

Polynuclear bismuth selenolates: rings *en route* to clusters

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BiBr_3 reacts with the silylated selenium reagent Se(Ph)-SiMe_3 in the presence of tertiary phosphines to yield polynuclear bismuth selenolate complexes that contain both terminal and bridging Se(Ph) ligands.

Despite the explosive growth in the chemistry of transition metal-chalcogenolate-polynuclear chemistry,¹ related developments in XV–XVI molecules of the heavier main group elements remain hitherto unprobed. In contrast to this absence of cluster chemistry, investigations into the synthesis and characterisation of solid state bismuth-selenides and -tellurides are numerous due to the materials' novel thermoelectric properties.² Bismuth-selenolate and -tellurolate complexes offer potential as low-temperature single-source precursors to related semiconductor materials.³ Our interest in the use of alkyl- and aryl-chalcogenolate ligands in stabilising polymetallic frameworks prompted us to begin an investigation into the polynuclear chemistry of bismuth and our initial findings are described herein. The synthesis and structural characterisation of the first examples of polynuclear bismuth-selenolates, $[\text{Bi}_4(\mu\text{-SePh})_5(\text{SePh})_8]^-$ **1** and $[\text{Bi}_6(\mu\text{-SePh})_6(\text{SePh})_{10}\text{Br}_2]^-$ **2**, are reported in this communication.

Se(Ph)SiMe_3 is an extremely useful reagent for the delivery of the PhSe^- moiety to transition and Group XI–XII metal centres *via* the formation of Me_3SiX ($\text{X} = \text{Cl}, \text{OAc}, \text{etc.}$).^{4–6} In an analogous vein, it has been demonstrated recently that silylated phosphines and arsines react with bismuth halides to yield solid BiP and BiAs materials^{7,8} and $\text{Bi(NMe}_2)_3$ has been shown to react with $\text{Te(SiMe}_3)_2$ to yield Bi_2Te_3 .⁹ To date however, it has not proven possible to isolate intermediates *en route* to the extended solids.

Tertiary phosphines coordinate readily to Bi(III) centres to yield a variety of neutral phosphorous donor complexes of BiBr_3 .¹⁰ The ability of R_3P ligands to thus stabilise reaction intermediates between bismuth salts and silylated chalcogen could allow for polynuclear species to be generated. When solutions of $\text{BiBr}_3:\text{P}^*\text{Pr}_3$ (1:2) are treated with three equivalents of Se(Ph)SiMe_3 and allowed to warm slowly to room temperature, a viscous red oil is formed. The oil can be taken up into THF–ethanol mixtures from which red/orange crystals of $[\text{Bi}_4(\text{SePh})_{13}]^-$ **1** form in moderate yield as the $[\text{HP}^*\text{Pr}_3]^+$ salt.† A single crystal X-ray analysis‡ provided full structural details (Fig. 1). There are two crystallographically independent yet chemically identical molecules in the asymmetric unit, and discussed bond lengths and angles refer to molecule 1. Complex **1** consists of four Bi centres, five bridging SePh groups and eight terminal Bi-SePh bonds. Each bismuth atom is bonded to two terminal SePh moieties (Bi-Se : 2.646(4)–2.737(4) Å). These distances are similar to those reported for the monomeric complex $[\text{2-(4,4-Me}_2\text{COCCH}_2\text{CN)C}_6\text{H}_4\text{Se}]_2\text{Bi}$ in which the six coordinate bismuth centre displays distorted octahedral geometry.¹¹ Each Bi in **1** is five coordinate and the overall geometry is close to square pyramidal with bismuth possessing a stereochemically active lone pair. The Se-Bi-Se angles are clustered about 90° (81.43(9)–98.31(11)°) and 180° (167.67(11)–173.54(10)°), the greatest deviations from idealized geometry associated with $\mu\text{-Se-Bi-}\mu\text{-Se}$. The lone pairs on the four bismuth centres are each oriented in the same direction relative to the Bi_4 (mean

