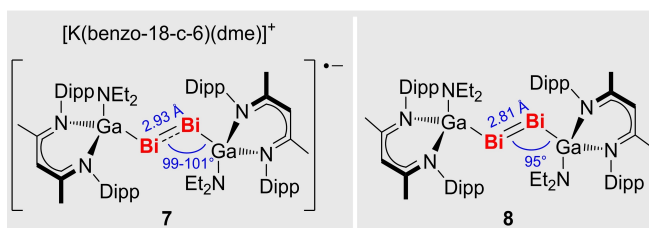
3.1.2. Dinuclear low-valent bismuth compounds

Dibismuthene radical anions have been reported to be highly sensitive species,^[46,162] and the first compound of this type has only recently been isolated and characterized in detail (**7**, Scheme 13, left).^[39] The Bi–Bi–Ga bond angle and the Bi–Bi bond length in **7** are larger than those in the neutral analog **8** (Scheme 13).^[163] The latter suggests a reduced Bi–Bi bond order in **7** compared to **8**, which was supported by DFT calculations and NBO analyses (e.g. WBI=1.35 (**7**), 1.81 (**8**)).^[39] The spin density in **7** is largely located on the Bi₂ fragment according to DFT calculations and EPR spectroscopy, i.e. the singly occupied molecular orbital can be interpreted to be the $\pi^*(\text{Bi}=\text{Bi})$ orbital.

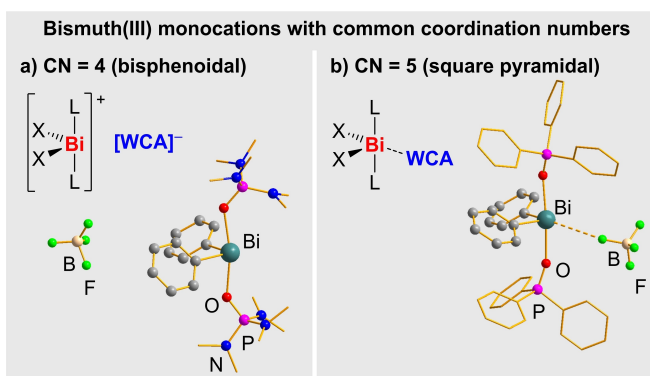
3.1.3. Bismuth(III) compounds

3.1.3.1. Cationic bismuth(III) species

Bismuth(III) monocations. The majority of monocationic bismuth(III) compounds show strong interactions with four bonding partners, resulting in a bisphenoidal coordination geometry with the tightly-bound anionic ligands in the



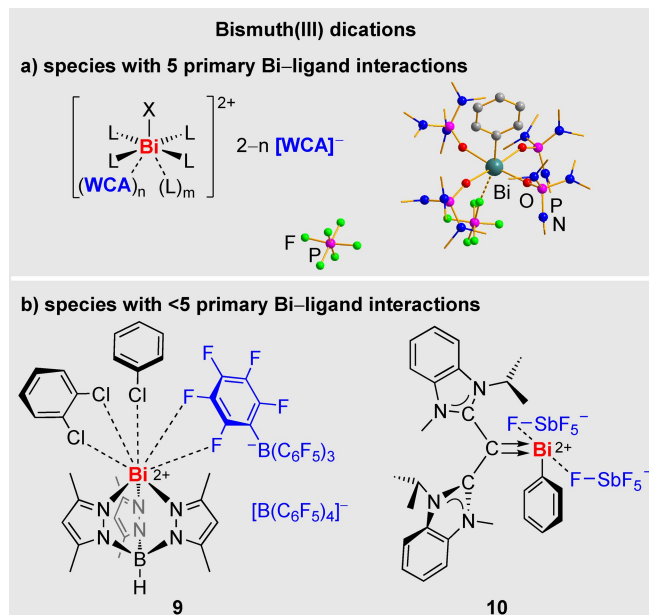
Scheme 13. Dibismuthene radical anion **7** (left) and its neutral parent compound **8** (right). Bond lengths and angles as determined by single-crystal X-ray diffraction analysis are shown in blue. Dipp = 2,6-*i*Pr₂-C₆H₃; benzo-18-c-6 = benzo-18-crown-6.



Scheme 14. Lewis drawing and an example of a molecular structure of a) a typical organobismuth monocation with CN = 4 and a bisphenoidal coordination geometry (example: [BiPh₂(OP(NMe₂)₃)₂][BF₄])^[164] and b) an organobismuth monocation featuring additional weak interactions with the counteranion leading to CN = 5 and a square pyramidal coordination geometry (example: [BiPh₂(OPPh₃)₂(BF₄)]).^[48] Hydrogen atoms in molecular structures are omitted for clarity.

equatorial positions (Scheme 14a).^[33,35,48,164,165] Lower and higher coordination numbers ranging from (formally) two^[157] to at least eight^[100,101] can be reached by applying strategies such as the introduction of bulky ligands,^[157] multidentate ligands^[100,101] or additional weak interactions (e.g.: a coordination number of five generated by weak interactions with the counteranion, Scheme 14b).^[35,48,166] An unusual case of a bismuth cation favoring a coordination number of seven has recently been reported. BiBr₂-(NC₅H₅)₃][B(3,5-(CF₃)₂-C₆H₃)₄] shows a regular pentagonal bipyramidal coordination geometry around bismuth with a stereochemically inactive lone pair.^[62] For a more detailed discussion of trends in structure and bonding of monocationic bismuth(III) compounds, the reader is directed to a recent review article on the topic.^[20]

Bismuth(III) dications. The number of well-defined dicationic bismuth compounds remains small compared to their monocationic counterparts. They are characterized by high coordination numbers. Typically, five primary metal-ligand-interactions are observed (Scheme 15a).^[37,38,48,49,63] This results in a (distorted) square pyramidal coordination geometry, which has previously been interpreted as a hint towards the presence of a stereochemically active lone pair.^[48] The coordination number in these compounds increases to 6–9 when their weaker secondary interactions to neutral ligands or counteranions are included, which (with a few exceptions)^[38] results in irregular coordination geometries due to sterics, geometric constraints of chelating ligands, and packing effects.^[37,48,49,51,63] A small number of examples has shown that the coordination chemistry of



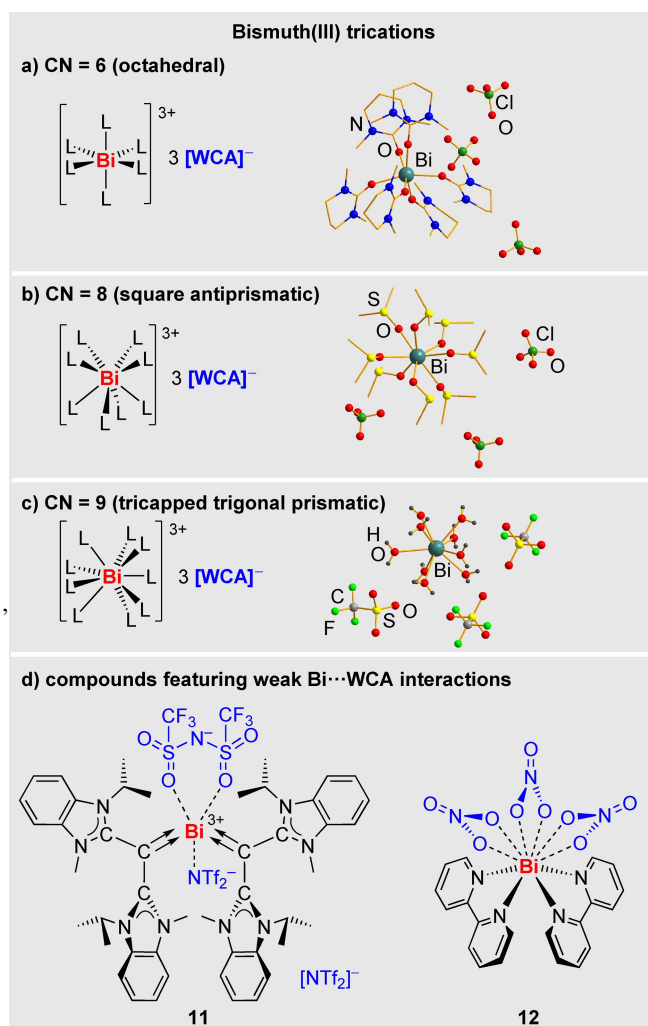
Scheme 15. a) Lewis drawing (left) and an example of a molecular structure ([BiPh(OP(NMe₂)₃)₄][PF₆]₂, right)^[48] of an organobismuth dication with five primary metal-ligand-interactions. b) Examples of molecular bismuth dications with less than five primary metal-ligand-interactions (additional weak Bi...FSbF₅ interactions are present in the solid state structure of **10** according to distance criteria). Hydrogen atoms in the molecular structure are omitted for clarity.

dicationic bismuth complexes can strongly be influenced by the use of bulky anionic or neutral ligands that effectively cover one coordination hemisphere of the bismuth atom (e.g.: **9**)^[36,50,61] or introduce Bi–C multiple bonding as a means to modify the electronic structure around bismuth (**10**; Scheme 15b).^[3,8] This led to a rare example of a bismuth dication stabilized by a tridentate tris(pyrazolyl)borate with only three primary metal ligand interactions (**9**).^[3,6] In the absence of strong Lewis bases, the electron demand of the bismuth center is satisfied by interactions with the weakly coordinating anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and the solvent molecules chlorobenzene and 1,2-dichlorobenzene, leading to a coordination number of eight.^[3,6] Similarly, a neutral carbodicarbene ligand gave access to the bismuth dication **10** that shows primary bonding interactions with only two ligands, and is further stabilized by multiple weak $\text{Bi}\cdots\text{F}\cdots\text{SbF}_5$ contacts in the solid state.^[38]

Dicationic bismuth compounds tend to adopt dinuclear or polymeric arrangements in the solid state when bearing counteranions such as $[\text{NO}_3]^-$, $[\text{CO}_3]^{2-}$, $[\text{SO}_4]^{2-}$, and $[\text{OTf}]^-$, which are inclined to show both relevant primary and secondary interactions with the central atom(s).^[49,50,63] Mononuclear dicationic bismuth dications are accessible by use of WCAs, such as $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{B}(3,5\text{-X}_2\text{C}_6\text{H}_3)_4]^-$ ($\text{X} = \text{Cl}, \text{CF}_3$), or $[\text{NTf}_2]^-$, that are less prone to show relevant primary bonding interactions with the central atom.^[36–38, 48, 50] WCAs such as $[\text{PF}_6]^-$ and $[\text{SbF}_6]^-$ appear to show a behavior on the borderline between these two extremes.^[38, 48]

Bismuth(III) trications. Tricationic bismuth compounds with monodentate σ -donating ligands and without significant interactions between the metal center and the counteranions commonly show coordination numbers of six,^[54,57,167] eight (most common),^[54–56,58,168a–d] or nine^[53] in the solid state. This results in octahedral, square anti-prismatic, and tri-capped trigonal prismatic coordination geometries (Scheme 16a–c). Lower coordination numbers of five can be obtained when bulky σ - and π -donating neutral ligands are used (**11**, Scheme 16d, left).^[3,8] When chelating ligands are exploited, tricationic bismuth compounds with higher coordination numbers of seven to ten are commonly obtained (**12**,^[59] Scheme 16d, right),^[59,169,170] while the coordination number can be reduced in some cases by removal of labile monodentate ligands under reduced pressure.^[169] In addition, considerable changes in the coordination chemistry of tricationic bismuth compounds have been reported upon going from the solid state to solutions in organic or inorganic solvents. While significant Bi–O bonding has been reported for solid $[\text{Bi}(\text{bipy})_2(\text{OTf})_3]$, free triflate anions were detected in acetonitrile solutions of this compound.^[170] Furthermore, extended X-ray absorption fine structure spectroscopy and large-angle X-ray scattering suggest that in acidic aqueous solutions of $[\text{Bi}(\text{H}_2\text{O})_n][\text{ClO}_4]_3$ and $[\text{Bi}(\text{H}_2\text{O})_n][\text{OTf}]_3$ the bismuth atom is eight-coordinate, while it shows a coordination number of nine in the solid state.^[54]

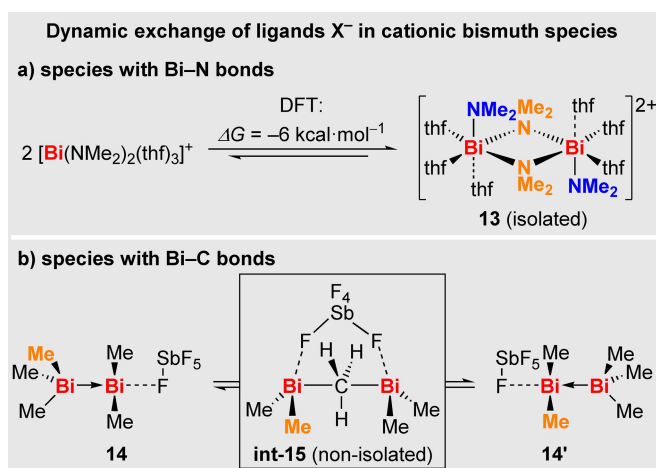
Dynamic exchange of anionic ligands. For neutral organometallic bismuth(III) compounds BiX_3 , the intermolecular exchange of anionic ligands X^- has been suggested to proceed through the formation of -ate complexes^[171] or through photochemically-induced processes.^[43] For mono-



Scheme 16. General Lewis drawing (left) and an example of a molecular structure (right) of a bismuth(III) trication with a) CN=6 (example: $[\text{Bi}(\text{dmpu})_6][\text{ClO}_4]_3$, $\text{dmpu} = N,N'$ -dimethylpropyleneurea),^[54] b) CN=8 (example: $[\text{Bi}(\text{dmsO})_8][\text{ClO}_4]_3$),^[54] and c) CN=9 (example: $[\text{Bi}(\text{OH}_2)_9][\text{OTf}]_3$).^[53] d) Tricationic bismuth compounds with weak Bi...WCA interactions. Carbon-bound hydrogen atoms in molecular structures are omitted for clarity.

and dicationic bismuth(III) compounds, which contain two and one monoanionic ligands X^- , respectively, alternative pathways appear to be accessible. When the Bi–X bond shows a considerable ionic contribution and access to a bridging coordination mode of the ligand X^- is reasonable (e.g.: $\text{X} = \text{NR}_2$, OR), exchange of the anionic ligands between two different bismuth atoms in a non-productive equilibrium reaction can be assumed to be feasible (e.g.: $[\text{BiX}_2]^+ + [\text{BiX}_2^*]^+ \rightleftharpoons 2[\text{BiXX}^*]^+$). This has been underlined by the isolation of species such as **13**, which shows a dinuclear arrangement in the solid state in combination with one and two distinct chemical environments of its NMe_2 groups at room temperature and -60°C , respectively (Scheme 17a).^[35]

Cationic bismuth(III) compounds containing more covalent Bi–C bonds have also been reported to be subject to

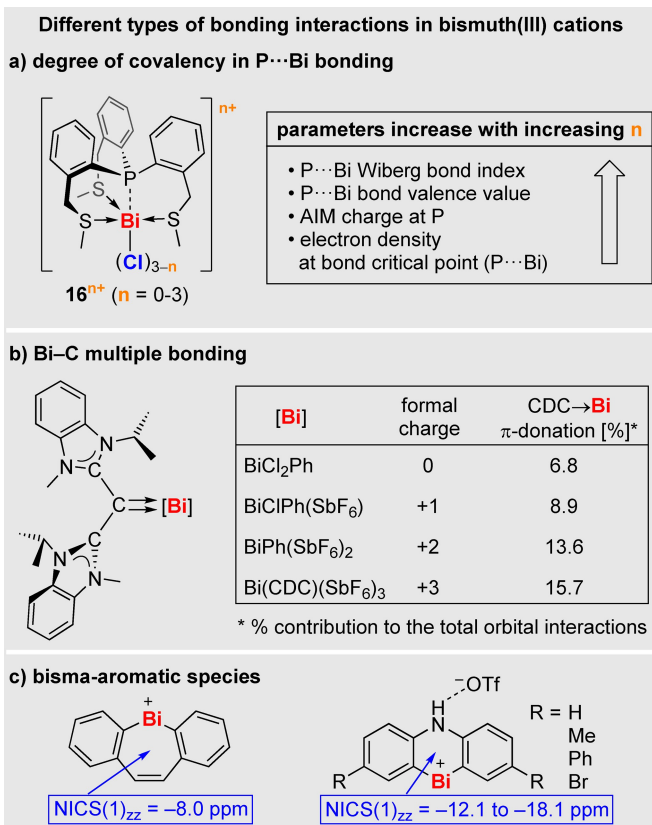


Scheme 17. Ligand exchange in cationic bismuth compounds: a) bismuth amide species (charge in isolated **13** balanced by $[\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_3)_4]$); b) organometallic bismuth species.

ligand exchange reactions, initiating the degradation of compounds such as $[\text{BiPh}(\text{hmpa})_4][\text{PF}_6]_2$.^[48] The dynamic bonding situation of allyl ligands in $[\text{Bi}(\text{C}_3\text{H}_5)_2(\text{thf})_2][\text{B}(3,5\text{-Cl}_2\text{-C}_6\text{H}_3)_4]$ has also been discussed in the context of dynamic Bi–C bond formation/cleavage (η^1/η^3 -isomerism), and has been suggested to proceed intramolecularly based on a positive activation entropy.^[3–3] A remarkably facile ($\Delta G^\ddagger(298 \text{ K}) = 13.5 \text{ kcal mol}^{-1}$) and reversible rupture and formation of Bi–C bonds has been reported for the dimethyl bismuth cation **14** bearing a labile BiMe_3 ligand (Scheme 17b).^[3–21] The scrambling of methyl groups in this compound has been suggested to proceed through the (non-isolated) intermediate **int-15** featuring a linear Bi–C–Bi unit with an sp^2 hybridized C^{methyl} atom.^[32]

Covalency and multiple bonding of neutral ligands. A series of model compounds 16^{n+} ($n=0\text{--}3$) has been investigated with a focus on the nature of the $\text{P}\cdots\text{Bi}$ interaction in response to the complex charge (Scheme 18a).^[172] As a result, theoretical methods including natural bond orbital (NBO) and atoms in molecules (AIM) analyses (backed up by experimental findings) suggest a gradual transition from predominantly non-covalent (16^{0+}) to predominantly dative bonding (16^{3+}). Thus, the stepwise increase of the formal charge of the compounds from 0 to +3 induces a steady increase of covalency (and strength) of the $\text{P}\cdots\text{Bi}$ interactions between the neutral ligand and the (charged) bismuth atom.

