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Preparation, Geometric and Electronic Structures of $[Bi_2Cu_4(SPh)_8(PPh_3)_4]$ with a Bi_2 Dumbbell, $[Bi_4Ag_3(SePh)_6Cl_3(PPh_3)_3]_2$ and $[Bi_4Ag_3(SePh)_6X_3(PPh\textit{i}Pr_2)_3]_2$ (X = Cl, Br) with a Bi_4 Unit

Heino Sommer,[a] Andreas Eichhöfer,[a] Nedko Drebov,[b] Reinhart Ahlrichs,*[b] and Dieter Fenske*[a,c]

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$BiBr_3$ and CuCl react with $S(Ph)SiMe_3$ in thf solution in the presence of PPh_3 to yield $[BiCu_2(SPh)_3Br_2(PPh_3)_3]$ (**1**). The reaction of **1** with 2 equiv. of NaSPh gives rise to $[Bi_2Cu_4(SPh)_8(PPh_3)_4]$ (**2**) containing a Bi_2 dumbbell. In this paper we further report the synthesis and characterization of the new cluster complexes $[Bi_4Ag_3(SePh)_6Cl_3(PPh_3)_3]_2$ (**3**) and $[Bi_4Ag_3(SePh)_6X_3(PPh\textit{i}Pr_2)_3]_2$ [X = Cl (**4**), Br (**5**)]. In the surprisingly formed species **3**–**5** a formal charged Bi_4^{6+} unit is observed. Compounds **3**–**5** were prepared by the reaction of BiX_3 (X = Cl, Br), $AgS\textit{t}Bu$, $Se(Ph)SiMe_3$ and phosphane (PPh_3, $PPh\textit{i}Pr_2$). The structures of the compounds were determined by single-crystal X-ray analysis. Additionally, theoretical investigations were preformed to rationalize the bonding situation in **2**–**5**.

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Introduction

Recently, we reported the preparation and structure of $(PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]$.[1] The ternary bismuth–copper–chalcogenolate anion $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ consists of a branched $[Bi_{10}]$ moiety embedded in a copper–sulfur shell. In this work we study the title compounds by a combined approach of theory and experimental methods, which was used previously[1] and for a series of transition metal complexes of the heavier group 13/15 elements. Examples are $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2$,[2] $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$,[3] $[Cu_{20}Sb_{10}(PCy_3)_8]$,[4] $[Cu_{28}Sb_{12}(PEt_3)_{12}\{Sb(SiMe_3)_2\}_2]$[5] and the largest copper–antimony cluster $[Cu_{45}Sb_{16}(PEt_2Me)_{16}]$ synthesized so far.[6] The structural analysis of some copper–antimony complexes proved to be impossible by X-ray crystallography alone, its structure was determined reliably by a combined approach of DFT calculations and X-ray crystallography.

Up to now only a limited number of molecular cluster compounds containing bismuth, a coinage metal and sulfur or selenium have been synthesized. The $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ anion for example can be prepared by the reaction of $Bi(SPh)_3$ with CuSPh and $S(Ph)SiMe_3$ in the presence of a phosphonium cation. Our approach to metal chalcogenolate clusters generally involves the reaction of a metal salt MX (M = transition metal; X = halide, carboxylate, alkoxide) with a trimethylsilyl derivative of a main group element in the presence of a tertiary phosphane. Herein we reported the synthesis and structure of $[BiCu_2(SPh)_3Br_2(PPh_3)_3]$ (**1**), $[Bi_2Cu_4(SPh)_8(PPh_3)_4]$ (**2**), $[Bi_4Ag_3(SePh)_3Cl_3(PPh_3)_3]_2$ (**3**) and $[Bi_4Ag_3(SePh)_3X_3(PPh\textit{i}Pr_2)_3]_2$ [X = Cl (**4**), Br (**5**)]. Theoretical investigations, described after the discussion of the experiments, were preformed for **2**–**5** to elucidate unusual features of the molecular and electronic structures.