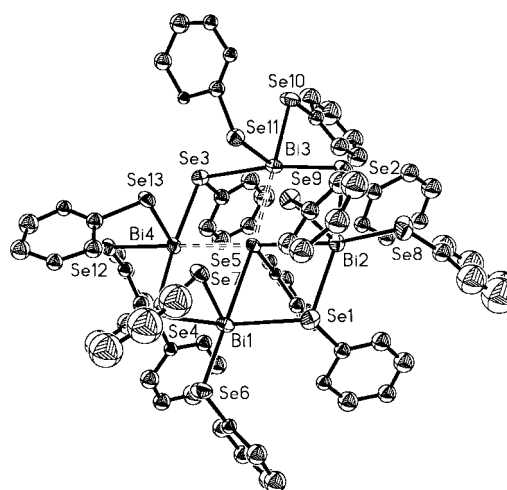


Fig. 1 The molecular structure of $[\text{Bi}_4(\mu\text{-SePh})_5(\text{SePh})_8]^-$ **1** (molecule 1), isolated as its $[\text{HP}^*\text{Pr}_3]^+$ salt, illustrating the near planar arrangement of the four Bi and five $\mu\text{-Se}$ centres. Selected bond lengths (Å) and angles (°): Se-C 1.87(3)–1.98(3), Bi1-Se7 2.657(3), Bi1-Se6 2.731(3), $\text{Bi1-}\mu\text{-Se}$ 2.890(3)–3.248(3), Bi2-Se9 2.646(4), Bi2-Se8 2.737(4), $\text{Bi2-}\mu\text{-Se}$ 2.974(3)–3.277(3), Bi3-Se11 2.649(3), Bi3-Se10 2.696(3), $\text{Bi3-}\mu\text{-Se}$ 2.984(4)–3.312(3), Bi4-Se13 2.655(3), Bi4-Se12 2.696(3), $\text{Bi4-}\mu\text{-Se}$ 2.962(3)–3.337(3); Bi1-Se1-Bi2 99.62(8), Bi1-Se5-Bi2 92.4(1), Se6-Bi1-Se7 93.0(1), Bi1-Se7-C 102.5(10), Se1-Bi1-Se7 86.4(1), Se1-Bi2-Se9 91.8(1), Se1-Bi2-Se2 167.7(1), Se2-Bi3-Se3 167.7(1), Se3-Bi4-Se4 168.88(9), Se1-Bi1-Se4 170.11(9).

deviation = 0.037 Å) plane. Four phenylselenolate ligands ($\text{Se7}, 9, 11, 13$) are *trans* to the lone pairs, with their C_6H_5 rings tilted away from the centre of the molecule. The five phenyl rings of the $\mu\text{-SePh}$ ligands lie on the opposite side of this Bi_4 framework. The bridging selenium atoms Se1-Se5 together with the four bismuth centres form a near planar (mean deviation = 0.085 Å) array. The Bi-Se bonding distances of the four “perimeter” $\mu\text{-SePh}$ groups in **1** (Se1-Se4) are markedly longer *versus* their terminal counterparts, ranging from 2.890(3)–3.172(4) Å. The Bi-Se5 distances are longer still (3.248(3)–3.337(3) Å) and each of these distances is greater than the sum of the Bi and Se covalent radii (2.69 Å).¹² The resultant geometry is such that the four Bi centres are separated by ≈ 4.6 Å.

If a similar reaction procedure for the preparation of **1** is repeated with PPh_3 , a completely different structural type is isolated with the formation of $[\text{Bi}_6(\mu\text{-SePh})_6(\text{SePh})_{10}\text{Br}_2]^-$ **2**. Complex **2**, which crystallises about an inversion centre in $P\bar{1}$, consists of a 12 membered Bi_6Se_6 ring that encircles two Br atoms ($\text{Bi}\cdots\text{Br} = 3.269(2)$ – $3.336(2)$ Å) (Fig. 2). As in **1**, the terminal Bi-Se bonds (2.666(2)–2.703(2) Å) are shorter than the $\mu\text{-Se}$ bridges (2.767(2)–3.110(2) Å). Unlike in **1** however, two of the bismuth centres in **2** (Bi3 and Bi3A) display but three Bi-Se bonds and exhibit the shortest Bi-Br distance. It is interesting to note that the three Bi-Se bonds at these centres vary little in length (terminal *versus* bridging, Bi3-Se6 : 2.666(2); Bi3-Se8 : 2.774(2); $\text{Bi3-}\mu\text{-Se2A}$: 2.767(2) Å) in contrast to the disparate distances at the four other Bi sites. The Se-Bi3-Se angles however vary little from 90° . The relative orientation of Se3/3A