Multiple bonding. Potential Bi–C multiple bonding has been investigated in neutral and cationic bismuth compounds stabilized by N-heterocyclic carbene (NHC), cyclic alkyl amino carbene (cAAC), or carbodicarbene (CDC) ligands.^[3–8] According to energy decomposition analysis (EDA) combined with the natural orbitals for chemical valence (NOCV) method, π -type $\text{C}\rightarrow\text{Bi}$ donation shows only minor contributions of 4–6 % to the overall stabilizing orbital interactions in monocationic bismuth complexes with NHC or cAAC ligands. The relevance of this interaction is higher in carbodicarbene complexes of bismuth and, as a trend, increases with increasing charge of the bismuth



Scheme 18. Investigations into the impact of formal charge on the nature of bismuth-L bonding and heteroaromaticity (L = neutral ligand, NICS = nucleus-independent chemical shift).

complex (Scheme 18b). As a result, it has been suggested to describe compounds $[\text{BiPh}(\text{SbF}_6)_2(\text{CDC})]$ (**10**, Scheme 15) and $[\text{Bi}(\text{NTf}_2)_3(\text{CDC})_2]$ (**11**, Scheme 16) as bisma-alkene cations (CDC = carbodicarbene). The compounds depicted in Scheme 18c have been shown to exhibit bisma-aromatic character and Bi–C bonds with σ - and π -type contributions according to DFT calculations, but could only be isolated as Lewis base adducts to date.^[3,173–175]

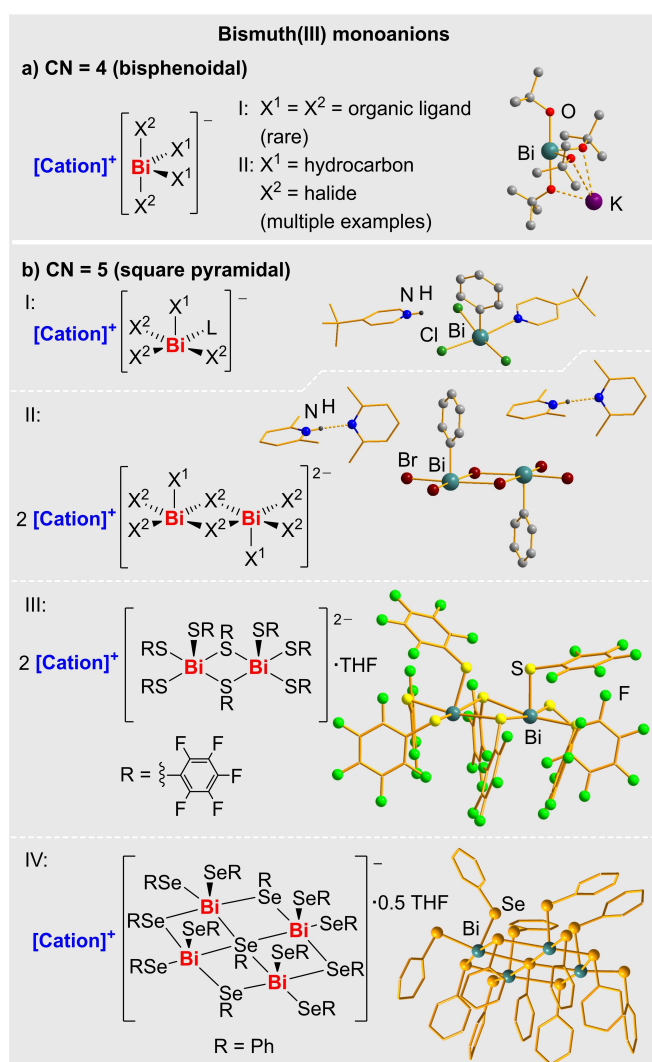
Cationic bismuth(III) complexes as electron donors. The Lewis acidic nature of cationic bismuth compounds is readily apparent.^[20,167,170,176] In view of the positive charge and the low energy of the $6s(\text{Bi})$ atomic orbital, it is somewhat counter-intuitive that these complexes can also act as Lewis bases towards moderately Lewis-acidic main group and transition metal species.^[177] According to theoretical calculations, deletion energies of up to 66 kcal mol^{-1} have been reported for the $\text{Bi}\rightarrow\text{M}$ interactions, indicating that this unusual type of donor/acceptor interaction can make a significant (>35 %) contribution to the overall interaction energies.

3.1.3.2. Anionic bismuth(III) species

Bismuth(III) monoanions. There are only a few homoleptic and mononuclear bismuth(III) anions in which the mono-

anionic ligands are not purely inorganic (*cf.* section 2.1.3). The alcoholate $[\text{KBi}(\text{O}t\text{Bu})_4]$ represents the only such example based on monodentate ligands (Scheme 19a, I).^[73] Compound $[\text{Li}(\text{thf})_4][\text{Bi}(\text{P}t\text{Bu})_3]_2$ bears dianionic bidentate phosphorus ligands,^[178] and both compounds show a bisphenoidal coordination geometry around bismuth.

The utilization of multidentate anionic ligands including additional neutral donor groups leads to larger coordination numbers. Examples include octahedral $[\text{KBi}(\text{pyridine-dipyrrolide})_2]$, square antiprismatic $\text{Na}[\text{Bi}(\text{DOTA})]$, and square (anti-)prismatic $[\text{N}(n\text{Bu})_4][\text{Bi}(\text{pc})_2] \cdot (\text{solv})_n$, where the coordination geometry can be controlled by the presence and nature of co-crystallized solvent molecules (pyridine-dipyrrolide = 2,6-(3-R',5-R-C₄HN)₂-C₅H₃N; R/R' = *t*Bu/*t*Bu or Mes/Ph; DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate; pc = phthalocyaninato).^[76,179]



Scheme 19. General Lewis drawing (left) and an example of a molecular structure (right) of bismuth(III) monoanions with a) CN = 4 (example: $[\text{KBi}(t\text{Bu})_4]$),^[73] b) CN = 5 (examples: $[4-t\text{Bu-NHC}_5\text{H}_4][\text{BiPhCl}_3(4-t\text{Bu-NC}_5\text{H}_4)]$, $[\text{H}(2,6-\text{Me}_2\text{NC}_5\text{H}_3)_2][\text{Bi}_2\text{Ph}_2\text{Br}_2]$, $[\text{Et}_4\text{N}][\text{Bi}_2(\text{SC}_6\text{F}_6)_2] \cdot \text{THF}$, and $[\text{HP}^i\text{Pr}_3][\text{Bi}_4(\text{SePh})_{13}] \cdot 0.5\text{THF}$).^[65,186,187] Carbon-bound hydrogen atoms in molecular structures are omitted for clarity.

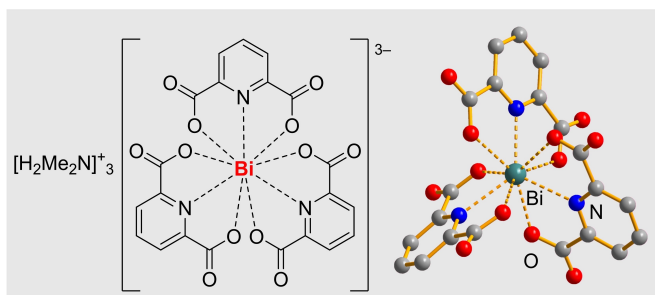
Heteroleptic monoanionic bismuth(III) compounds with two aryl groups and two anionic ligands based on more electronegative elements such as halides, nitrogen, or oxygen are well-documented.^[38,66,69,70,72,74,90,180–182] These species commonly show a coordination number of four and a bisphenoidal coordination geometry around the central atom with the carbon-based ligands in the equatorial positions (Scheme 19a, II). A rare case of a monoanionic dinuclear bismuth compound featuring perfluorinated ethyl ligands, $[\text{PPh}_4][\text{Bi}_2(\text{C}_2\text{F}_5)_4\text{I}_3]$, has also been reported.^[183]

Heteroleptic bismuth(III) compounds bearing one anionic hydrocarbon ligand and three halide ligands per bismuth atom show a strong tendency to realize a coordination number of five. They are either coordinated by an additional neutral ligand leading to mononuclear structures (Scheme 19b, I)^[65,75] or have dinuclear structures with two bridging halide ligands in the solid state (Scheme 19b, II).^[65–67,72,77,180,184] Square pyramidal coordination geometries around bismuth are observed with the hydrocarbon ligand(s) in the apical position(s) (and on opposite sides of the Bi_2X_6 -plane in the case of the dinuclear species).^[68,185] In dinuclear complexes with different types of halide ligands, the heavier halides adopt the bridging positions.^[67] While ions of the type $[\text{Bi}_2\text{Ph}_3\text{X}_6]^{2-}$ (including a compound with the $[\text{Bi}_2\text{Ph}_2\text{I}_6]^{2-}$ dianion)^[184] usually show a planar Bi_2X_6 unit, $[\text{NEt}_4]_2[\text{Bi}_2\text{Ph}_2\text{I}_6]$ has been reported to show a strongly bent geometry with both of the hydrocarbon ligands on the convex side of the Bi_2I_6 unit.^[180]

Aggregation phenomena have also been observed for homoleptic anionic bismuth(III) chalcogenolato complexes, representative examples of which are shown in Scheme 19b, III, IV. The coordination geometry around bismuth is typically square pyramidal. In contrast to the dinuclear species described in Scheme 19b, II, all apical substituents are found on the same side of the plane defined by the square base of the coordination polyhedra, which may be ascribed to unfavorable steric interactions between the substituents at the chalcogen atoms.^[186–188]

Dianions, Trianions, and Tetraanions. Well-defined, di-, tri-, and tetraanionic bismuth(III) compounds with monodentate organic ligands remain elusive. However, a small number of dianionic species with halides and organic ligands bound to bismuth have been reported. Examples include $[\text{BiMeBr}_4]^{2-}$, $[\text{Bi}(\text{O}-2,6\text{-Xyl})_3\text{Br}_2]^{2-}$, and $[\text{Bi}(\text{O-Mes})_2\text{Br}_3]^{2-}$, which show a square pyramidal coordination geometry around bismuth (Xyl = 2,6-Me₂-C₆H₃; Mes = 2,4,6-Me₃-C₆H₂).^[68,71] The use of chelating dianionic ligands allows access to trianionic and tetraanionic species such as $[\text{NH}_2\text{Me}_2][\text{Bi}(2,6\text{-pdc})_3]$ (Scheme 20) and $\text{K}_4[\text{Bi}(2,5\text{-pdc})_3 \cdot (2,5\text{-Hpdc})]$ with a holo-directed^[189] and a capped pentagonal bipyramidal coordination geometry, respectively (H_2pdc = pyridinedicarboxylic acid).^[190,191]

Bonding analysis. The bisphenoidal coordination geometry of ten-electron-complexes of type EX_4 with purely σ -donating ligands has been rationalized on the basis of qualitative molecular orbital analyses.^[180,192] The occupation of the axial positions by the most electronegative bonding partners is in agreement with mixing of 3a₁ and 4a₁ molecular orbitals of the complexes in C_{2v} symmetry.^[192]



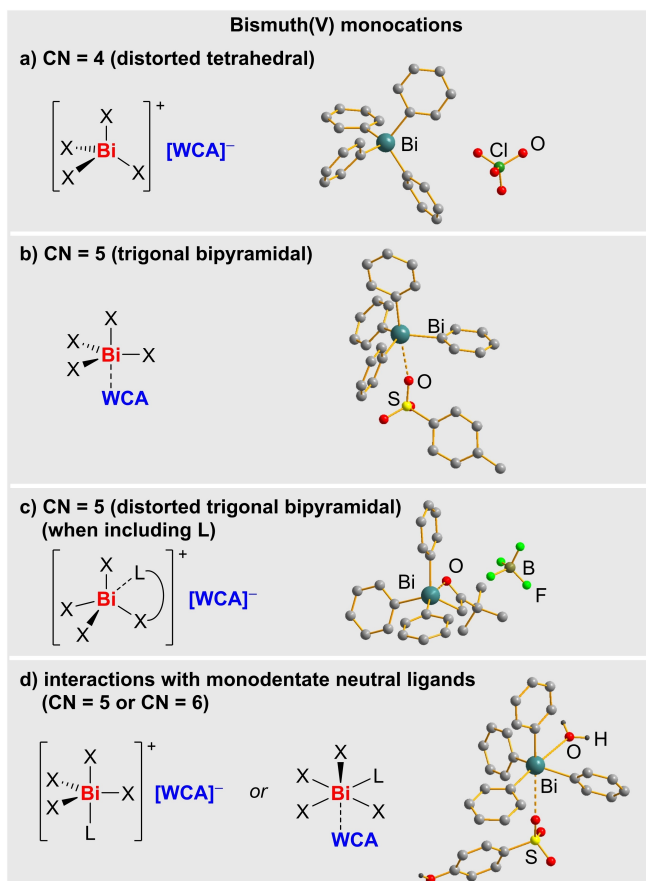
Scheme 20. Example of a trianionic Bi complex with a tridentate ligand: $[\text{H}_2\text{Me}_2\text{N}]_3[\text{Bi}(2,6\text{-pdc})_3]$ ($2,6\text{-H}_2\text{pdc} = 2,6\text{-pyridinedicarboxylic acid}$).^[191]

Monometallic anionic bismuth(III) compounds have so far only been isolated with at least two sufficiently electronegative ligands such as halides or alcoholates. One of the factors leading to this observation is certainly the poor Lewis acidity of bismuth compounds BiR_3 ($\text{R} = \text{hydrocarbon}$) due to the absence of an energetically low-lying $\sigma^*(\text{Bi}-\text{R})$ orbital. This has been circumvented by the synthesis of tris(2-pyridyl) bismuth compounds. Upon coordination of Ag^+ in the N,N,N -binding pocket, the bismuth-based Lewis acidity is enhanced to an extent that $\text{Bi}\cdots\text{X}$ and $\text{Bi}\cdots\text{L}$ interactions with anions such as triflate and neutral donors such as acetonitrile are realized in the solid state.^[182]

3.1.4. Bismuth(V) compounds

3.1.4.1. Cationic bismuth(V) species

Bismuth(V) monocations. The compound class of monocationic bismuth(V) species is dominated by complexes bearing at least three aryl substituents. The largest group comprises species with four aryl ligands,^[82,84,85,90,91,95,193a,b,194,195–201] a considerable number of compounds with three aryl and one alkynyl-,^[86] vinyl-,^[202] alkyl,^[87,92,93,203] or halide^[204] moiety are known, and only one example with four alkyl groups at bismuth has been reported.^[94] Most of these compounds show distorted tetrahedral coordination geometries around the metal center based on the use of WCAs such as $[\text{BF}_4]^-$, $[\text{ClO}_4]^-$, $[\text{PF}_6]^-$ or complex halo-bismuthates (Scheme 21a).^[82,87,199,200] When counteranions with a less pronounced charge delocalization such as $[\text{OTs}]^-$ are applied, additional weak $\text{Bi}\cdots\text{WCA}$ interactions are commonly realized to give five-coordinate species with a trigonal bipyramidal coordination geometry around bismuth (Scheme 21b).^[90] In view of the difficulties to prevent the interaction of bismuth atoms with neutral ligands in Bi^{III} monocations, it may appear surprising to note that such interactions are only rarely reported for the bismuth(V) analogs. This may be ascribed to the fact that a coordination number of at least four is inherently obtained for bismuth(V) monocations in the absence of additional neutral ligands. When bismuth(V) cations contain an intramolecular donor functionality such as a carbonyl group, a weak interaction with the central atom has been suggested based on distance criteria and bond angles.^[92,93,203] This

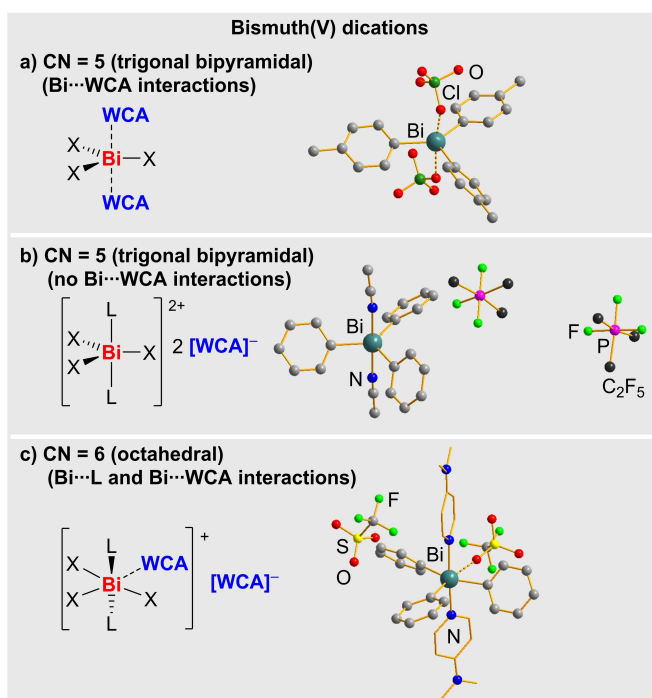


Scheme 21. General Lewis drawings (left) and examples of molecular structures (right) of bismuth(V) monocations with a) $\text{CN} = 4$ (example: $[\text{BiPh}_4][\text{ClO}_4]$),^[199] b) $\text{CN} = 5$ including $\text{Bi}\cdots\text{WCA}$ interactions (example: $[\text{BiPh}_4(\text{OTs})]$),^[90] c) $\text{CN} = 5$ without $\text{Bi}\cdots\text{WCA}$ interactions (example: $[\text{BiPh}_3(\text{CH}_2\text{C}(\text{O})\text{tBu})][\text{BF}_4]$),^[203] and d) monodentate neutral ligands bound to bismuth (example: $[\text{BiPh}_4(4\text{-OH-C}_6\text{H}_4\text{SO}_3)(\text{H}_2\text{O})]$).^[198] Carbon-bound hydrogen atoms in molecular structures are omitted for clarity.