Results and Discussion

The reaction of $BiBr_3$ with CuCl, PPh_3 and $S(Ph)SiMe_3$ in a molar ratio of 1:3:6:6 in tetrahydrofuran (thf) yielded red crystals of $[BiCu_2(SPh)_3Br_2(PPh_3)_3]$ (**1**) (Scheme 1). The elimination of the bromido ligands with NaSPh in a mixture of thf and hexane resulted in the formation of very small black crystals of $[Bi_2Cu_4(SPh)_8(PPh_3)_4]$ (**2**) with a Bi_2^{4+} dumbbell in the molecular centre (Scheme 1).

$$BiBr_3 + 3\,CuCl + 6\,PPh_3 + 6\,S(Ph)SiMe_3 \xrightarrow[\text{thf}]{} [BiCu_2(SPh)_3Br_2(PPh_3)_3]\ (\mathbf{1})$$

$$[BiCu_2(SPh)_3Br_2(PPh_3)_3]\ (\mathbf{1}) + 2\,NaSPh \xrightarrow[\text{thf}]{} [Bi_2Cu_4(SPh)_8(PPh_3)_4]\ (\mathbf{2})$$

Scheme 1. Synthesis of **1** and **2**.

Further chalcogenide-bridged bismuth/coinage metal complexes were prepared by the reaction of $BiCl_3$ with $AgS\textit{t}Bu$ and $Se(Ph)SiMe_3$ in the presence of a tertiary phosphane (PPh_3). From the resulting deep red solution and the

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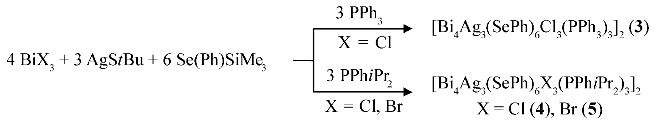
[a] Institut für Nanotechnologie, Forschungszentrum Karlsruhe,
Postfach 3640, 76021 Karlsruhe, Germany
[b] Institut für Physikalische Chemie, Universität Karlsruhe,
Fritz-Haber-Weg 4, 76131 Karlsruhe, Germany
E-mail: reinhart.ahlrichs@chemie.uni-karlsruhe.de
[c] Institut für Anorganische Chemie, Universität Karlsruhe,
Engesserstr. 15, 76131 Karlsruhe, Germany
Fax: +49-721-608-8440
E-mail: dieter.fenske@chemie.uni-karlsruhe.de

brown precipitate, deep red crystals of $[Bi_4Ag_3(SePh)_6Cl_3(PPh_3)_3]_2$ (**3**) were formed after 24 h. The use of $PPhiPr_2$ instead of PPh_3 and BiX_3 (X = Cl, Br) in a similar reaction led to the formation of deep red crystals of structurally related compounds $[Bi_4Ag_3(SePh)_6X_3(PPhiPr_2)_3]_2$ [X = Cl (**4**), Br (**5**) (Scheme 2)].



Scheme 2. Synthesis of **3**–**5**.

The redox reactions leading to the Bi_4^{6+} unit in **3**–**5** are unclear at present. The only assumption we can offer is the intermediate formation of $Bi(SePh)_3$, which through a cleavage of Bi–Se bonds leads to the formation of $Bi_4(SePh)_6$ and $(SePh)_2$, and further reaction with AgS*t*Bu and $Se(Ph)SiMe_3$ yield **3**–**5**.

Compound **1** (Figure 1) crystallizes in the triclinic space group $P\bar{1}$ with one molecule and four thf molecules in the unit cell. The bismuth atom is coordinated by two bromido ligands and three sulfur atoms of the phenylthiolato ligands in a distorted square-pyramidal coordination. The deformation of the pyramid is indicated by the two different