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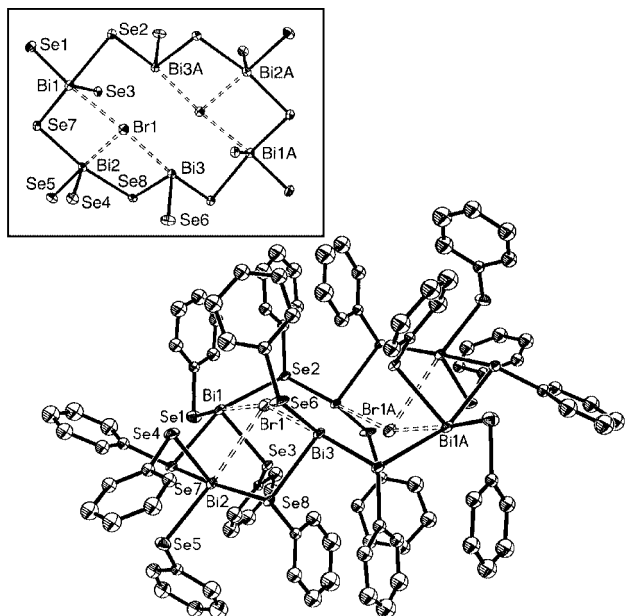


Fig. 2 The molecular structure of $[\text{Bi}_6(\mu\text{-SePh})_6(\text{SePh})_{10}\text{Br}_2]$ **2**. Selected bond lengths (Å) and angles (°): Bi1–Se1 2.670(2), Bi1–Se3 2.703(2), Bi1–μ-Se2 3.110(2), Bi1–μ-Se7 2.820(2), Bi1–Br1 3.279(2), Bi2–Se4 2.650(2), Bi2–Se5 2.663(2), Bi2–μ-Se7 3.009(2), Bi2–μ-Se8 2.999(2), Bi2–Br1 3.336(2), Bi3–Se6 2.666(2), Bi3–Se8 2.774(2), Bi2–μ-Se2A 2.767(2), Bi2–Br1 3.269(2); Se1–Bi1–Se3 101.34(6), Se1–Bi1–Se7 88.84(6), Se3–Bi1–Se7 80.41(5), Se1–Bi1–Se2 85.08(5), Se3–Bi1–Se2 79.60(5), Se7–Bi1–Se2 157.50(5), Se4–Bi2–Se5 93.11(6), Se4–Bi2–Se8 89.53(5), Se5–Bi2–Se8 95.19(6), Se4–Bi2–Se7 98.12(5), Se5–Bi2–Se7 91.87(6), Se8–Bi2–Se7 169.30(5), Se6–Bi3–Se2A 189.31(6), Se6–Bi3–Se8 87.46(5), Se2A–Bi3–Se8 91.30(5), Bi3A–Se2–Bi1 92.65(5), Bi1–Se7–Bi2 94.63(5), Bi3–Se8–Bi2 101.26(5).

(bonded to Bi1/1A) is unusual in that it clearly distorts inwards towards the centre of the Bi₆Se₆ ring such that Se1–Bi1–Se3 is 101.34(6)°, whilst Se1–Bi1–Se7 and Se1–Bi1–Se2 are 88.84(6) and 85.08(5)°, respectively (*i.e.* close to orthogonal). In contrast, the related angle Se4–Bi2–Se5 is 93.11(6)°. The Se2...Se8 and Se7...Se7A distances are 8.350 and 12.283 Å, respectively. Although there is no direct structural relationship between **1** and **2**, the structure of **2** can be considered as two coplanar Bi₃(μ-Se)₂ units linked by Se2 and Se2A (Fig. 2, insert).