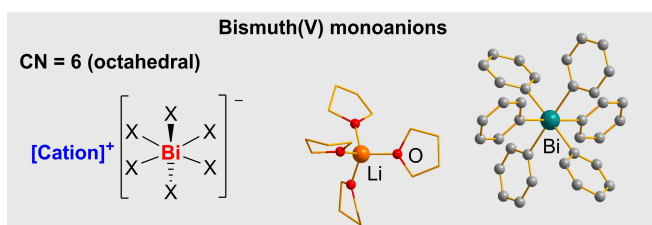
would result in a coordination number of five with a distorted trigonal bipyramidal coordination geometry, with the distortion being due to geometric ligand constraints (Scheme 21c; $1 > \tau^5 > 0.5$).

In addition, a handful of bismuth(V) monocations featuring bonding interactions with neutral monodentate ligands has been reported, including $[\text{BiPh}_4(\text{dmsO})][\text{PtBr}_3(\text{dmsO})]$, $[\text{BiPh}_4(4\text{-OH-C}_6\text{H}_4\text{SO}_3)(\text{H}_2\text{O})]$, $[\text{BiPh}_4(\text{OCMe}_2)]_2$, $[\text{BiPh}_4]_2[\text{Bi}_4\text{I}_{16}]$, and $[\text{BiPh}_4(\text{H}_2\text{O})][\text{NO}_3]$ (Scheme 21d).^[91,196–198] Compounds with such $\text{Bi}-\text{L}$ bonding seem to correspond to one of multiple minimum structures on a flat energy landscape: (i) the $[\text{BiPh}_4]^+$ moiety with a $[4\text{-OH-C}_6\text{H}_4\text{SO}_3]^-$ counteranion is coordinated by H_2O in the solid state,^[198] while the $[\text{BiPh}_4]^+$ moiety with a $[2,5\text{-Me}_2\text{-C}_6\text{H}_3\text{SO}_3]^-$ counteranion bears H_2O molecules without significant $\text{Bi}\cdots\text{OH}_2$ bonding in the crystal lattice,^[201] (ii) “water-free” $[\text{BiPh}_4(\text{NO}_3)]$ molecules co-crystallized with $[\text{BiPh}_4(\text{H}_2\text{O})][\text{NO}_3]$ from aqueous solutions^[91] and (iii) the cations $[\text{BiPh}_4]^+$ and $[\text{BiPh}_4(\text{OCMe}_2)]^+$ co-crystallized with the counteranion $[\text{Bi}_4\text{I}_{16}]^{4-}$.^[196]

Bismuth(V) dications. Among mononuclear bismuth(V) dications, compounds bearing three aryl groups at the metal center are clearly dominating. When significant bonding interactions with both anions are realized, the bismuth atom adopts a trigonal bipyramidal coordination geometry with the aryl groups in the equatorial plane (Scheme 22a).^[78,201,205,206] The counteranions can be substituted for strongly σ -donating monodentate neutral ligands with the overall coordination geometry remaining unchanged (Scheme 22b),^[78,204] or to give hexa-coordinate species due to one weak Bi...WCA contact (Scheme 22c).^[78] Forcing the neutral donors into *cis*-position by use of chelating ligands presumably also gives compounds with distorted octahedral coordination geometries.^[78]



Scheme 22. General Lewis drawings (left) and examples of molecular structures (right) of bismuth(V) dications with a) CN = 5 including Bi...WCA interactions (example: $[\text{Bi}(\text{4-Me-C}_6\text{H}_4)_3][\text{ClO}_4]_2$;^[206] b) CN = 5 without Bi...WCA interactions (example: $[\text{BiPh}_3(\text{NCMe})_2][\text{PF}_6(\text{C}_2\text{F}_5)_3]_2$;^[204] c) CN = 6 (example: $[\text{BiPh}_3(\text{OTf})(\text{4-NMe}_2\text{-NC}_5\text{H}_4)_2][\text{OTf}]\text{dmap}$).^[78] Hydrogen atoms in molecular structures are omitted for clarity.



Scheme 23. General Lewis drawing (left) and an example of the molecular structure (right) of bismuth(V) monoanions with CN = 6 (example: $[\text{Li}(\text{thf})_4][\text{BiPh}_6]$).^[98] Hydrogen atoms in the molecular structure are omitted for clarity.

3.1.4.2. Anionic bismuth(V) species

Bismuth(V) monoanions. Monoanionic bismuth(V) compounds with monodentate organic ligands are rare and have been reported to show octahedral coordination geometries (Scheme 23).^[94,97,98] While the Bi–C bond lengths in compound $[\text{Li}(\text{thf})_4][\text{BiMe}_6]$ (2.30–2.36 Å)^[94] are similar to those in the neutral parent compound BiMe_5 (2.27–2.30 Å) (trigonal bipyramidal),^[94] the Bi–C bond lengths in $[\text{Li}(\text{thf})_4][\text{BiPh}_6]$ (2.27–2.30 Å)^[98] are longer than the Bi–C^{apical} (2.22 Å) and similar to the Bi–C^{equatorial} (2.32 Å) bond lengths in neutral BiPh_5 (square pyramidal).^[207] This highlights the impact of both, charge and coordination geometry, on structural parameters in this class of compounds.

Stability and equilibria of bismuth(V) monoanions. The literature-known organometallic bismuth(V) anions $[\text{Li}(\text{thf})_4][\text{BiMe}_6]$ and $[\text{Li}(\text{thf})_4][\text{BiPh}_6]$ are unstable to an extent that solution spectroscopic data have not been reported.^[94,97,98] Stoichiometric considerations, the reversible color change of solutions of $\text{Li}[\text{BiPh}_6]$ upon heating/cooling, and quenching experiments suggest that there is an equilibrium reaction $\text{LiR} + \text{BiR}_5 \rightleftharpoons \text{Li}[\text{BiR}_6]$, which is shifted to the bismuthate side in the cold and in the presence of an excess of the lithium reagent.^[97,98]

3.2. Complexes with inorganic ligands

The structures of bismuth complexes with inorganic ligands highlight fundamental aspects of the coordination chemistry of these compounds, but also show an astounding variability with regard to mono- and multinuclear motifs. Here, we summarize representative examples of charged bismuth compounds with inorganic ligands taking over a key role to showcase these and related important aspects of structure and bonding.

3.2.1. Bismuth(III) species

3.2.1.1. Cationic bismuth(III) species

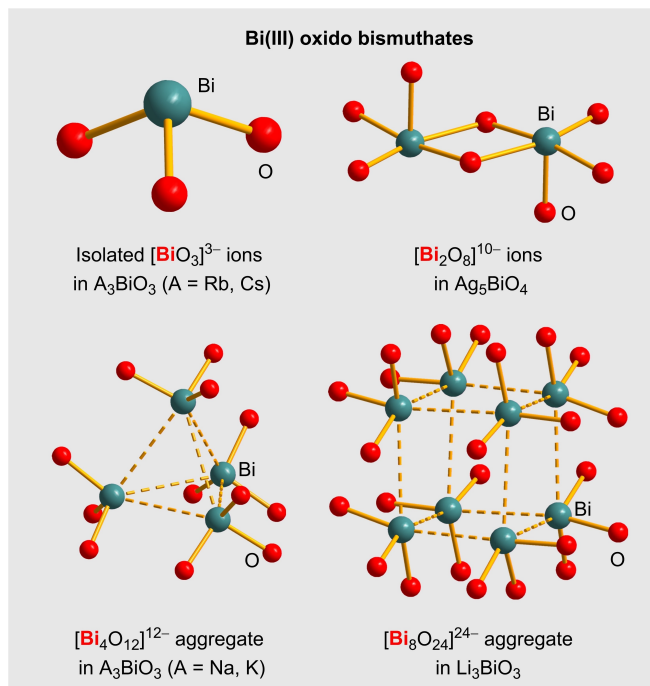
As a sole example of a well-defined molecular bismuth cation with purely inorganic ligands, the tricationic complex $[\text{Bi}(\text{H}_2\text{O})_9]^{3+}$ has been discussed in section 3.1.3.1 (Scheme 16) along with related species bearing organic ligands.^[53]

3.2.1.2. Anionic bismuth(III) species

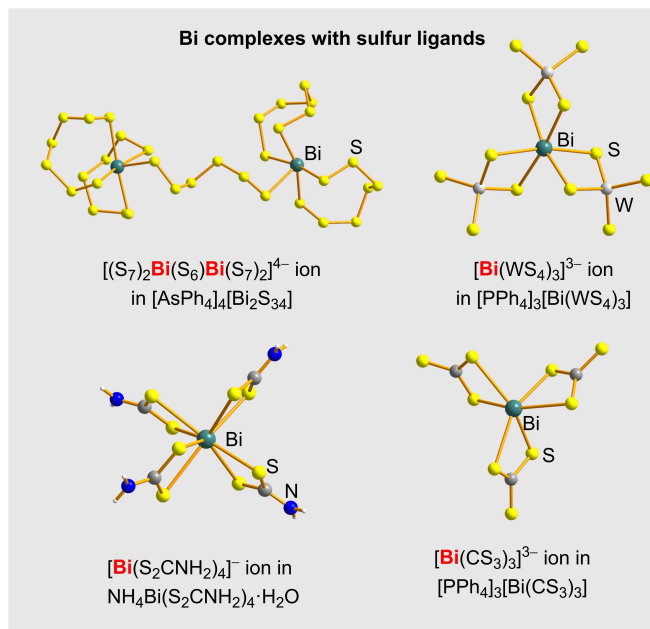
Oxido species. Many oxido bismuthates feature extended anionic substructures, but some representatives with isolated, molecular anions are also known. They can be understood as the salts of the oxo acids H_3BiO_3 and H_3BiO_4 as well as their different aggregation products. In A_3BiO_3 with $\text{A} = \text{Li–Cs}$, isolated $[\text{BiO}_3]^{3-}$ units can be observed.^[208–211] Depending on A, different aggregates can be found in the single crystal structure, as shown in

Scheme 24. Here, $[\text{BiO}_3]^{3-}$ units form cubic or tetrahedral substructures with Bi...Bi distances below the sum of the van der Waals radii.^[212] Ag_5BiO_4 contains highly charged dinuclear $[\text{Bi}_2\text{O}_8]^{10-}$ units,^[112,113] also shown in Scheme 24.

Sulfido species. In contrast to the oxido bismuthates, the corresponding compounds with the heavier chalcogens exclusively feature extended anionic substructures, for



Scheme 24. Examples of molecular oxido bismuthates(III).^[112,113,208–211]



Scheme 25. Examples of Bi complexes with sulfur-based ligands.^[214,215,218,219]

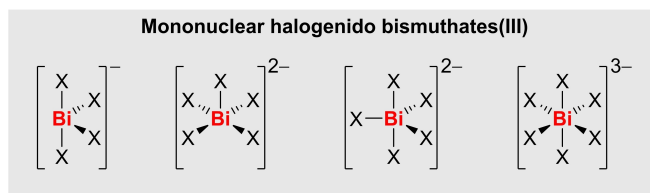
example a 3D anion with channels in RbBi_3S_5 .^[213] However, molecular anions with more complex chalcogen based ligands are known. These include $[\text{Bi}_2\text{S}_{34}]^{4-}$, a dinuclear complex with four bidentate S_7^{2-} ligands and one bridging S_6^{2-} ligand.^[214] The complex $[\text{Bi}(\text{WS}_4)_3]^{3-}$, isolated as its $[\text{PPh}_4]^+$ salt, represents an example of a bismuth complex with $[\text{WS}_4]^{2-}$ ligands.^[215] This has remained the only example of a molecular complex with a typical thio metalate anion. $[\text{Me}_2\text{NH}_2][\text{BiGeS}_4]$ represents the only other compound with an organic counterion in this class, although in this case a layered anion is observed.^[216] This is remarkable, as heterometallic main group chalcogenido metalates represent a large and well-studied family of compounds.^[217] Additionally, simple, formally inorganic dithiocarbamate^[218] and thiocarbonate^[219] complexes are known, which can serve as precursors to Bi_2S_3 . All sulfur-ligand based complexes are summarized in Scheme 25.

Halogenido species. Halogenido bismuthates represent by far the largest and most varied class among bismuth complexes with inorganic ligands, and even a mineral from this class of compounds has been reported, namely argesite $(\text{NH}_4)_7\text{Bi}_3\text{Cl}_{16}$.^[220]

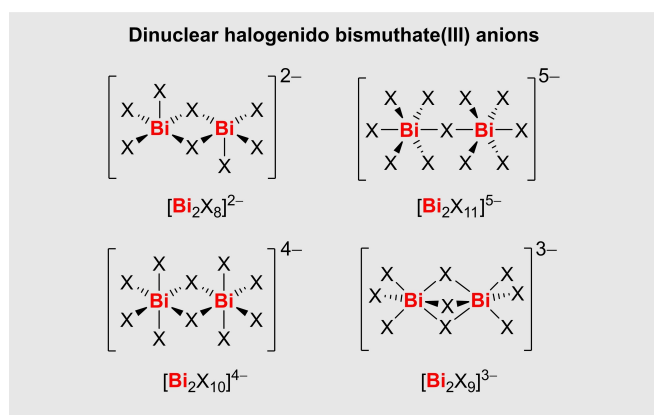
A clear differentiation can be made between the fluorides and the heavier halogenides: On the one hand, fluorido bismuthates(III) featuring molecular anions have not been prepared, yet, and on the other hand analogous compounds of the heavier halogens are easily accessible. Only a number of fluorido bismuthates(III) with extended anions such as K_2BiF_5 , which features a chain-like anion composed of distorted, edge-sharing pentagonal-bipyramidal $\{\text{BiF}_7\}$ units, have been reported.^[221] Fluorido bismuthates-(V) (discussed in section 3.2.1) can be obtained in a straightforward manner, which again contrasts with the accessibility of the heavier homologs.

The structures and chemistry of halogenido bismuthates with the heavier halogens have been reviewed on several occasions.^[99,116,222] Thus, we only want to give a representative overview here. Generally, the chemistry of chlorido, bromido and iodido bismuthates is closely related. Typical mononuclear complexes $[\text{BiX}_4]^-$ (bisphenoidal), $[\text{BiX}_5]^{2-}$ (square-pyramidal or trigonal-bipyramidal) and $[\text{BiX}_6]^{3-}$ (octahedral) are summarized in Scheme 26 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

$\{\text{BiX}_6\}$ units represent the most common building block of multinuclear anions, with dinuclear ions with corner-, edge- and face-sharing shown in Scheme 27, together with $[\text{Bi}_2\text{X}_8]^{2-}$, a rare anion type composed of two square-pyramidal $\{\text{BiX}_5\}$ units connected through edge-sharing.



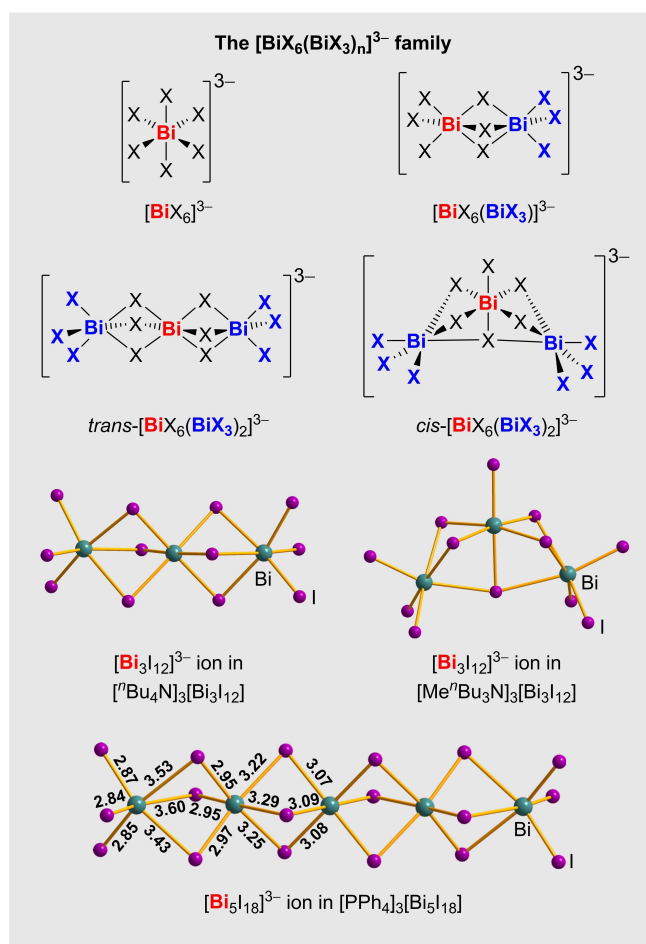
Scheme 26. Mononuclear halogenido bismuthate(III) anions for $\text{X} = \text{Cl}, \text{Br}, \text{I}$. Note that not all types of anions are known for all X .



