



## Review

## Coordination chemistry of homoatomic ligands of bismuth, selenium and tellurium

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## Contents

1. Introduction.....	1
2. Bismuth.....	2
2.1. Uncharged or anionic clusters.....	2
2.2. Polycations as ligands and hosts.....	2
3. Selenium and tellurium.....	5
3.1. Polycationic ligands.....	6
3.2. Polyanionic ligands.....	7
3.3. Uncharged ligands.....	7
4. Resume.....	8
Acknowledgements.....	9
References.....	9

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## ABSTRACT

Multi-centre-bonds as well as conventional two-centre two-electron bonds are the basis for charged or uncharged homoatomic molecules of the heavy main-group elements bismuth, selenium and tellurium. In many cases these homoatomic species are not fairly isolated in the structures but make use of their paired or unpaired p-electrons and, if available, of their  $\pi$ -systems to establish (strong) heteropolar covalent donor bonds to metal cations. Such coordination can have retroactive effect on the bonding inside the ligand and even stabilises new homonuclear species such as the  $\text{Bi}_{10}^{4+}$  antiprism or the  $\text{Te}_{10}$ -tricycle. Moreover, these homoatomic ligands can be highly connecting, since all of their atoms are potential donors. Here we give an overview of recent developments in the coordination chemistry of oligo- and polyatomic selenium, tellurium and bismuth ligands.

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## 1. Introduction

The virtually infinite chemistry of carbon eclipses the diversity of the chemistry of all other elements. The position in the first eight-membered period with four valence orbitals filled by four electrons offers the widest range of options for homoatomic covalent bonding. For the likewise valence electron-rich but heavier main group elements of the p-block the ability to form stable covalent two-centre two-electron (2c2e) bonds declines and

multi-centre-bonding becomes an attractive alternative, as is demonstrated by the metallic  $\beta$ -form of tin and the metal lead. Using both options, localised 2c2e bonds as well as delocalised multi-centre bonds, makes the chemistry of elements such as bismuth, tellurium or selenium surprisingly rich and somewhat unpredictable. This holds especially if their oxidation states do not deviate much from zero, i.e. for low-valent compounds with homoatomic bonds between these elements. Besides, uncharged molecules with or without organyl or organoheteryl groups, a multitude of polyanions and the less abundant polycations define the field. In many cases these homoatomic species are not fairly isolated in the structures, but make use of their lone-pairs to establish heteropolar covalent donor bonds to metal atoms. Since all of their atoms are potential donors, these homoatomic ligands

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can be highly connecting. In the following we want to give an overview of recent developments in the coordination chemistry of oligo- and polyatomic selenium, tellurium and bismuth ligands. We will exclude intermetallic and organometallic compounds although there are no inherent borderlines. For aspects that lead away from the narrow scope we will give references to some of the numerous reviews and countless original articles that are more or less associated with the topic of this review.

## 2. Bismuth

### 2.1. Uncharged or anionic clusters

Bismuth and platinum metals (*M*) have rather similar electronegativity values. By acquiring electrons, the latter can complete their filling of the d-shell and formal electron counts of 16 or 18 are achieved. Quantum-chemical calculations show that such *M*–Bi bonds are slightly polar with bismuth carrying a small positive partial charge.