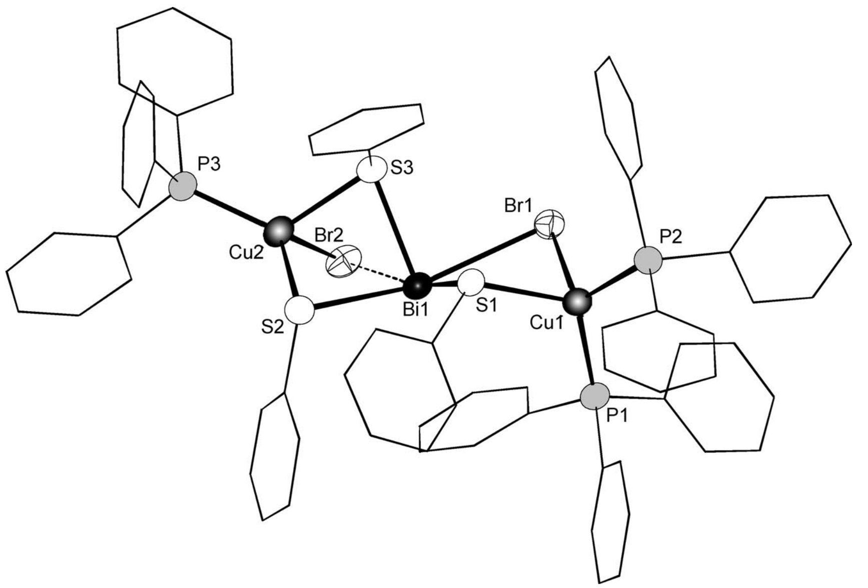


Figure 1. Molecular structure of **1** (50%-ellipsoids). Selected bond lengths [pm] and angles [°]: Bi1–S1 267.0(3), Bi1–S2 269.4(3), Bi1–S2 260.5(2), Bi1–Br1 304.4(2), Bi1–Br2 313.1(2), Bi1–Cu1 371.2(1), Bi1–Cu2 318.5(2), Cu1–S1 238.3(4) Cu1–Br1 255.4(3), Cu2–S2 238.0(4), Cu2–S3 245.4(3), Cu2–Br2 248.6(3), Cu–P 227.9(4)–221.0(1); S–Bi–S 80.6(1)–96.4(1), S–Bi–Br$_{cis}$ 86.5(1)–106.8(1), Br–Bi–Br 107.4(1), S–Cu–P 108.5(1)–120.7(1), S–Cu–Br 86.5(1)–106.8(1).

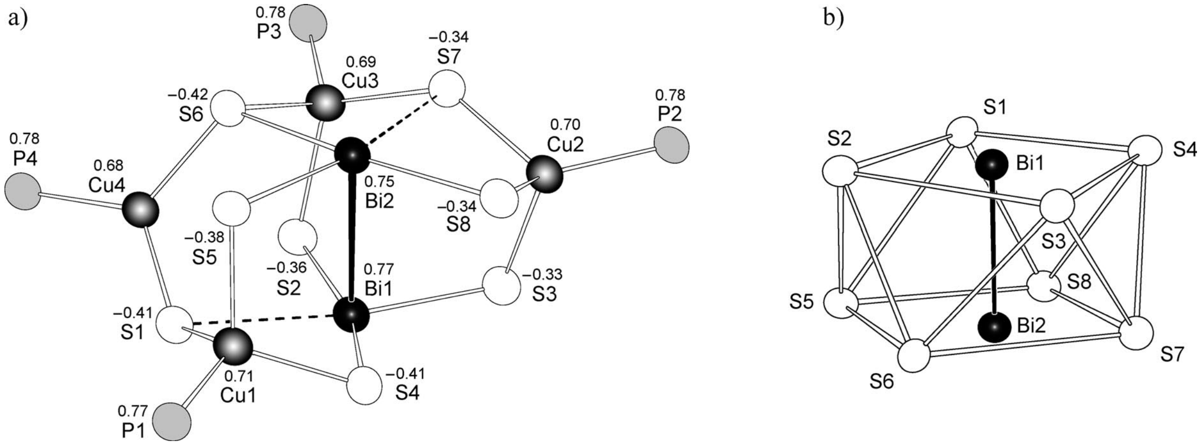


Figure 2. (a) Molecular structure of **2** (50%-ellipsoids, C and H atoms are omitted for clarity). Calculated partial charges are given above the atom labels. (b) S_8 antiprism (schematic polyhedron). Selected bond lengths [pm] and angles [°] (calculated values in brackets): Bi1–Bi2 306.4(10) [311.0], Bi1–S1 307.0(4) [308.6], Bi1–S2 285.9(7) [288.2], Bi1–S3 269.9(4) [274.8], Bi1–S4 276.7(7) [281.8], Bi2–S5 278.1(5) [282.3], Bi2–S6 285,7(6) [293.3], Bi2–S7 298.8(6) [298.5], Bi2–S8 282.8(5) [281.0] Cu1–S1 249.1(1) [249.1], Cu1–S4 236.1(5) [235.6], Cu1–S5 232.6(5) [233.8], Cu2–S3 233.3(5) [235.5], Cu2–S7 249.8(6) [256.4], Cu2–S8 237.1(7) [237.2],Cu3–S2 233.5(5) [234.3], Cu3–S6 243.5(5) [251.5], Cu3–S7 243.9(5) [242.7], Cu4–S1 226.4(1) [229.7], Cu4–S6 226.8(5) [230.1], Cu–P 224.2(7)–225.1(1) [226.4–228.1]; S–Bi–S$_{cis}$ 80.0(2)–109.1(3), S–Cu–S 85.5(3)–117.3(3), S–Cu–P 112.5(2)–122.9(3).