Scheme 27. Dinuclear halogenido bismuthate(III) anions for X = Cl, Br, I.

We have analyzed 824 halogenido bismuthates deposited in the CCDC database^[223] to obtain some general trends in this class of compounds, as far as this can be judged from the compounds that have been characterized up to now (see Supporting Information for details). The large majority of compounds features molecular anions. Of these, the majority features either a mono- or dinuclear anion motif. From Cl to Br and I the tendency to form less highly charged anions (with regard to the charge per bismuth atom) increases through the formation of face-sharing connections between $\{\text{BiX}_6\}$ units or polymeric polynuclear anions. Currently, the highest observed nuclearity in molecular halogenido bismuthate anions is eight, although this may increase if suitable cations can be found to stabilize anions of higher nuclearity.

In contrast to the lead halide perovskites, where families of related anion motifs can be derived via hypothetical cuts of the perovskite aristotype,^[224] finding such families within the halogenido bismuthates has been more difficult, mostly due to their great structural variability. Nonetheless, we want to introduce two specific families that represent commonly observed motifs for all heavier halogens. The $[\text{BiX}_6(\text{BiX}_3)_n]^{3-}$ family can be derived from the octahedral $[\text{BiX}_6]^{3-}$ anion by successively attaching additional BiX_3 units so that a face-sharing chain of octahedra results (Scheme 28). Compounds featuring the $n=1$ member of the family are quite ubiquitous (see Supporting Information). $[\text{Bi}_3\text{X}_{12}]^{3-}$ anions can be found for all X,^[225,57] although they are predominantly observed for X=I. Through different attachment positions, a *cis*^[226] and a *trans*^[57] motif can be obtained for $n=2$. Tetranuclear anions with $n=3$ have not yet been observed, but several examples of compounds with pentanuclear $[\text{Bi}_5\text{I}_{18}]^{3-}$ ions with $n=4$ have been reported.^[227] For both, the trinuclear $[\text{Bi}_3\text{X}_{12}]^{3-}$ and the pentanuclear $[\text{Bi}_5\text{I}_{18}]^{3-}$ ions, long bridging Bi–X bonds *trans* to the terminal ones can be observed, reflecting the concept of attaching BiX_3 units as the anions are extended. If the *trans* attachment is continued with n approaching infinity, a hypothetical chain-like polymorph of BiX_3 is obtained. This has been realized in the solvate $\text{Bi}_2\text{I}_6(\text{sulfolane})_2$ (sulfo-

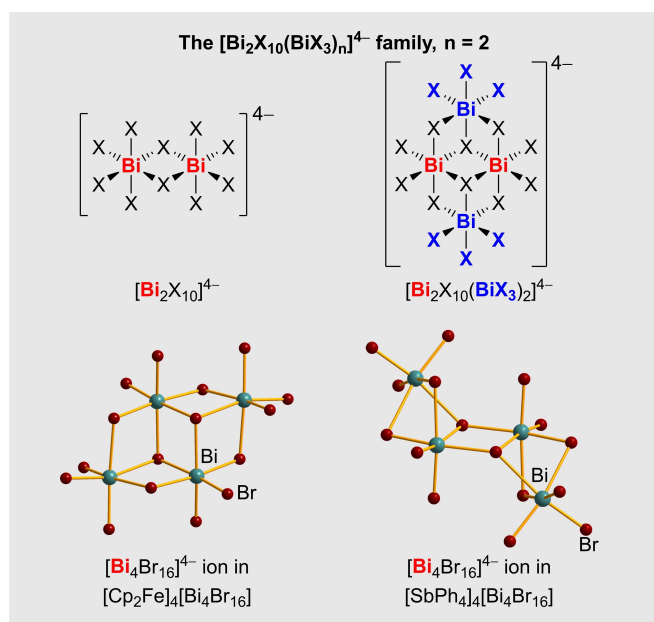


Scheme 28. Concept and representatives of the $[(\text{BiX}_6)(\text{BiX}_3)_n]^{3-}$ family.^[57, 226, 227]

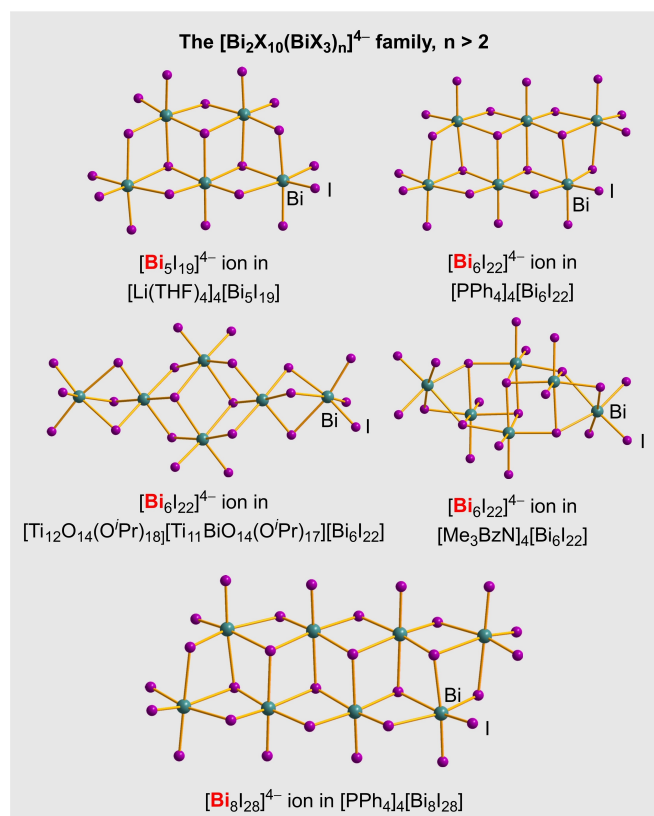
lane = tetrahydrothiophene 1,1-dioxide, $\text{C}_4\text{H}_8\text{O}_2\text{S}$),^[55] which features $[\text{BiI}_3]_{\infty}$ chains.

A second representative family of anions with the composition $[\text{Bi}_2\text{X}_{10}(\text{BiX}_3)_n]^{4-}$ can be derived from the dinuclear $[\text{Bi}_2\text{X}_{10}]^{4-}$ ion by formally attaching BiX_3 units, typically in an edge-sharing, but occasionally also in a face-sharing fashion. The attachment points can be varied, leading to isomeric anions, for example in compounds with $[\text{Bi}_4\text{Br}_{16}]^{4-}$ ions ($n=2$), where two isomers are known,^[228,229] and those with $[\text{Bi}_6\text{I}_{22}]^{4-}$ ions ($n=4$), where three different isomers are known.^[227,230,231] Still, there appears to be a preference for arrangements that can be understood as cut-outs of the CdI_2 -structure type^[232] with a purely edge-sharing connection of $\{\text{BiX}_6\}$ octahedra, with the members for $n=2$, 3, 4 and 6 being known^[230,233] in addition to a fair number of compounds with the simple dinuclear $[\text{Bi}_2\text{X}_{10}]^{4-}$ ion (see Supporting Information), as shown in Schemes 29 and 30.

In addition to these two families, a number of unique molecular anion motifs have been obtained, some of which we want to present here. The hexanuclear anion $[\text{Bi}_6\text{Cl}_{26}]^{8-}$, isolated as its $[\text{N},\text{N}'\text{-Me}_2\text{-4,4'-bipyridinium}]^{2+}$ (MV^{2+}) salt^[111] is composed of three $\{\text{Bi}_2\text{Cl}_{10}\}$ units connected via corner-sharing of *trans*-standing chloride ligands of the

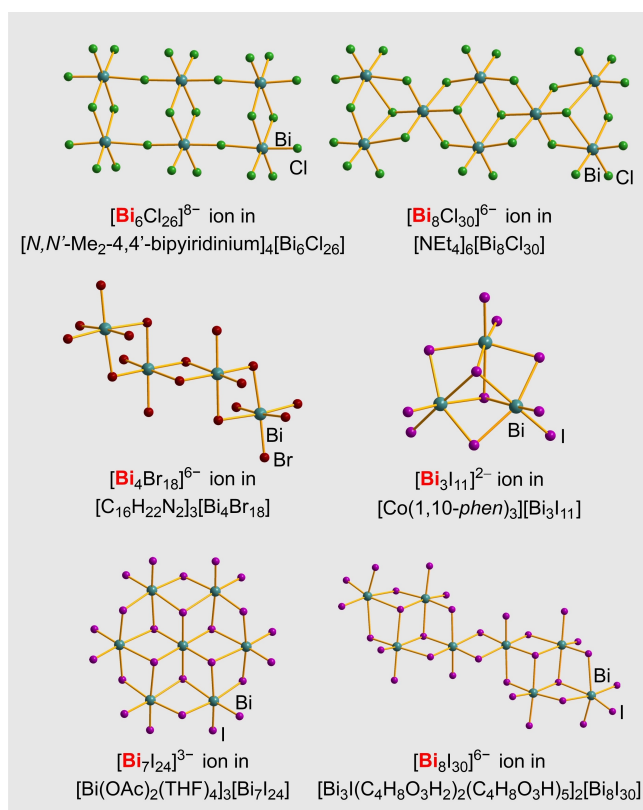


Scheme 29. Concept and representatives of the $[\text{Bi}_2\text{X}_{10}(\text{BiX}_3)_n]^{4-}$ family with $n = 2$.^[228, 229]



Scheme 30. Representatives of the $[\text{Bi}_2\text{X}_{10}(\text{BiX}_3)_n]^{4-}$ family with $n > 2$.^[227, 230, 231, 233]

central unit, shown in Scheme 31. This hexanuclear anion can be viewed as a cut-out of the ladder-like chain anion $\{[\text{Bi}_2\text{Cl}_8]^{2-}\}_\infty$, which is also available as a MV^{2+} salt.^[23, 4] The



Scheme 31. Additional examples of multinuclear halogenido bismuthates (III).^[111, 235, 237, 239, 240, 242]

corresponding tetranuclear anion with only two $\{\text{Bi}_2\text{Cl}_{10}\}$ units is known as a MV^{2+} salt as well.^[111]

The $[\text{Bi}_8\text{Cl}_{30}]^{6-}$ anion, isolated as its $[\text{NEt}_4]^+$ salt,^[235] represents a complex anion motif built from three $\{\text{Bi}_2\text{Cl}_{10}\}$ units connected through edge-sharing with two additional $\{\text{BiCl}_6\}$ units, as shown in Scheme 31. A related anion motif has also been found in compounds with extended chains, although these have remained limited to iodides such as $(\text{N-MePy})\{[\text{Bi}_3\text{I}_{10}]\}$.^[236]

The $[\text{Bi}_4\text{Br}_{18}]^{6-}$ anion can be prepared as its 1,1'-(ethane-1,2-diyl)bis(3,5-dimethylpyridin-1-ium) salt^[237] and is composed of a chain fragment built from four edge-sharing $\{\text{BiBr}_6\}$ octahedra. A number of compounds with similar extended anions built from edge-sharing octahedra have been reported, such as $[\text{HPy}][\text{BiBr}_4]$.^[238]

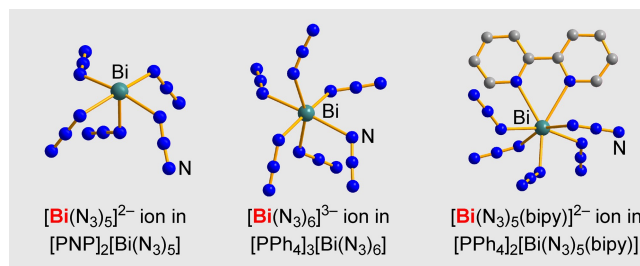
These three examples suggest that larger molecular motifs can represent a “snapshot” of the formation of chain-like anions.

We want to introduce three examples of iodido bismuthate anions with unique motifs: The $[\text{Bi}_3\text{I}_{11}]^{2-}$ ion is found in a series of compounds $[\text{M}(1,10\text{-phen})_3][\text{Bi}_3\text{I}_{11}]$ ($\text{M} = \text{Fe}, \text{Co}, \text{Zn}$),^[239] and displays a high degree of condensation, featuring three $\{\text{BiI}_6\}$ units that are connected with each other through face-sharing (see Scheme 31). The $[\text{Bi}_7\text{I}_{24}]^{3-}$ ion found in $[\text{Bi}(\text{OAc})_2(\text{THF})_4]_3[\text{Bi}_7\text{I}_{24}]$ ^[240] is a unique example of a halogenido bismuthate anion adopting the motif of a typical Anderson type polyoxometalate.^[241] The $[\text{Bi}_8\text{I}_{30}]^{6-}$ ion found in

$[\text{Bi}_3\text{I}(\text{C}_4\text{H}_8\text{O}_3\text{H}_2)_2(\text{C}_4\text{H}_8\text{O}_3\text{H})_5]_2[\text{Bi}_8\text{I}_3]^{[242]}$ represents the largest currently known molecular iodo bismuthate (Scheme 31). It is composed of two $\{\text{Bi}_2\text{X}_{10}(\text{BiX}_3)_2\}$ units, as described above, connected via edge-sharing. Once again, this can be viewed as a fragment of a chain-like anion motif, as found in $[\text{N}(n\text{Bu}_4)][\text{Bi}_2\text{I}_7]^{[233]}$

With regard to the wide variety of motifs observed in the halogenido bismuthates, the solution behavior of these complexes is of great interest and has been a subject of investigation for more than 50 years.^[243] Studies have been conducted either in acetonitrile, ensuring the formation of charged species by the addition of an additional source of halide ions, or in aqueous solutions of hydrohalic acids. Depending on the concentration of halide ions, different species were identified using UV/Vis and Raman spectroscopy. In acetonitrile, the presence of $[\text{BiX}_4]^-$, $[\text{BiX}_6]^{3-}$, $[\text{BiI}_7]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) has been proposed.^[244a,b,245] In $\text{HX}(\text{aq})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the species $[\text{BiX}_4(\text{H}_2\text{O})_2]^-$ (only for $\text{X} = \text{Cl}, \text{Br}$), $[\text{BiX}_5]^{2-}$, and $[\text{BiX}_6]^{3-}$ have been reported.^[246] A number of challenges are associated with the solution behavior and precise speciation of halogenido bismuthates, including the lability of the $\text{Bi}-\text{X}$ bond and the determination of the exact nature of the species present. For example, the existence of a $[\text{BiI}_8]^{5-}$ ion in aqueous solution was proposed,^[247] which could not be confirmed in later works,^[246] although the use of different conditions may contribute to this disparity. However, no $\{\text{BiI}_7\}$ or $\{\text{BiI}_8\}$ building units have ever been observed in the solid state. Some helpful hints towards additional aspects of solution behavior, including the formation of multinuclear ions, halogen exchange reactions and the formation of mixed halogen species, and interactions with cations can be found in a recent study on halogenido bismuthate-based ionic liquids.^[248] While the species formed in dilute solutions and in ionic liquids where $[\text{BiX}_n]^{q-}$ ions are a constituent component^[249] cannot be equated, some of the quantum chemical investigations in the study were conducted by modelling a solution-like environment for the ions. These point toward the facile formation of di- and trinuclear species like $[\text{Bi}_3\text{X}_{12}]^{3-}$ and the presence of conformers with similar energies, for example a tetrahedral and a bisphenoidal arrangement of ligands in $[\text{BiX}_4]^-$. This is well in line with typical observations on the rich structural chemistry of species commonly found in the solid state. Overall, the solution behavior of halogenido bismuthates remains under-explored and thus a worthwhile direction for future investigations, especially regarding the generally under-utilized fluorido bismuthates. A deeper insight would allow for a better understanding of how the species in solution act as building blocks for solid halogenido bismuthates obtained through solution synthesis.