Typical examples are cuboctahedral cluster anions of the type  $[M\text{Bi}_6X_{12}]^{n-}$  (Fig. 1a). The transition metal atom (*M* = Ru, Rh, Ir, Pt) centres an octahedron of six bismuth atoms. These are in (more or less) square-planar coordination by halogen atoms (*X* = Cl, Br, I) that bridge the edges of the octahedron and thereby define the vertices of a cuboctahedron. Interatomic distances (*M*–Bi 265 to 275 pm) and quantum-chemical calculations indicate that the *M*–Bi interactions are strong covalent 2c2e bonds. Direct Bi–Bi bonds are not present (Bi...Bi > 380 pm) and thereby these bismuth clusters differ from isomorphous filled  $M_6X_{12}$  clusters known from the chemistry of metal-rich halides of d- and f-elements [1,2]. The bonding mode of the bismuth atoms in the  $[M\text{Bi}_6X_{12}]^{n-}$  cluster is quite similar to that of the peripheral bismuth(II) atoms in the  $^{1\infty}[X_{4/2}\text{Bi}^{\text{II}}\text{Bi}^{\text{I}}\text{Bi}^{\text{I}}\text{Bi}^{\text{II}}X_{4/2}]$  strands in bismuth monobromide [3] or monoiodide [4] (Fig. 1b). The square coordination by *X* anions (Bi–*X* 280 to 310 pm) is based on linear 3c4e bonds, while the remaining electron in the orthogonal 6p-orbital is involved in *M*–Bi bonding. Hence, the bismuth atoms are one-electron donors to the transition metal atom. By ascribing the oxidation state +II to the bismuth atoms, the  $M^{\text{II}}_6X_{12}$  cluster shell is formally uncharged and the overall charge of the cluster is projected on the central *M* atom. In the case of  $[\text{PtBi}_6X_{12}]^{2-}$ , several compounds are known that leave no doubt about the total cluster charge [5,6]. The electron count for platinum in the oxidation state –II is thus 10 (valence electrons of the atom) + 2 (charge) + 6 (from 6 Bi) = 18. In fact, all quantum-chemical methods for partitioning the electron density assign a small negative charge to the platinum atom, which therefore has to be called a platinumide. Similar results are obtained for other *M* atoms, such as ruthenium, rhodium or iridium.

The  $[M\text{Bi}_6X_{12}]^{n-}$  clusters can be regarded as cut-outs of the NaCl structure type, yet with strong (heteropolar) covalent bonding and optimised electron count. It is not surprising that these quite stable units turn up in many compounds with varying *M*, *X* and charge. An expanded version is also known, the  $[M\text{Bi}_6X_{13}]^{(n+1)-}$  cluster, which bears an additional  $\mu_3$ -bridging *X* anion above one face of the bismuth octahedron (Fig. 1c) [7,8]. In some cases the plausible charge of such an anionic cluster has been used to derive the less predictable counter-charge of a polycation in the structure.

In most cases, the cuboctahedral clusters are widely isolated in the crystal structures and therefore can be regarded as non-coordinating anions that provide charge balance for the neighbouring cations, which are typically bismuth polycations. In the case of the counter ions are simply  $\text{Bi}^{3+}$  cations, coordinating as well as non-coordinating situations have been found. In monoclinic  $\text{Bi}_2[\text{PtBi}_6\text{Br}_{12}]_3$  and triclinic  $\text{Bi}_2[\text{PtBi}_6\text{I}_{12}]_3$  three cluster anions are concatenated into uncharged linear trimers by two

octahedrally coordinated  $\text{Bi}^{3+}$  cations ( $\text{Bi}^{3+}\text{--Br} \geq 279$  pm;  $\text{Bi}^{3+}\text{--I} \geq 300$  pm; Fig. 1d) [6]. In rhombohedral  $\text{Bi}_2[\text{PtBi}_6\text{Cl}_{12}]_3$  the cluster anions form a pseudo-cubic framework connected by numerous secondary bonds ( $\text{Bi}^{\text{II}}\text{...Cl}$  370 to 385 pm), a so-called (i–a)-bridging [9]. Therein comparatively large cavities are defined by 24 chloride ions and host only weakly bonded  $\text{Bi}^{3+}$  cations on diverse statistically occupied sites ( $\text{Bi}^{3+}\text{...Cl} > 335$  pm) [5].