bond lengths [Bi–μ_2-Br 304.4(2)–313.1(2) pm, Bi–μ_2-S 260.5(3)–267.0(3) pm]. Figure 1 displays the distorted tetrahedral coordination of the copper atoms. Cu1 is coordinated by the phosphorus atoms of two phosphane ligands as well as by S1 and Br1, whereas Cu2 is coordinated by one phosphane ligand, two sulfur atoms (S2, S3) and Br2. The non-bonding Bi–Cu distances in **1** [Bi1–Cu2 318.5(2) pm, Bi1–Cu1 371.2(1) pm] are about 40–100 pm longer than those previously reported for the covalent Bi–Cu bond in [$(Me_3Si)_2BiCu(PMe_3)_3$] [274.9(1) pm].[7]

Compound **2** (Figure 2) crystallizes in the monoclinic space group $P2_1/c$ with four molecules together with eight thf solvent molecules in the unit cell. The structure can be described as a distorted S_8 antiprism with a Bi_2 dumbbell [Bi–Bi 306.4(1) pm] in the molecular centre.

The bismuth atoms are coordinated by four sulfur atoms with three shorter bonds [270.1(6)–286.2(1) pm] and a longer one [Bi1–S1 307.1(6) pm, Bi2–S7 299.1(8) pm]. These distances are longer than the sum of the Bi and S covalent radii (250 pm). The Cu1, Cu2 and Cu3 atoms are coordinated by three S atoms and one phosphane ligand in a distorted tetrahedral coordination, whereas Cu4 is coordinated in a distorted trigonal-planar mode by two S atoms and one phosphane ligand.

A similar bismuth–sulfur fragment is observed in the ternary bismuth(II)–chalcogenometalate $Bi_2[M_4E_8]$ (M = Al, Ga; E = S, Se), with a Bi–Bi bond (314 pm) just 8 pm longer than in **2**.[8]

A comparison of measured and calculated bond lengths for **2**, given in Figure 2, reveals a very satisfying picture: deviations in excess of 5 pm are found only for the relatively weak bonds Bi2–S6, Cu2–S7, and Cu3–S6, but even here discrepancies are less than 8 pm.

Compounds **3** and **5** crystallize in the triclinic space group $P\bar{1}$. The X-ray analysis shows dimers of monomer units of [$Bi_4Ag_3(SePh)_6Cl_3(PPh_3)_3$] (**3**) and [$Bi_4Ag_3(SePh)_6Br_3(PPh\mathit{i}Pr_2)_3$] (**5**), respectively. The analogous compound **4** crystallizes in the monoclinic space group $P2_1/n$. The structure refinement yields a dimer ([$Bi_4Ag_3(SePh)_6Cl_3(PPh\mathit{i}Pr_2)_3]_2$) and two $Bi(SePh)_3$ molecules. The structures further differ in the connectivity of the parallel monomers, as displayed in Figure 3.

The dimer building blocks are held together by weak dispersive and electrostatic interactions (**3**: Bi2···Se2′ 355.6 pm, Bi2···Se3′ 360 pm), as detailed below. The intermolecular Bi–Se distances are still longer in **4** and **5** (**4**: Bi2···Se11/Se12 371.4/363.9 pm, Bi6···Se4/Se5 361.6/368.3 pm; **5**: Bi2···Se2′ 382.9 pm, Bi2···Se3′ 370.3 pm) than those in $Bi(SePh)_3$ (348–358 pm).[9] According to the structure refinement results there are no further interactions between the dimers as shown in Figure 4.