Pseudo- and polyhalide species. A natural extension of the chemistry of halogenido bismuthates is the use of pseudo- and polyhalide ligands. A number of azido bismuthates have been reported, including $[\text{Bi}(\text{N}_3)_5]^{2-}$ and $[\text{Bi}(\text{N}_3)_6]^{3-}$, as well as complexes featuring additional coordination by donor solvents or 2,2'-*bipy*, shown in Scheme 32, or chain-like polymeric anions like $[\text{Bi}(\text{N}_3)_4]^-$.^[107,250,251] The formation of anionic azido species affords compounds that are comparably more stable than their neutral analogues;



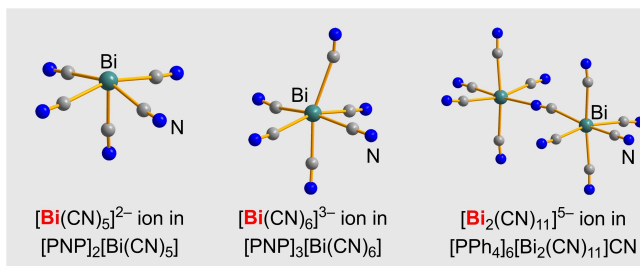
Scheme 32. Molecular azido bismuthate(III) complexes.^[250]

while it has been reported that $\text{Bi}(\text{N}_3)_3$ is “extremely shock-sensitive and can explode violently upon the slightest provocation”,^[107] $[\text{PPh}_4]_3[\text{Bi}(\text{N}_3)_6]$ is “neither heat- nor shock-sensitive”.^[107]

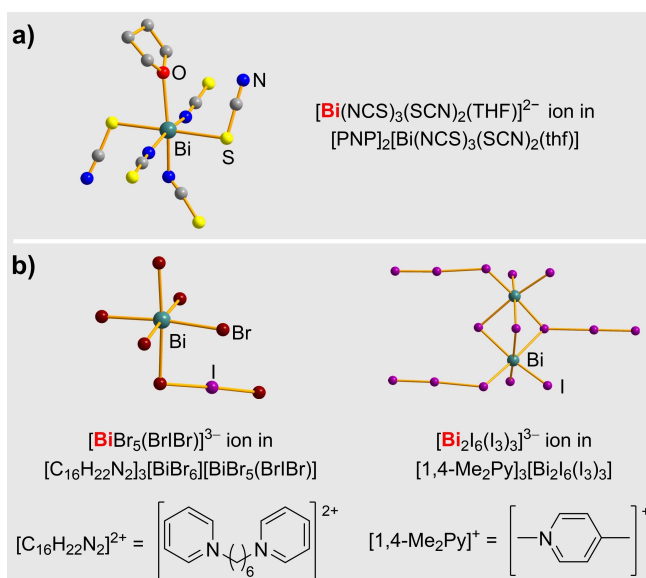
In a similar approach as for the azido compounds, molecular cyanido bismuthate ions have been isolated using large $[\text{PPh}_4]^+$ and $[\text{PNP}]^+$ cations. Here, $[\text{Bi}(\text{CN})_5]^{2-}$, $[\text{Bi}(\text{CN})_6]^{3-}$ and the dinuclear $[\text{Bi}_2(\text{CN})_{11}]^{5-}$ ion are known, as shown in Scheme 33.^[252] Interestingly, both C and N coordination is observed for the bridging cyanido ligand in $[\text{Bi}_2(\text{CN})_{11}]^{5-}$.

While polymeric thiocyanato bismuthates have been explored, for example in the context of Prussian Blue analogues,^[253] molecular species have remained limited to $[\text{Bi}(\text{NCS})_3(\text{SCN})_2(\text{THF})]^{2-}$ (Scheme 34a), a complex showing coordination of the thiocyanato ligand both via the nitrogen and via the sulfur atom underscoring that Bi^{3+} ions can act as Lewis acids of intermediate hardness despite their significant oxophilicity.^[106] Examples of halogenido bismuthates with polyhalide ligands, shown in Scheme 34b, include the complexes $[\text{BiBr}_5(\text{Br}_3)]^{3-}$,^[254] $[\text{BiBr}_5(\text{BrI})]^{3-}$,^[255] and $[\text{Bi}_2\text{I}_6(\text{I}_3)]^{3-}$.^[256] Often, additional halogen-halogen contacts below the sum of the van der Waals radii are observed in the compounds featuring these anions, extending the anionic substructure. Depending on the specific case, they can also be understood as regular halogenido bismuthates with trapped dihalogen molecules, which may also be used for halogenation reactions.^[257]

Bismuthates with other simple inorganic ligands have been reported, for example the nitrato complexes $[\text{Bi}(\text{NO}_3)_5]^{2-}$,^[258] featuring exclusively bidentate coordination of the nitrato ligands, and $[\text{Bi}(\text{NO}_3)_6]^{3-}$,^[259] featuring four nitrato ligands with bidentate and two with monodentate

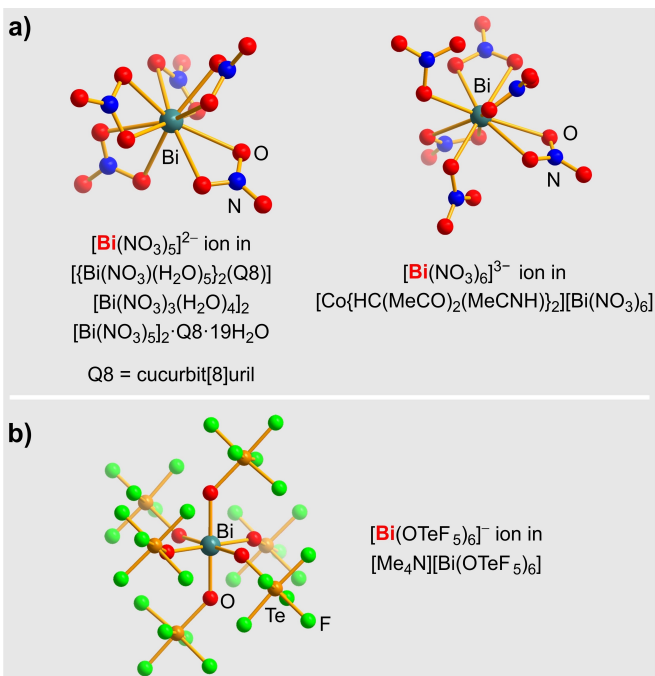


Scheme 33. Molecular cyanido bismuthate(III) complexes.^[252]



Scheme 34. Examples of molecular thiocyanato and polyhalogenido bismuthates(III).^[106, 255, 256]

coordination (Scheme 35a). This underlines the highly flexible coordination chemistry of these compounds, including the ability of charged bismuth complexes to adopt various coordination numbers. A singular example of an inorganic Bi^{V} complex that does not feature fluoro or oxido ligands has been reported with $[\text{Bi}(\text{OTeF}_5)_6]^-$,^[260] shown in Scheme 35b.



Scheme 35. a) Examples of homoleptic nitrato bismuthates(III).^[258, 259] b) Structure of the $[\text{Bi}(\text{OTeF}_5)_6]^-$ anion, an example of a bismuthate(V) that is not an oxido or fluorido complex.^[260]

3.2.2. Bismuth(V) species

Oxido species. A number of Bi^{V} oxido bismuthates are known and include compounds with the molecular anions $[\text{BiO}_4]^{3-}$ found in the mixed valence bismuthate $\text{K}_9[\text{Bi}^{\text{V}}\text{O}_4][\text{Bi}^{\text{III}}_4\text{O}_9]$,^[114] $[\text{BiO}_6]^{7-}$ found in Li_7BiO_6 ,^[261, 262] and $[\text{Bi}_2\text{O}_8]^{6-}$ found in K_3BiO_4 ,^[263] shown in Scheme 36.

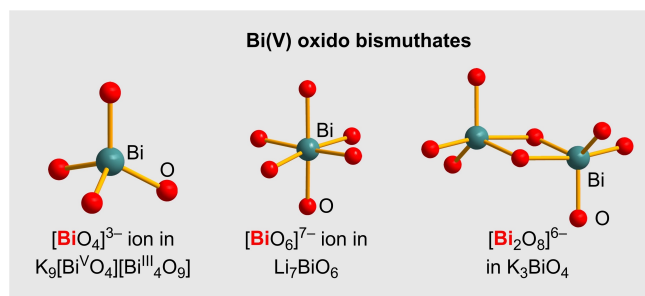
Fluorido species. Most of the fluorido bismuthates(V) are purely inorganic and feature coordination numbers greater than six. ABiF_6 ($\text{A} = \text{Li}-\text{Cs}$)^[264] and A_2BiF_7 ($\text{A} = \text{Na}-\text{Cs}$, NMe_4 , NO_2)^[115] are two series of fluorido bismuthates(V) that form monoanionic octahedral and dianionic pentagonal-bipyramidal molecular entities (Scheme 37).

3.3. Low-valent bismuth-based cluster compounds

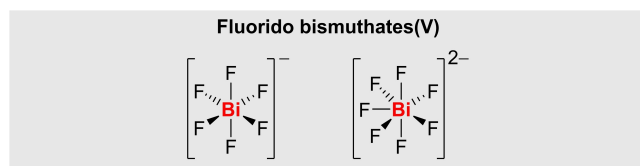
Multimetallic cluster molecules in which bismuth atoms are directly bonded to other (semi)metal atoms have several structural features in common, which at first glance is independent of either a positive or negative total charge. However, a closer look indicates that the total charge, thus an overall deficient number of electrons (cations) or an electron excess (anions), is key to the bonding situation within the clusters. This in turn affects structural details and reactivity and stability of the molecules—in the crystalline compounds, in solution, or in the gas phase. Here, we refer to some seminal contributions that illustrate such differences and their consequences.

3.3.1. Compounds with polycationic cluster molecules

The first structural determination of a polycationic bismuth cluster was that of Bi_9^{5+} observed in a crystal of composition



Scheme 36. Examples of molecular oxido bismuthates(V).^[114, 261–263]



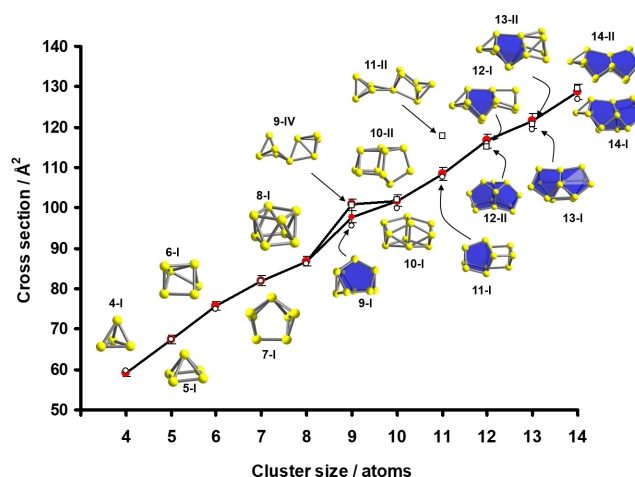
Scheme 37. Mononuclear fluorido bismuthate mono- and di-anions.

$\text{Bi}_{12}\text{Cl}_{14}$.^[120] The same cation was later found in the compound $\text{Bi}_{10}(\text{HfCl}_6)_3$, which contained a combination of Bi^+ and Bi_9^{5+} cations.^[122] In both cases, the Bi_9^{5+} cluster adopted a tricapped trigonal prismatic structure reminiscent of Ge_9^{2-} , not conforming to the Wade-Mingos rules which would predict a *nido*-deltahedron as opposed to the observed *closo*-deltahedron. This, however, cannot rule out the possibility of fluctuation between cluster structural motifs when not restricted by the dominating effect of crystal packing that has a great influence in the solid-state. The influence of the counteranion is already reflected in the known structures, as the presence of $(\text{BiCl}_5)^{2-}$ and $(\text{Bi}_2\text{Cl}_8)^{2-}$ counterions in the first example led to a distortion of the polycation. In contrast, when partnered with the relatively weakly coordinating $(\text{HfCl}_6)^{2-}$ anion, Bi_9^{5+} is significantly more symmetric, close to a C_{3h} symmetry though not at the required idealized D_{3h} symmetry. It was not until the isolation of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ in 2010, some fifty years later, that the Bi_9^{5+} cation was observed with C_{4v} symmetry and the expected *nido*-deltahedron structure, the only example to date for Bi_9^{5+} .^[265] The dication Bi_8^{2+} in $\text{Bi}_8(\text{AlCl}_4)_2$ has a square-antiprismatic structure, consistent with the removal of one “ Bi^{3+} ” vertex from the tricapped trigonal prism of Bi_9^{5+} .^[123] Originally determined from powder X-ray diffraction data, and later confirmed by single crystal X-ray diffraction, Bi_5^{3+} has an almost perfect trigonal bipyramidal structure,^[125] whilst the Bi_5^{3+} has the square-based pyramidal *nido*-cluster architecture,^[266] all in compliance with the Wade-Mingos rules. Completing the set of known Bi_x^{q+} , the very rare Bi_6^{2+} has a distorted octahedron structure.^[267] The above-mentioned examples and variants of homoatomic Bi_n^{q+} clusters are illustrated in Scheme 38.

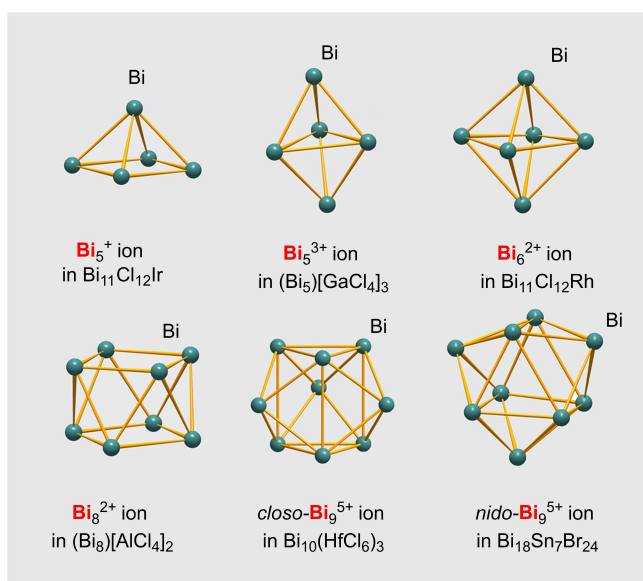
Ion mobility spectrometry paired with trapped ion electron diffraction, and density functional theory calculations have revealed a whole series of Bi_n^+ species ($n \leq 13$) to

exist in the gas phase,^[269] which seem to follow clear structural rules (Scheme 39).

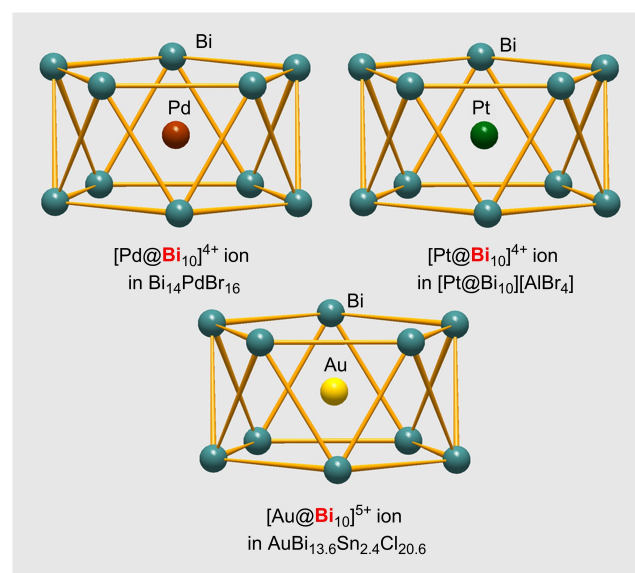
The three cationic intermetalloid clusters, $[\text{Au}@\text{Bi}_{10}]^{5+}$, $[\text{Pd}@\text{Bi}_{10}]^{4+}$ and $[\text{Pt}@\text{Bi}_{10}]^{4+}$, have been investigated by quantum chemical calculations.^[130–134] All three species are described as Bi_{10}^{4+} pentagonal antiprismatic clusters encapsulating a Au^+ , a Pd^0 , and a Pt^0 atom, respectively. It is this encapsulation of a d^{10} metal that drives the formation of the overall cluster structure (Scheme 40). This is typified by the fact that the synthesis of $[\text{Pd}@\text{Bi}_{10}]^{4+}$ in $\text{Bi}_{14}\text{PdBr}_{16}$ only



Scheme 39. Collision cross sections of Bi_n^+ cations with $n=4-14$ as a function of the cluster size (experimental values from mass spectrometric measurements: full circles with error bars; calculated values for global minimum structures (DFT): open circles, for other relevant isomers (DFT): open squares). Calculations of cross sections were done with the SEDI-model using the coordinates from DFT calculations. Reproduced from ref. [269] with permission by the American Institute of Physics.



Scheme 38. Structures of polybismuth cations.^[123, 126–129, 265–268]



Scheme 40. Structures of intermetalloid polybismuth cations containing a d^{10} metal and Bi_{10}^{4+} cage.^[267, 134]

occurs upon melting Bi₂Pd with Bi and Br, whilst using the individual elements exclusively yields PdBr₂ and Bi₆Br₇.

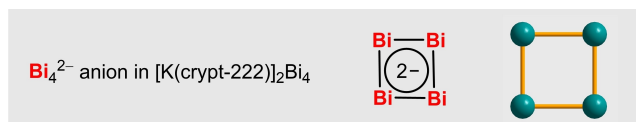
Both experimental and theoretical work indicated that cationic bismuth clusters generally show a similarity with regards to their geometrical and electronic situation to germanium Zintl clusters. It is of no surprise that their connection can be derived from the isoelectronic relationship between Bi and Ge[−] (or any other group 14 element) with five valence electrons per cluster atom; similar analogies are found between clusters of Ge⁰ and (BH) units, which also share the same electron count (of four valence electrons here) per cluster atom. Assigning an oxidation state to the bismuth atoms in these clusters is not a trivial task, and provides very little insight into the nature of these compounds. Quantum chemical studies followed by population analysis of the canonical molecular orbitals can help to get an idea of “natural charges” (NBO analyses)^[270] or “Mulliken charges” (Mulliken analyses),^[271] for instance. However, as all types of population analyses are based on (different) definitions of the end of one atoms and the beginning of the next, the meaningfulness of the numbers are often not high—and the values are often even inverse for different methods applied. Therefore, it is much more worthwhile to comment on the overall charge of the cluster molecules which plays a major role in the structures observed.