This entry into the quasi two-dimensional polynuclear chemistry of bismuth-chalcogenolates using coordinatively flexible, selenolate ligands opens the door to a development of this area of cluster research. The wealth of chemistry in related, lighter congeners of bismuth-Group XVI complexes suggests a rich and varied chemistry.¹³ We are actively pursuing this avenue of research.

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Notes and references

† Preparation of **1**: A 0.32 g (0.71 mmol) sample of BiBr₃ was suspended in 35 mL of diethyl ether with 1.4 mmol of P⁺Pr₃ at 0 °C, and cooled to –60 °C. 0.53 mL (2.14 mmol) of Se(Ph)SiMe₃ was added and the yellow suspension was warmed slowly to room temperature to yield a clear orange solution, a red viscous oil and an insoluble black material with a metallic luster. The solvent was removed *in vacuo* and the oil was dissolved in 18 mL of EtOH–THF (2:1), filtered and stored at –5 °C to yield 0.12 g (22%) of red/orange needles of [Bi₄(SePh)₁₃]₂[HPP⁺Pr₃]. A similar procedure using PPh₃ and 2.5 equivalents of Se(Ph)SiMe₃ yielded red crystals of [Bi₆(μ-SePh)₆(SePh)₁₀Br₂] **2** in 25% yield. Anal calc. (found) for [C₇₈H₆₅Bi₆Se₁₃][HPC₉H₉]₂·0.5THF **1**: %C 34.9 (34.5); %H 2.98 (2.49). For C₉₆H₈₀Bi₆Se₁₆Br₂ **2**: %C 29.5 (29.5); %H 2.06 (1.77).

† Crystal data for **1**: [C₇H_{6.5}Bi₄Se₁₃][HPC₉H₂₁]-0.5THF, red/orange needle, 0.07 × 0.09 × 0.27 mm, *M* = 3061.99, triclinic, space group *P* $\bar{1}$, *a* = 13.9032(7), *b* = 23.4916(13), *c* = 30.3394(11) Å, *a* = 79.858(3), *β* = 83.279(3), *γ* = 78.716(2)°, *V* = 9530.7(8) Å³, at 200 K, *Z* = 4, ρ_{calc} = 2.134 g cm⁻³, μ = 12.387 mm⁻¹, $2\theta_{\text{max}}$ = 39.6, 17094 independent reflections measured (*R*_{int} = 0.123) on an Enraf-Nonius Kappa-CCD diffractometer. The structure was solved by direct methods and refined on *F*² using SHELXL software.¹⁴ All P, Bi and Se atoms were refined anisotropically, all C atoms isotropically to yield *R* = 0.0799, *wR*₂ = 0.1907, GoF = 0.976 for 9413 data [*F*_o > 2σ(*F*_o)].

Crystal data for **2**: [C₉₆H₈₀Bi₆Se₁₆Br₂], red plate, 0.27 × 0.20 × 0.06 mm, *M* = 3910.66, triclinic, space group *P*1̄, *a* = 11.5913(7), *b* = 14.9695(16), *c* = 16.6252(18) Å, *a* = 66.260(4), *β* = 83.972(6), *γ* = 81.496(6)°, *V* = 2592.1(4) Å³, at 200 K, *Z* = 1, *ρ*_{calc} = 2.505 g cm^{−3}, *μ* = 16.578 mm^{−1}, 2*θ*_{max} = 42.2°, 5576 independent reflections measured (*R*_{int} = 0.092). The structure was solved and refined on *F*² as for **1** to yield *R* = 0.0484, *wR*₂ = 0.1118, GoF = 0.982 for 4211 data [*F*_o > 4σ*F*_o]. CCDC reference number 186/1887. See <http://www.rsc.org/suppdata/dt/b0/b001417f> for crystallographic files in .cif format.

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