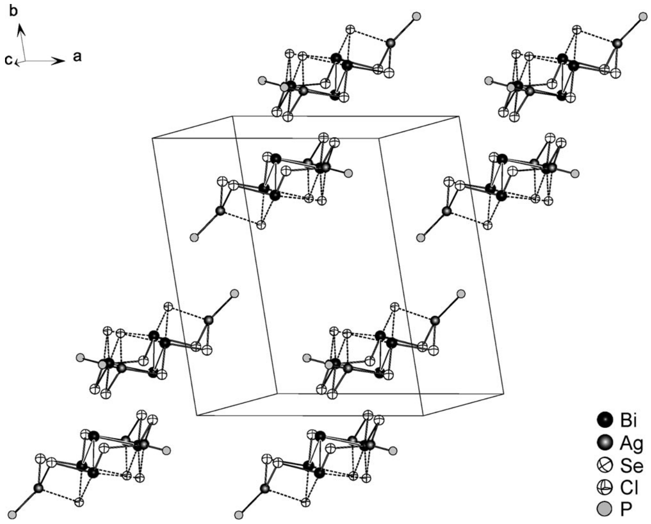


Figure 4. Several molecular units of **3** in the crystal. Carbon and hydrogen atoms are omitted for clarity.

The striking structural motif in **3**–**5** is a Bi_4 unit, which is linked by μ_2-PhSe⁻ ligands to silver atoms (Figure 5). The bismuth atoms form a trigonal pyramid in which the apical

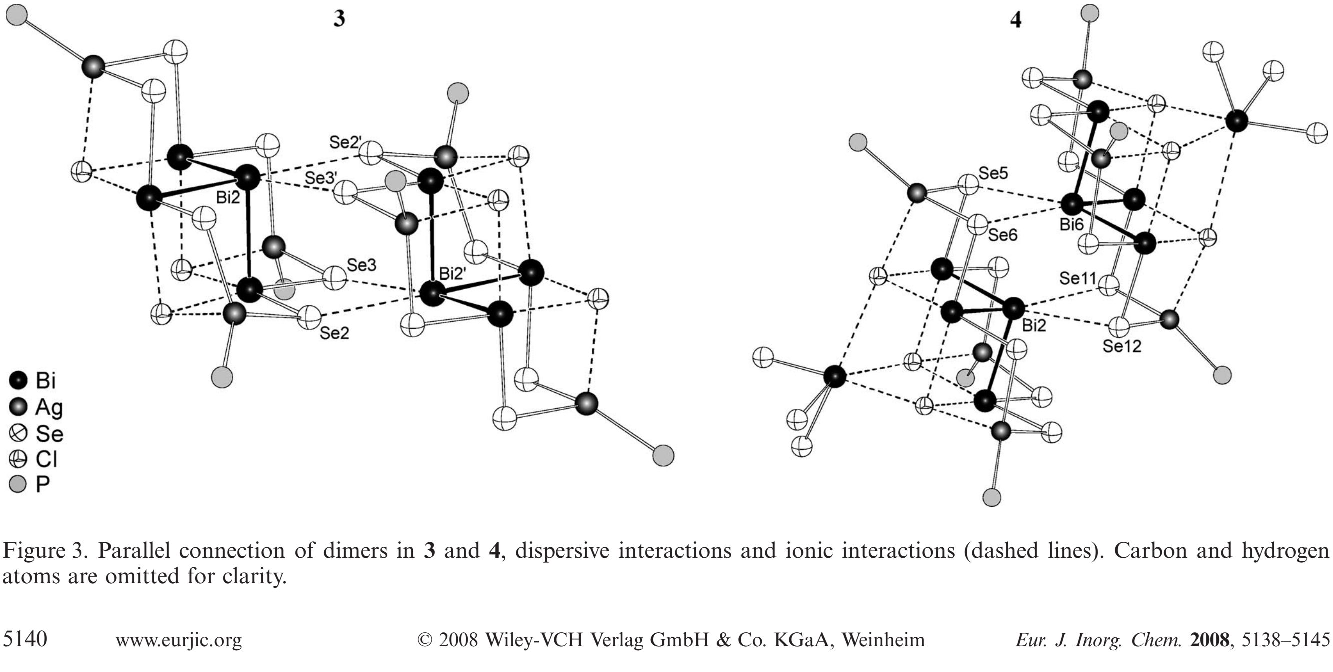


Figure 3. Parallel connection of dimers in **3** and **4**, dispersive interactions and ionic interactions (dashed lines). Carbon and hydrogen atoms are omitted for clarity.