3.3.2. Compounds with polyanionic cluster molecules

As was previously mentioned, Bi₂^{2−} is not strictly a cluster molecule, however is one of the most well-studied polybismuthides. The crystal structure of the [K(222-crypt)]₂Bi₂ showed a significantly short Bi–Bi bond of 2.838 Å, which prompted investigation into the electronic structure of the molecule.^[272] By first principles, it can be described as isoelectronic to O₂ with a triplet ground state, and was initially revealed to be the case by the first quantum calculations performed on the molecule. However, conflicting EPR data suggested the compound to be diamagnetic and the calculations were disregarded on the basis of the difficulty of modelling anionic bismuth molecules at the time. A later theoretical study showed that, on considering spin-orbit coupling and relativistic effects, the diamagnetic ground state is the energetic minimum for Bi₂^{2−}, whilst the lighter congeners of group 15 all have paramagnetic ground states.^[273] Bi₄^{2−} has a square planar structure, and the presence of 6π electrons invokes the question whether such a molecule can be defined as aromatic (Scheme 41).^[13, 6] The average Bi–Bi bond length of 2.939 Å is notably shorter than that of a typical Bi–Bi single bond. However, DFT calculations revealed a small degree of antiaromatic character.^[274–276]

The only other known homoatomic polybismuth anions, Bi₇^{3−} and Bi₁₁^{3−}, possess nortricyclane- and ufosane-type structures, respectively, like the equivalent phosphorus compounds.^[138, 139]

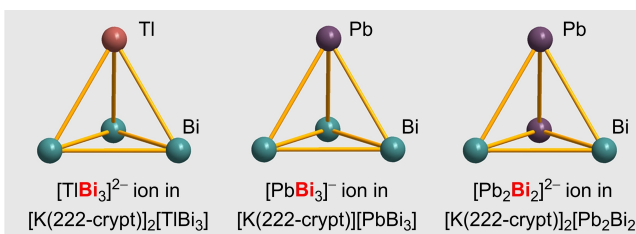
Heteronuclear *pseudo*-tetrahedral anions involving bismuth atoms with either a group 13 (Tr) or 14 element (Tt)



Scheme 41. Regular square planar structure of the Bi₄^{2−} anion in crystalline [K(crypt-222)]₂Bi₄,^[136] which can be formally considered as a 6π aromatic molecule. However, in contrast to its lighter Pn₄^{2−} congeners with Pn being P or As,^[277] which show diatropic ring currents indicative for π-aromaticity, calculations of ring currents indicate that both Sb₄^{2−}^[278] and Bi₄^{2−} are weakly antiaromatic instead.^[274–276]

with a total valence electron count of 20 (thus *pseudo*-P₄) are excellent starting materials for the generation of larger polybismuthides (Scheme 42). Of the eight combinations of (TrBi₃)^{2−} and (Tt₂Bi₂)^{2−} possible, three remain elusive, (Al, Si and Ge). This is a comment on their relative stabilities drawn from the size of the atoms and the electron distribution within the heteronuclear bonds.^[144] The ratio of the covalent radii between the atoms involved gives a strong indication in this manner. Atoms of a similar size to Bi, namely Tl and Pb in this case, have a ratio close to 1 and afford the most stable anions. Deviations from this ideal exact ratio are more strongly felt for (Tt₂Bi₂)^{2−} anions than (TrBi₃)^{2−}. This can be explained by the nature of the structure of the molecule. (TrBi₃)^{2−} has a triangular base of three bismuth atoms in which the Tr atom can sit above, resulting in favorable orbital overlap, whereas (Tt₂Bi₂)^{2−} can be viewed as composed of two homoatomic dumbbells with no such stabilizing factor. The result is seen in the fact that (GaBi₃)^{2−} has been synthesized and (Ge₂Bi₂)^{2−} has not despite having similar covalent radii ratios (0.82 vs 0.81, respectively). Very recently, the first isoelectronic anion with a single charge only, (PbBi₃)[−] was added to this collection.^[279]

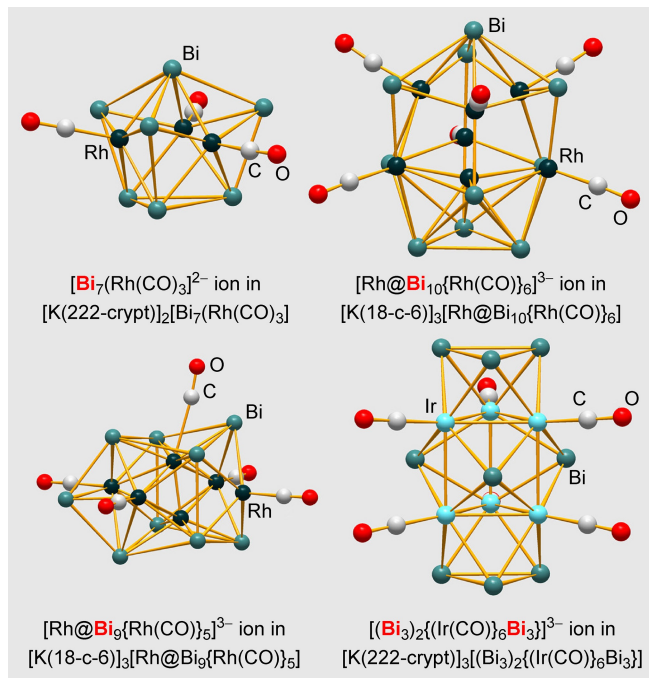
While the structures of homoatomic polybismuth anions are typically electron-precise (comprising 5*n* valence electrons) and thus dominated by the 8-*N* rule with three-connected atoms,^[280] binary compositions allow for more flexibility, as shown in systematic theoretical studies of binary clusters of the general formula Pb_{*n*}Bi_{*x*} and (Pb_{*n*}Bi_{*x*})⁺ (*n* = 3–13).^[281] The study indicated that uncharged species and their charged isoelectronic counterparts often have similar or even identical structures, but relative



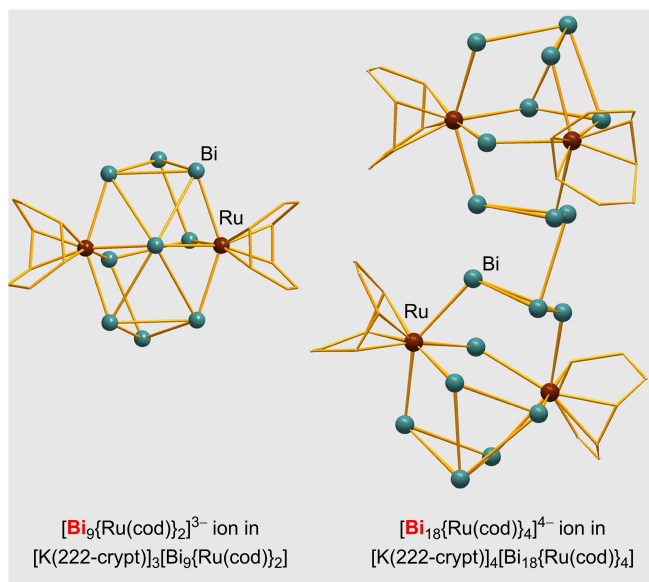
Scheme 42. Structures of *pseudo*-tetrahedral binary group 13/15 or group 14/15 anions with 20 valence electrons involving bismuth atoms, given for anions involving atoms from exclusively period six as representatives (from left): (TlBi₃)^{2−}, (PbBi₃)[−], (Pb₂Bi₂)^{2−}.^[142, 143, 279]

energies of isomers may be swapped—which could lead to very different reactivities in the gas phase.

Inclusion of transition metal complexes into polybismuthides has yielded a diverse number of structures depending on the nature of the transition metal fragment involved in the cluster framework. Monovalent $\{M(CO)\}^+$ ($M = Co, Rh, Ir$) fragments,^[282–284] where electrons from the metal can be



Scheme 43. Structures of non-deltahedral heterometallic(carbonyl) clusters containing bismuth showing a variety of $\{Bi_3\}$, $\{Bi_4\}$ and $\{Bi_6\}$ substructures.^[282–284]

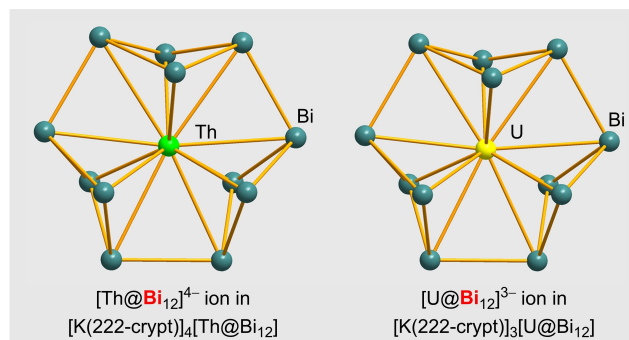


Scheme 44. Structures of $[Bi_9\{Ru(cod)\}_2]^{3-}$ and $[Bi_{18}\{Ru(cod)\}_4]^{4-}$. The larger structure can be viewed as the oxidatively coupled dimer of the parent $[Bi_9\{Ru(cod)\}_2]^{3-}$ cluster.^[140–143, 288]

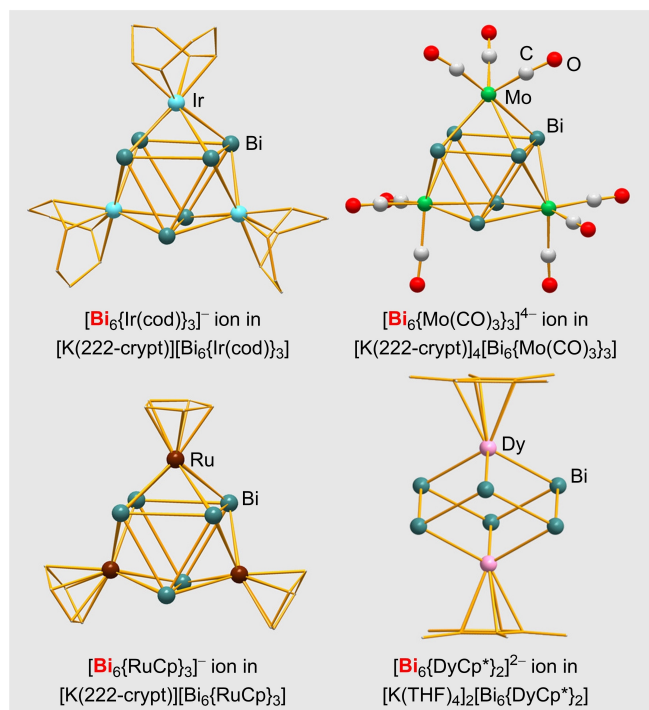
incorporated into the cluster bonding, afford structures that do not conform with traditional deltahedral clusters.^[285–287] The anion $[Bi_7\{M(CO)\}_3]^{2-}$ (Co or Rh) has a structure where the metal fragment lies in the puckered pentagonal face of the $\{Bi_7\}$ nortricyclane (Scheme 43). Additionally, using an alternate source for the $\{Rh(CO)\}^+$, $[Rh@Bi_{10}\{Rh(CO)\}_6]^{3-}$ or $[Rh@Bi_9\{Rh(CO)\}_5]^{3-}$ anions made up of $\{Bi_6\}$ and $\{Bi_4\}$, and $\{Bi_2\}$ and $\{Bi_3\}$ fragments, respectively, could be isolated (Scheme 43). In the case of $\{Ir(CO)\}^+$, the obtained $[(Bi_3)_2\{(Ir(CO))_6Bi_3\}]^{3-}$ anion has a nine atom vertex tricapped trigonal prismatic structure sandwiched between two $\{Bi_3\}$ triangles.

Switching to 12 electron transition metal complex fragments, namely $[Ni(CO)]$, $[Cr(CO)_3]$ and $[Mo(CO)_3]$, there is a shift towards *closo*-deltahedron clusters containing small anionic $\{Bi_n\}$ fragments ($n = 3, 4$ or 6). These polybismuthides vary in structure with ozone-like and cyclo- Bi_3^{3-} , square and butterfly $\{Bi_4\}$, and chair and trigonal prismatic $\{Bi_6\}$ motifs all observed.^[285–287, 289] Much larger heteroatomic polybismuthides have also been isolated, with the record currently standing at 18 bismuth atoms in the example of $[(Ru(cod))_4Bi_{18}]^{4-}$, the oxidatively coupled dimer of $[(Ru(cod))_2Bi_9]^{3-}$ (Scheme 44; $cod = 1,5$ -cyclooctadiene).^[288]

Arguably the most interesting species with regards to structure and bonding are the intermetalloid clusters containing f-block metals, $[Th@Bi_{12}]^{4-}$ and $[U@Bi_{12}]^{3-}$ (Scheme 45) and the series of $[(L_nM)_3Bi_6]^{q-}$ complexes which contain $\{Bi_6\}$ trigonal prisms (Scheme 46).^[276, 289–291] The intermetalloid structures can be described as a Bi_{12}^{8-} cluster built up from three slightly folded four-membered rings connected at opposing corners affording a torus-shaped $\{Bi_{12}\}$ ring encapsulating the actinide ion. Due to the open-shell configuration of $[U@Bi_{12}]^{3-}$, the analysis of ring currents was not possible by quantum chemical calculations in those days. However, in the Th case, calculations revealed the presence of a significant π -aromaticity. Additionally, the $\{Bi_6\}$ trigonal prisms in $[(L_nM)_3Bi_6]^{q-}$, depending on the regularity of the prism, show an unprecedented aromatic behavior. $[Mo(CO)_3Bi_6]^{4-}$ and $[Ir(cod)_3Bi_6]^-$ both possess slightly irregular prismatic structures, whereas the $[(RuCp)_3Bi_6]^-$ anion features a near perfect triangular prism and consequently shows a unique non-localizable molecular orbital with f_z^3 symmetry producing a corresponding aromatic ring current, which has therefore been described as ϕ -



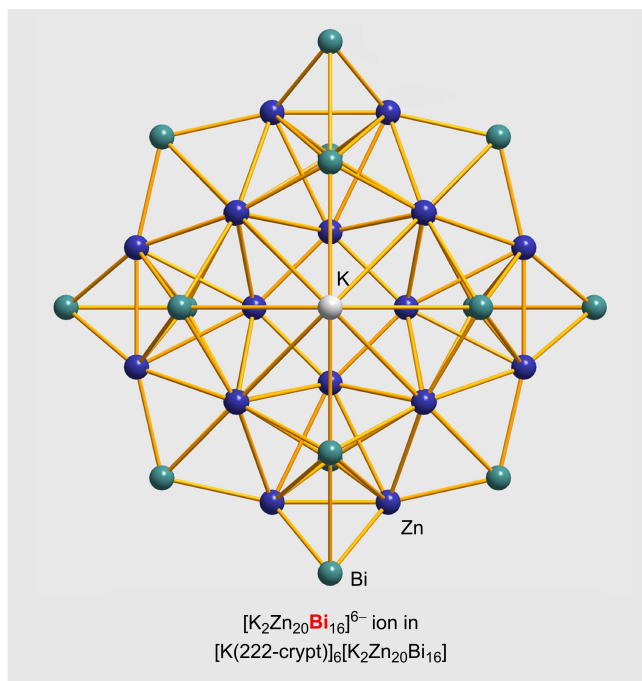
Scheme 45. Structures of intermetalloid actinide bismuth clusters.^[276, 290]



Scheme 46. Structures of heterometallic clusters containing $\{\text{Bi}_6\}$ trigonal prisms and a chair conformation, respectively. $[\text{Bi}_6\{\text{Ir}(\text{cod})\}_3]^-$ and $[\text{Bi}_6\{\text{Mo}(\text{CO})_3\}_3]^{4-}$ have slightly irregular prisms, while the near perfect prism in $[\text{Bi}_6\{\text{Ru}(\text{Cp})\}_3]^-$ shows a diatropic ring current of f_z^3 -symmetry.^[289, 291] The arrangement of the bismuth atoms in $[\{\text{Cp}^*\text{Ln}\}_2\text{Bi}_6]^{2-}$ can be described as a chair conformation, analogous to that of isoelectronic, neutral S_6 .^[292]

type aromaticity ($\text{Cp} = \text{C}_5\text{H}_5$). This was the first time such an observation has been made in an isolable compound—with the charge of the underlying $\{\text{Bi}_6\}^{q-}$ proven to play a major role in the nature of this behavior. Another $\{\text{Bi}_6\}$ unit, with a chair-like structure, has recently been observed in the heterometallocubanes $[\text{K}(\text{THF})_4]_2[\{\text{Cp}^*\text{Ln}\}_2\text{Bi}_6]$ ($\text{Ln} = \text{Tb}, \text{Dy}; \text{Cp}^* = \text{C}_5\text{Me}_5$). These compounds are the first examples of single molecular magnets containing Bi donors. The Bi_6^{6-} fragment, which is isoelectronic with neutral S_6 , acts as a bridge between the two lanthanoid centers, supporting strong ferromagnetic coupling.^[292] Polybismuthide frameworks have also found success in stabilizing unique metalloid fragments, as shown in the example of $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$ which contains a $\{\text{Zn}_{12}\}$ fragment within a larger polymetallide cage (Scheme 47).^[293] Population analyses suggest a low-valent situation for both the $\{\text{Zn}_{12}\}$ unit (stable as such with total charges of ± 0 to $+6$) and the polymetallide shell. None of the Bi atoms accumulates more than ≈ 1.6 charges according to NBO analyses.^[270]

Similar to cationic bismuth clusters, oxidation states of the bismuth atoms are not obvious in such compounds, which limits the usefulness of their assignment. However, it is obvious that charged clusters allow for the preparation of all metal species with little to no supporting ligands and provide unique insight into metal-metal bonding. The diverse range of structural motifs that have been identified to date demonstrate that anionic polybismuth units confer a



Scheme 47. Structure of $[\text{K}_2\text{Zn}_{20}\text{Bi}_{16}]^{6-}$ which has a unique $\{\text{Zn}_{12}\}$ contained with a large polymetallide cage.^[293]

remarkable degree of structural flexibility to homo- and heteroatomic clusters.