Up to now, there are only two examples of direct concatenation of  $[M\text{Bi}_6X_{12}]^{n-}$  clusters by bridging. The elimination of two *X* anions (together with their charge) is compensated by sharing four of the *X* anions with adjacent clusters. In the  $^{1\infty}[\text{PtBi}_6X_8X_{4/2}]$  cis-trans cluster chains of  $\text{PtBi}_6\text{Cl}_{10}$  and  $\text{PtBi}_6\text{Br}_{10}$  the cuboctahedral cluster shape is preserved, yet with some distortion (Fig. 1e) [10]. Chemical bonding and the 18-electron-count for the platinum atoms are the same as in the isolated clusters. Despite their high metal content and their polymeric character, the compounds are semi-conducting since all valence electrons are localised in the electron precise clusters.

Similar to the cuboctahedral clusters in many aspects but nevertheless unique is the uncharged molecule  $\text{RhBi}_7\text{Br}_8$  (Fig. 1f) [11]. Therein the rhodium atom is surrounded by seven bismuth atoms in the shape of a pentagonal bipyramid. The apical bismuth atoms are again in square-planar coordination by bromine atoms. The inherent symmetry mismatch between these  $[\text{BiBr}_4]$  squares and the equatorial bismuth pentagon generates a tricky multi-centre Bi–Br bonding situation. Moreover, *ab initio* calculations revealed an unprecedented 5c4e bond in the equatorial bismuth ring (Bi–Bi 320 to 330 pm) [12] which was later discussed as an example of a five-atom Möbius aromatic system with an inverted term scheme compared to the common Hückel aromatic system [13]. The remaining electrons that are neither part of the Bi–Bi bonding system nor transferred to the Br atoms are available for Bi–Rh bonds, yielding again the electron count 18 for the rhodium atom.

### 2.2. Polycations as ligands and hosts

Since the first structural characterisation of a bismuth polycation [14] fifty years ago, this and others were located in many new compounds. Despite various synthetic approaches such as chemical gas-phase transport, reactions in high-temperature melts, in liquid  $\text{SO}_2$ , in benzene or lately in ionic liquids the diversity of species remained surprisingly limited. Today, seven different homoatomic bismuth polycations are known:  $\text{Bi}_2^{4+}$ ,  $\text{Bi}_5^+$ ,  $\text{Bi}_5^{3+}$ ,  $\text{Bi}_6^{2+}$ ,  $\text{Bi}_8^{2+}$ ,  $\text{Bi}_9^{5+}$  and  $\text{Bi}_{10}^{4+}$  (Table 1, Fig. 2). In the case of antimony, only  $\text{Sb}_8^{2+}$  has been isolated in the form of its tetrachloridogallate salt [15]. Except for  $\text{Bi}_2^{4+}$ , all bismuth polycations are polyhedral clusters.

Very recently, the first anionic bismuth polyhedron, the Zintl anion  $\text{Bi}_{11}^{3-}$ , has been isolated [16]. Besides the observation of anionic bismuth Zintl ions, such as  $\text{Bi}_7^{3-}$ , in the gas-phase were reported [17]. The newly discovered chain  $\text{Bi}_4^{6-}$  is the bismuth polyanion with the highest known charge per atom obtained from solution [18]. Moreover, a large variety of organobismuth compounds with homonuclear bonds are known [19,20].

Typically for the chemistry of bismuth in oxidation state +III or lower, only the three 6p electrons are used (and counted) for bonding, while the two electrons in the 6s form an inactive lone-pair. Modifications of Wade's rules, which were originally developed for hydroboranes [21,22], help to understand the chemical bonding and to correlate electron count with shape [23]. Formal replacement of *n* B–H *exo*-bonds by *n* Bi 6s lone-pairs also results in  $2n + m$  skeletal electrons (SE), i.e. the optimum electron count for *n*-atomic *closo* (*m* = 2), *nido* (*m* = 4), or *arachno* polyhedra (*m* = 6). In fact, electron count and cluster shape match for the square pyramid  $\text{Bi}_5^+$  (*nido*, 14 SE), for the trigonal bipyramid  $\text{Bi}_5^{3+}$  (*closo*, 12 SE), the opened octahedron  $\text{Bi}_6^{2+}$  (*nido*, 16 SE), the square antiprism  $\text{Bi}_8^{2+}$

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