4. Physical and chemical properties

4.1. Lewis acidity of cationic bismuth complexes

Lewis acidity is one of the key parameters in order to understand the chemical properties of cationic bismuth species (*cf.* section 4.2).^[20] It has recently been quantified for a number of compounds using the Gutmann-Beckett (GB) method,^[36, 170, 175, 176, 294, 295] which assesses the interaction of the Lewis acid with OPET_3 as a probe. According to this method, the following trends can be delineated: (i) positively charged complexes show a higher Lewis acidity than their neutral analogs,^[20, 175, 295–297] (ii) an increase of the formal charge ($+1/+2/+3$) does not necessarily result in a higher Lewis acidity,^[297] because (iii) the Lewis acidity towards the probe OPET_3 may be reduced by the presence of strongly electron donating neutral ligands that are often used to stabilize such compounds;^[297] (iv) the Lewis acidity of cationic bismuth compounds can be tuned by applying geometric constraints;^[176] (v) monodentate neutral donors in the coordination sphere of bismuth Lewis acids tend to be subject to dynamic exchange reactions;^[20, 36, 167] (vi) more than one Lewis acidic site may be accessible,^[36, 167, 297] and (vii) blocking one lobe of a vacant bismuth-centered p orbital by steric crowding can be a way to increase the Lewis acidity of the cationic complex.^[298] Contrary to the trend of the Lewis acidity increasing with an increasing atomic number of group 15 compounds, cationic antimony species

have been reported to show a higher Lewis acidity than their bismuth congeners according to the GB method in a few cases.^[294,297] This has been explained by the Sb-centered vacant p-orbital of complex fragments $[\text{PnR}_2]^+$ being lower in energy than that in its bismuth counterpart ($\text{Pn}=\text{Sb}, \text{Bi}$), which results in a better orbital-energy-fit with the donor orbital of the Lewis base OPeEt_3 .^[294] Importantly, cationic species can also be formed in situ from neutral compounds by disproportionation reactions. So even when neutral bismuth compounds are meant to be employed as Lewis acids, it is possible that ionic species are generated and then represent the most Lewis acidic component, facilitating catalytic reactions. Such disproportionations have recently been demonstrated for simple bismuth halides according to $2\text{BiX}_3 + 7\text{solv} \rightleftharpoons [\text{BiX}_2(\text{solV})_5][\text{BiX}_4(\text{solV})_2]$ ($\text{X}=\text{halide}$, $\text{solV}=\text{polar solvent}$).^[62] This leads to the unusual situation that the use of polar solvents (which favor the disproportionation reaction) can increase the Lewis acidity of bismuth compounds—a so-called inverse solvent effect in Lewis acidity.

Modifications of the GB method have been established, which apply SPMe_3 and SePMe_3 as probes, highlighting the importance of the acid-base-pair-fit between the analyte (i.e. the bismuth cation) and the probe according to Pearson's concept of hard and soft acids bases (HSAB).^[167] According to this approach, monocationic bismuth species are strong and soft Lewis acids. Based on these findings, the first example of a $\text{Bi} \rightarrow \text{Bi}$ donor-acceptor bond has been realized in $[\text{BiMe}_2(\text{BiMe}_3)(\text{SbF}_6)]$, where BiMe_3 acts as a soft Lewis base.^[32]

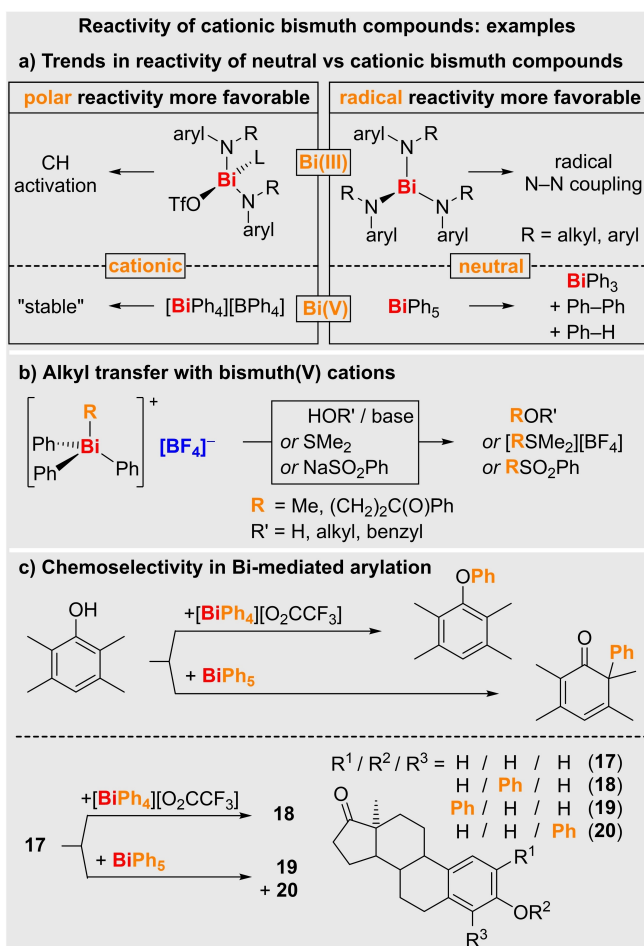
4.2. Trends in reactivity and applications

Cationic species. The considerable Lewis acidity of cationic bismuth compounds plays a central role in their reactivity.^[20] Cationic bismuth(III) compounds such as $[\text{Bi}(\text{C}_3\text{H}_5)_2(\text{thf})_2]^+[\text{B}(\text{C}_6\text{H}_3\text{Cl}_2)_4]^-$ and $[\text{Bi}(\text{NiPr}_2)_2(\text{thf})_3]^+[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]^-$ selectively insert substrates such as aldehydes, aldimines, and carbodiimides into their $\text{Bi}-\text{C}/\text{Bi}-\text{N}$ bonds, while their neutral parent compounds are unreactive under identical conditions.^[33,35] Likewise, the soft Lewis acidity of cationic bismuth compounds enables alkyl exchange via an unusual $\text{S}_{\text{E}}2$ mechanism (*cf.* Scheme 17, section 3.1.3.1^[8])^[2] and has been shown to contribute to the feasibility of CO insertion into a $\text{Bi}-\text{N}$ bond, as well as to the activation of CH bonds in arene substituents.^[173,174,299] The relevance of arene activation by cationic bismuth species has been further supported by the detailed analysis of a cationic bismuth-arene σ -complex.^[3,300] In addition to CH activation, the activation of a $\text{B}-\text{H}$ bond in $[\text{B}_{12}\text{H}_{12}]^{2-}$ to give a dicationic bismuth species $[\text{BiB}_{12}\text{H}_{11}]$ has also been reported.^[301]

The cationic character of bismuth compounds does not only have the potential to increase their reactivity, but it can also have an impact on selectivity. When unsymmetric heterocumulenes such as ketenes ($\text{Me}_2\text{C}=\text{C}=\text{O}$) and (thio)isocyanates ($\text{O}/\text{S}=\text{C}=\text{NR}$) insert into $\text{Bi}-\text{N}$ bonds of cationic species, the electrophilic bismuth atom may interact with either one of the nucleophilic terminal positions of the

heterocumulenes, but tends to favor interactions with the softer Lewis basic site (Me_2C over O ; NR over O ; S over NR).^[302]

While the neutral or charged nature of a compound is certainly only one factor affecting its reactivity, cationic bismuth(III) species can effectively pre-coordinate and polarize substrate molecules, and therefore access polar reaction pathways more readily than their neutral parent compounds. On the contrary, cationic species tend to be less prone to radical reactions than their neutral parent compounds. This has been exemplified in a case study of neutral and cationic bismuth amides, where neutral compounds $[\text{Bi}(\text{N}(\text{aryl})_2)_3]$ undergo radical reactions and their in situ generated cationic derivatives react in a polar fashion (Scheme 48a).^[173,174,303] Along these lines, it should be noted that cationic bismuth(V) compounds such as $[\text{BiPh}_4][\text{BPh}_4]$ are more stable than their parent compounds—in this case BiPh_5 , which has been reported to decompose with formation of BiPh_3 , biphenyl, and benzene.^[79] It is suggested that the relative stability of the ionic species is due to radical reaction pathways related to $\text{Bi}-\text{Ph}$ homolysis being higher in energy than in the case of BiPh_5 (Scheme 48a).



Scheme 48. Examples documenting trends in the reactivity of cationic bismuth compounds.

Cationic bismuth(V) compounds have been exploited in functional group transfer reactions. With cationic bismuth(V) species of type $[\text{Bi}(\text{aryl})_3(\text{alkyl})]^+$ and $[\text{Bi}(\text{aryl})_3(\text{allyl})]^+$, for instance, nucleophilic substrates such as arylsulfonates, thioethers, alcohols, and water can be alkylated and allylated (e.g.: Scheme 48b).^[87,93,304] According to kinetic investigations, the methylation of benzyl alcohol proceeds about two times faster with the bismuthonium salt $[\text{BiMePh}_3][\text{BF}_4]$ than with methyl triflate, establishing BiPh_3 as a more effective leaving group than triflate in this reaction.^[87] The arylation of aryl alcohols with bismuth(V) species has been investigated in some detail.^[89,305] Generally, *C*- or *O*-arylation is possible, and the chemoselectivity depends on the electronic properties of the substrate and the bismuth reagent. For substrates with alkyl groups in the *ortho*-position and for estrone as an example of a natural product, cationic bismuth(V) species give *O*-arylated products, while BiPh_3 gives *C*-arylated products (Scheme 48c).^[89] A nucleophilic attack of the alcohol at the bismuth-bound aryl moiety has been suggested as a mechanism leading to the *O*-arylated product.^[89] In related reactions, the transfer of a vinyl group from $[\text{Bi}(\text{aryl})_3(\text{vinyl})][\text{BF}_4]$ to phenols and β -dicarbonyl compounds is also feasible.^[306]

The Lewis acidity of bismuth(V) compounds has also been exploited in the field of anion transport. Tetra-aryl bismuth cations $[\text{BiPh}_3\text{R}][\text{BF}_4]$ have been shown to act as anion transporters across phospholipid bilayers, as demonstrated in a model system with egg yolk phosphatidylcholine-based large unilamellar vesicles ($\text{R} = \text{Ph}$, 2-naphthalenyl, 9-anthracenyl, 1-pyrenyl).^[195] They proved to be less effective in fluoride ion transport than their antimony analogs, which has been ascribed to a poor HSAB pair fit between the soft bismuth and the hard fluorine atoms.

The large ionic and covalent radii of bismuth allow the realization of high coordination numbers and the accommodation of bulky ligands in the coordination sphere of this element (*cf.* section 3). Nevertheless, the reactivity of cationic bismuth compounds can still be fine-tuned by modulating the sterics of ligands and substrates. This effect has been demonstrated in various types of reactions such as insertion reactions with cationic bismuth(III) amides^[35] and the oxidation of alcohols to aldehydes with cationic bismuth(V) compounds.^[194]

Anionic species. The reactivity of homoleptic anionic bismuth(I), bismuth(III), and bismuth(V) species with organic ligands has only been studied to a limited extent, presumably due to the sensitivity of such compounds. In situ-generated compounds of type $[\text{BiR}_2]^-$ have been reported to undergo alkylation and arylation with alkyl and aryl halides.^[41,43,44] This reflects an increase in nucleophilicity compared to the neutral parent compounds, since they are inert towards alkyl- and aryl halides.

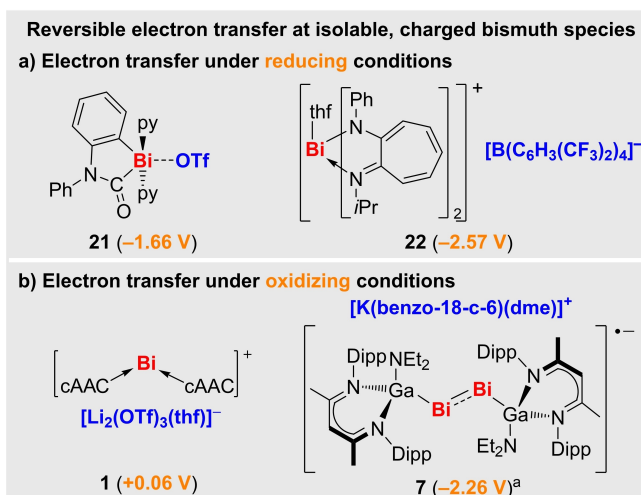
An intriguing counterion dependence has been reported for the reactivity of $\text{Bi}(\text{OrBu})_3$ with MOrBu ($\text{M} = \text{Li-K}$): no reaction is observed for $\text{M} = \text{Li}$, the formation of the expected -ate complex $[\text{KBi}(\text{OrBu})_4]$ is obtained for $\text{M} = \text{K}$, and the oxoalkoxide $[\text{Na}_4\text{Bi}_2\text{O}(\text{OrBu})_8]$ has been isolated for $\text{M} = \text{Na}$.^[73] In the case of $\text{M} = \text{Na}$, mechanistic investigations suggest that $[\text{NaBi}(\text{OrBu})_4]$ is formed initially, but undergoes

elimination of isobutene to give $[\text{NaBi}(\text{OrBu})_3(\text{OH})]$ as an intermediate en route to $[\text{Na}_4\text{Bi}_2\text{O}(\text{OrBu})_8]$.

Cluster compounds. While anionic or cationic multi-metallic clusters have mostly been studied with regards to formation, structures, and uncommon bonding situations until now, a tendency toward more functional studies can be seen in the recent literature. First reports on bond activation and even the catalytic activity of polyanionic clusters have been published, some of which involved bismuth-based Zintl clusters.^[139,307] In addition, the use of polyanionic cages as starting materials for a diversity of new solids has been reported for Ge_9^{4-} ^[308,309] and Si_n^{4-} ($n = 4, 9$).^[310] However, for polyanions or polycations involving bismuth atoms, such studies are still in their infancy. There has been only one report to date indicating that intermediate Bi_2^{2-} plays a role in the electrochemical cathodic corrosion process used to form bismuthene sheets for sodium ion storage.^[311]

4.3. Electron transfer reactions

Reversible electron transfer reactions in bismuth compounds remains rare to date. For neutral species, this has been achieved by exploiting dinuclear compounds and/or ligands containing a redox-active ferrocenyl group, at which the electron transfer proceeds.^[47,312] Cationic bismuth(III) species offer additional possibilities for the stabilization of radical species through electron delocalization in an extended π -electron system with participation of a vacant $p(\text{Bi})$ orbital. Under reducing conditions, this has recently been exploited for a small number of cationic bismuth compounds such as **21** and **22** (Scheme 49a).^[295,299] Under oxidative conditions, the isolable low-valent bismuth compounds **1** and **7** have been reported to undergo reversible electron transfer (Scheme 49b).^[39,40]



Scheme 49. Isolable, charged bismuth compounds that have been reported to undergo reversible electron transfer reactions. Numbers in orange indicate half wave potential vs ferrocene/ferrocenium (a: Determined starting from the corresponding neutral parent compound). cAAC = cyclic alkyl amino carbene.

Very recently, the dianionic bismuthate $[\text{BiCl}_5]^{2-}$ has been reported to show reversible behavior in cyclic voltammetry with a reduction wave at approximately -0.8 V vs ferrocene/ferrocenium (the exact number is not given in the literature).^[313] This has been exploited in the context of photocatalysis (see section 4.4).

4.4. Catalysis

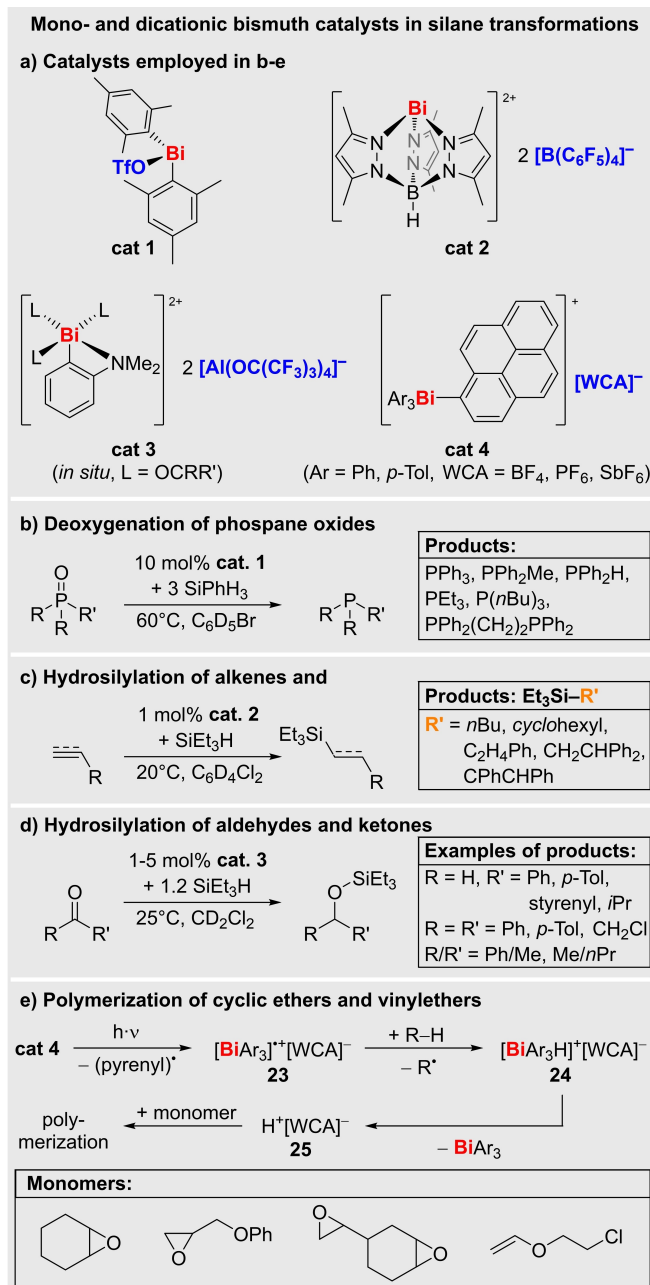
Homogeneous catalysis. Well-defined monocationic bismuth(III) compounds have been utilized as catalysts in three major domains: i) organic synthesis, making use of their Lewis acidity,^[20] ii) organic synthesis with the bismuth(III) compound being part of $\text{Bi}^{\text{I}}/\text{Bi}^{\text{III}}$ or $\text{Bi}^{\text{III}}/\text{Bi}^{\text{V}}$ redox cycles,^[20,314] and iii) polymerization catalysis exploiting the ability of bismuth compounds to release stabilized radical species under forcing conditions.^[20,315] Since these fields have recently been reviewed, this section highlights charged bismuth catalysts that are not in the focus of the above-mentioned fields or have been reported very recently.

The monocationic bismuth compound $[\text{Bi}(\text{Mes})_2(\text{OTf})]$ (**cat 1**) has been shown to be a rare example of a heavy main group compound which catalyzes the deoxygenation of phosphane oxides (Scheme 50a,b).^[294] Unexpectedly, the antimony analog is more active as a catalyst, which was assigned to the better HSAB pair fit between a vacant $p(\text{Sb})$ orbital and the phosphane oxide donor. Dicationic bismuth(III) compounds **cat 2** and **cat 3** have been exploited for the hydrosilylation of aldehydes, ketones,^[37] and alkenes,^[36] respectively (Scheme 50c,d). In agreement with the twofold positive charge lending a harder character to the bismuth center, the carbonyl compounds (in aldehyde/ketone hydrosilylation) and the silane (in alkene hydrosilylation) are activated by the bismuth Lewis acid.

Cationic bismuth(V) compounds $[\text{Bi}(\text{aryl})_3(\text{pyrenyl})]^+$ [**WCA**] (**cat 4**) initiate the photopolymerization of cyclic ethers and vinyl ethers (Scheme 50e). The pyrenyl group is suggested to act as an antenna moiety, enabling the photochemically initiated homolytic $\text{Bi}-\text{C}^{\text{pyrenyl}}$ bond cleavage to give a bismuth(IV) radical **23**, which abstracts a hydrogen atom from the reaction medium, resulting in the formation of **24**. The suggested intermediate **24** is proposed to eliminate $\text{H}[\text{WCA}]$ (**25**), which initiates the cationic polymerization.^[85]

Photocatalysis. Photocatalytic approaches with well-defined molecular bismuth compounds have first been reported for neutral species in the context of dehydrocoupling reactions between silanes and tetramethylpiperidinyloxy (TEMPO).^[316] Very recently, however, simple dianionic bismuthates $[\text{BiCl}_5]^{2-}$ have been shown to catalyze Giese-type C–C coupling reactions of hydrocarbons, such as cyclohexane, with electron-poor alkenes, such as acrylonitrile, when irradiated at $\lambda = 385$ nm.^[313] A mechanism based on atom transfer reactions has been suggested for these transformations.

Heterogeneous catalysis. The use of bismuth compounds in heterogeneous catalysis is oftentimes accomplished in a photocatalysis approach^[3 17] based on non-molecular oxides.



Scheme 50. Mono- and dicationic bismuth catalysts in deoxygenation, hydrosilylation, and polymerization reactions.

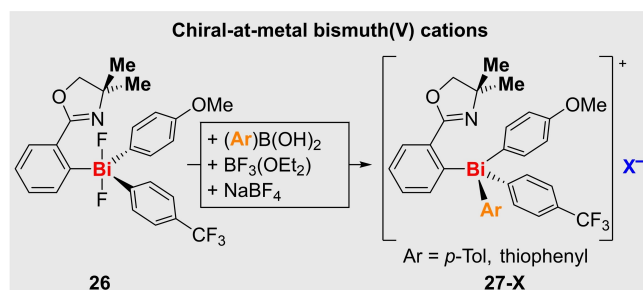
However, it has been shown in a recent study that Bi_2O_3 can act as a pre-catalyst for the formation of soluble, molecular species like $[\text{Bi}_x\text{Br}_y]^{q-}$ which are the true catalysts.^[318] Additionally, heterogeneous photocatalysts based on molecular halogenido bismuthates have been investigated in the context of metal halide perovskite semiconductors.^[319] Examples include $\text{Cs}_3\text{Bi}_2\text{I}_9$,^[320] $\text{MA}_3\text{Bi}_2\text{I}_9$,^[321] and (3-ethylbenzo[d]thiazol-3-ium) $_4\text{Bi}_2\text{I}_{10}$,^[322] which were used for photocatalytic CO_2 reduction in the presence of water to methane and CO, organic pollutant degradation, and hydrogen generation from hydroiodic acid. One of the major challenges in this field is the identification of the catalytically

active species. The formation of soluble species and surface alterations like the formation of BiOX shells can be difficult to identify and are likely to contribute to the catalytic activity in some cases.

Electrocatalysis. Bismuth-containing electrode materials such as in situ deposited Bi⁰, atomically thin bismuthene layers, bismuth oxide nanosheets, BiOCl nanosheets, and Bi/Mo bimetallic chalcogenides have been applied successfully in the field of electrocatalysis. Examples include the electrochemical reduction of CO₂ to give CO, (HCO₂)[−], or H₃COH selectively and with high Faradaic efficiencies.^[323,324] Driving forces for these approaches are the tunability of the electrode material, the possibility to realize moderate overpotentials,^[325] and the replacement of expensive electrode materials such as silver and gold.^[324] In the electron transfer steps of these reactions, charged bismuth compounds can be expected to play an important role, but are inherently difficult to characterize, since even the characterization of the neutral electrode materials can be challenging.

4.5. Chirality in bismuth(V) cations

The synthesis of bismuth(V) cations with four different substituents has been reported.^[83,84] In addition to the boron-mediated synthetic route (Scheme 51), a tin-based procedure is also viable. The bismuth atom in compounds such as **27-X** is a stereogenic center. Direct evidence for the bismuth-centered chirality in cations of type [BiAr¹Ar²Ar³Ar⁴]⁺ (e.g. through the formation and separation of diastereomers by introduction of a chiral counteranion) could not be delivered to date. The diastereotopic nature of the methyl groups in the oxazolyl substituent in **27-X** served as an indirect proof of the chirality of these compounds. The inversion barrier in **27-X** has been shown to depend on the polarity of the solvent and the nature of the counteranion, with weakly coordinating anions and polar solvents leading to higher energy barriers. In NMR spectroscopic investigations, inversion barriers of >23 kcal mol^{−1} and >21 kcal mol^{−1} have been approximated for **27-BF₄** (with Ar = *p*-Tol) in 1,2-dichlorobenzene and pyridine, respectively.^[83]



Scheme 51. Examples of chiral bismuth(V) cations; X = Cl, Br, I, OTs, BF₄.

4.6. Absorption and emission behavior in molecular bismuthate(III) anions

The specific absorption behavior of bismuthates has been utilized for more than 150 years. In 1872, Georg Dragendorff reported a reagent prepared from bismuth oxynitrate, tartaric acid and potassium iodide.^[326] When the reagent is mixed with alkaloids or other tertiary amines, the amine is protonated to form an ammonium salt [NHR₃]⁺, which reacts with the iodido bismuthate complexes in the reagent to form insoluble salts of nominal composition [NHR₃][BiI₄]. Each specific alkaloid results in a different color, allowing for their identification in forensic chemistry. Dragendorff's reagent is still used today, mainly as a stain in thin layer chromatography.^[326]

Naturally, the identity of the ligand in a specific bismuthate has a significant influence on the absorption properties, and thus the optical band gap and color of the resulting compound. For example, chlorido bismuthates are typically colorless, bromido bismuthates yellow and iodido bismuthates orange or red.^[327] Initial studies of the specific nature of the transitions involved in these absorption phenomena, as well as the broad emission that is observed in some cases, were conducted nearly forty years ago.^[328] Depending on the specific complex, one or several absorption and emission mechanisms may be identified. Metal-centered (MC) transitions were initially explored for Bi³⁺ ions doped into oxide hosts.^[329] They can be derived from those found in the free Bi³⁺ ion and other *ns*² ions. The ground state is 6s² (¹S₀) and the excited state is 6s¹6p¹ (³P₀, ³P₁, ³P₂ and ¹P₁). Marked absorption is observed for the spin-allowed transition from ¹S₀ to ¹P₁ (A band) and the transition from ¹S₀ to ³P₁ (C band), which is partially allowed due to spin-orbit coupling. Some authors also discuss the presence of a transition from ¹S₀ to ³P₂ (B band).^[245] In complexes such as [BiX₆]^{3−} (X = Cl, Br, I), ligand-to-metal charge transfer (LMCT) is observed in addition to MC transitions, complicating band assignment.^[330] In other cases, such as Hphen[Bi₂(HPDC)₂(PDC)₂(NO₃)₃·4H₂O (PDC = 2,6-pyridinedicarboxylate, phen = 1,10-phenanthroline), the bismuth atom can facilitate intersystem crossing and subsequently the observation of long-lived organic phosphorescence in the phenanthroline cation.^[331] When electron-poor ligands such as 2,2'-bipyridine (bipy) are used, for example in [BiCl₄(bipy)][−], metal-to-ligand charge transfer (MLCT) can be observed.^[332] Finally, self-trapped exciton (STE) emission, a luminescence phenomenon initially studied in alkali metal halides^[333] has been identified in halogenido bismuthates as well, for example in a compound featuring [Bi₂Cl₁₁]^{5−} ions,^[334] and is currently receiving broad attention.^[335] Here, excitons create a transient lattice defect which acts as a trap. This can result in a broad and strongly Stokes-shifted luminescence band and materials suitable for white-light generation. Overall, the mechanisms behind absorption and emission phenomena in bismuthates are quite varied, and it is often difficult to make assignments with certainty unless detailed spectroscopic and quantum chemical studies are conducted.

In addition to emission phenomena or thermal relaxation, a third pathway, photoreactivity, can be found in some bismuthates. For example, the formation of X_3^- and elemental bismuth is observed when bromido or iodido bismuthates are photoexcited in solution.^[245,333] Mechanistic details of the photoexcitation of $[BiI_6]^{3-}$ have been the subject of two recent studies,^[333] elucidating the initial formation of a bismuth-coordinated $(I_2)^{\bullet-}$ radical.

In a small number of compounds, additional optical phenomena can be observed. Many iodido bismuthates such as $[Co(1,10\text{-phen})_3][Bi_3I_{11}]$ (1,10-phen = 1,10-phenanthroline) show a distinct thermochromism, changing their color continuously upon cooling from dark red at room temperature to light orange at 77 K.^[239] In compounds where alkylviologens such as *N,N'*-dimethyl-4,4'-bipyridinium are used as cations, photochromism upon irradiation with UV light can be observed. For example, colorless crystals of $[HBzV]_2[Bi_2Cl_{10}]$ ($HBzV^{2+}$ = 1-Benzyl-4,4'-bipyridine-1,1'-dium) turn green upon irradiation, while heating to 100 °C returns the crystals to their original color.^[338]

4.7. Semiconducting properties

In addition to photocatalysis, the semiconductor properties of bismuthates, especially halogenido complexes, have been broadly explored for different uses. While the exploration of molecular iodido bismuthates for the use in solar cells has remained challenging and has been lagging behind lead halide perovskites to date,^[339] successful applications include the use in memristors,^[340] supercapacitors,^[341] photodetectors,^[342] and radiation detectors.^[343]

4.8. Material Synthesis

Cluster molecules have long been seen as intermediates on the way from molecules to materials. This has been reflected in the use of Ge Zintl anions to generate different, and new, modifications of Ge materials.^[308,309b,344] Currently, the only report where this principle has been considered with bismuth clusters, cationic or anionic, is by the electrochemical oxidation of bismuth to bismuthene via Bi_2^{2-} .^[311] In situ Raman spectroscopic, ESI-MS and GC-MS measurements identified the presence of Bi_2^{2-} before it was oxidized to the final bismuthene product. It was found that bismuthene prepared in this way displayed excellent electrochemical properties upon sodiation of the material, with stability and performance far superior to that of amorphous Bi nanoparticles. However, the nature of the electrolyte used in the fabrication process had a considerable effect on the properties of the material, with tetraethylammonium salts leading the way in terms of electrochemical performance compared with other alkylammonium salts. Other bismuth clusters would potentially show the same usefulness in this regard, however due to their limited accessibility this remains an open question.

4.9. Photoluminescence

As bismuth clusters, both anionic and cationic, are molecules containing only bismuth atoms, the properties inherent to the metal and bulk solid are equally transferred to these compounds. Thus, researchers aim to take advantage of the optical properties of this element in order to generate chemically and thermally stable materials, which may be exploited in applications such as sensors.^[345] The photoluminescent properties of these materials are reflected in the photoluminescent properties of bismuth clusters, which can be viewed as model compounds that can shed light onto the mechanisms of these phenomena in material systems. Only three clusters have been investigated for photoluminescent properties to date, again due to a lack of accessibility of other bismuth clusters, Bi_5^{3+} , Bi_8^{2+} and Bi_2^{2-} .^[346] All three have been shown to be NIR emitters. Crystals containing Bi_5^{3+} and either $(GaCl_4)^-$ or $(AlCl_4)^-$ as counterions showed slightly different behaviors, however this was partially attributed to possible defects or very minor impurities on the surface of the crystals due to the crystallization process. Two excitation-emission regions were observed for the Bi_5^{3+} cation with excitation maxima of 530 and 800 nm, and a further ultrabroad emission ranging between 1000 and 2700 nm. Assigning the processes that give rise to these bands has not been fully achieved owing to limitations in the quantum chemical packages used for the calculations. Measurements recorded on a sample of $Bi_8(AlCl_4)_2$ displayed a single broad emission centered around 1180 nm, however the presence of a tail in the spectra was attributed to a minor impurity of $Bi_5(AlCl_4)_3$. Further investigation into the reflectance spectra of both $Bi_5(AlCl_4)_3$ and $Bi_8(AlCl_4)_2$ allowed for a comment on the composition of the $Bi_8(AlCl_4)_2$ sample, and the conclusion drawn that the NIR emission behavior was attributable to both Bi_5^{3+} and Bi_8^{2+} . $[K(222\text{-crypt})]_2Bi_2$ displayed an emission peak at 1190 nm with two notable shoulders determined by Gaussian decomposition to be at 1047 and 1331 nm.^[137] These emissions were found to be of lower energy compared to the corresponding absorption energies (990, 1090, 1273 nm), attributable to a nonradiative decay of excess vibrational energy. The NIR luminescence was calculated to arise from spin-forbidden transition between three $^1\Sigma$ singlet excited states to the $^3\Pi$ ground or first two excited $^3\Pi$ states, however could only be considered as an approximation as it was not completely consistent with the recorded spectra.

Generally, changes are seen when going from extended bulk phases to molecules (both within a solid or in solution), owing to the transition from extended band structures to molecular orbital schemes with discrete levels of the electronic energy states. It is obvious that charges of molecular species must have an impact on their optoelectronic properties, as the occupation or vacancy of a corresponding molecular orbital is directly correlated to the excitation and emission behavior of that molecule. In this regard, the development of new charged bismuth cluster compounds can help to fine-tune the luminescence characteristics.

5. Summary and outlook

Charged molecular bismuth compounds have increasingly been identified as attractive target molecules in recent years. It has been realized that turning neutral compounds into well-defined ionic species is a powerful tool to modulate their characteristics. Since the introduction of Coulomb interactions touches the fundamental aspects of molecular interactions, this strategy can be exploited to make an impact on a broad spectrum of properties. This includes i) the accessibility, ii) physico-chemical properties (melting point, solubility), iii) coordination chemistry (increasing coordination chemical complexity, aggregation), iv) bonding (new structural motifs based on low-valent species, hetero-aromaticity, bismuth-carbon multiple bonding, and heavy p-block metal-only-Lewis pairs), v) and chemical properties (Lewis acidity, reversible bond formation/cleavage) of bismuth compounds.

In the hands of dedicated synthetic chemists, these strategies have given new spirit to seemingly established fields such as monocationic organobismuth complexes and inorganic bismuthates and granted access to exciting new classes of compounds such as charged low-valent complexes and charged clusters containing bismuth as a key element. It is especially important to point out that the recent developments centered around charged bismuth species span a broad range of compounds—from bismuth atoms in organic ligand environments through bismuth atoms surrounded by inorganic ligands all the way to bismuth clusters. This has inevitably given new impulses to diverse fields of research including CH activation, small molecule activation, Lewis acid design, catalytic applications, concepts in catalysis, and materials science.

It is anticipated that the summary of well-established and state of the art synthetic strategies for the synthesis of charged bismuth compounds and the analyses of their distinct physico-chemical properties and unique characteristics in structure, bonding, and reactivity will be a valuable guideline and source of inspiration for researchers aiming to exploit the fascinating properties of charged bismuth compounds.

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Conflict of Interest

The authors declare no conflict of interest.

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