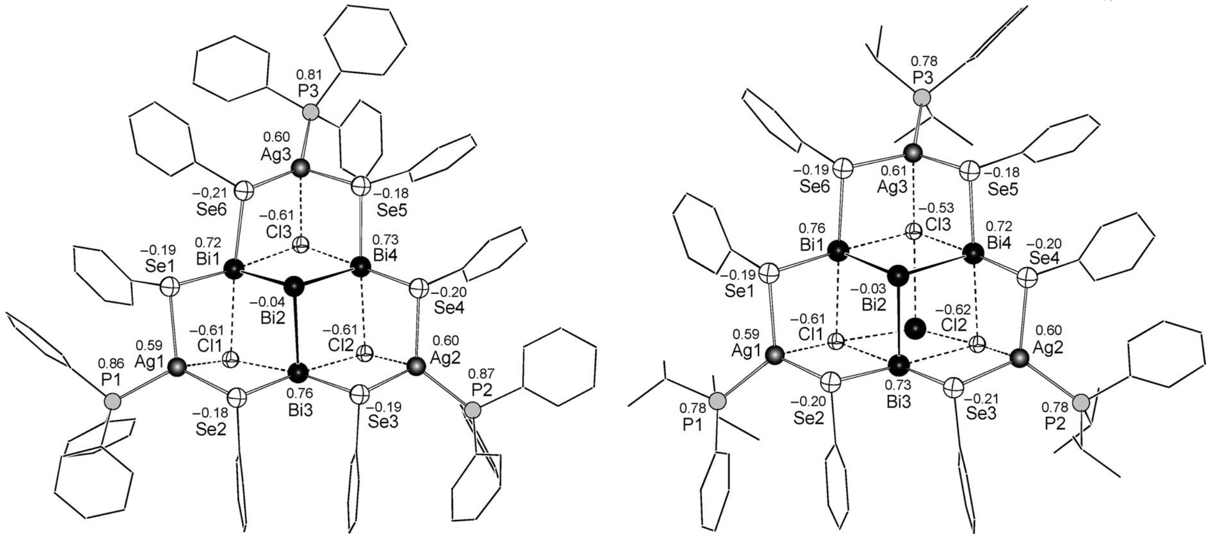


Figure 5. Molecular structure of the monomer unit in **3** (left) and **4**, which shows the same topology as **5** (right). Calculated partial charges are given above the atom labels.

Bi2 atom is bonded to Bi1, Bi3 and Bi4 with bond lengths of 299.9(9)–302.9(1) pm. The bond lengths in **3**–**5** are in the range of Bi–Bi distances reported for the dibismuthanes Ph_4Bi_2,[10] $(Me_3Si)_4Bi_2$,[11] $[2\text{-}(Me_3Si)_2CH]_4Bi_2$[12] and α-Bi (Bi–Bi 307.2 pm, Bi–Bi–Bi 95.4°).[13] The Bi1, Bi3 and Bi4 atoms are each surrounded by two μ_2-Se atoms of the $PhSe^-$ ligands and two chlorido ligands in a distorted square coordination sphere. Each of the three μ_3-capped halide atoms is linked to one silver and two bismuth atoms. The Ag–μ_3-Cl distances range from 275.5(4) to 286.5(4) pm [Ag–μ_3-Br 283.2(1)–293.1(1) pm], whereas the Bi–μ_3-Cl distances are 299.2(3)–305.8(4) pm [Bi–μ_3-Br 316.1(8)–327.3(1) pm]. These distances are much longer than the sums of covalent radii (Bi–Cl 246 pm, Bi–Br 260 pm, Ag–Cl 253 pm, Ag–Br 267 pm). Commonly observed Ag–X distances are 255.2(1) pm in $[AgCl(PPh_3)_3]$[14] and 269 pm in $[AgBr(PPh_3)_3]$.[15] Many of the structurally characterized chlorido- and bromidobismuthates show similar Bi–μ_3-X distances;[16,17] for example, in $[Bi_6(SePh)_{16}Br_2]$ the Bi–Br distances are 326.9(2)–333.6(2) pm.[18]

Computed structure parameters for **3**–**5** show close agreement with experimental values for all Bi–Bi and Ag–Se bond lengths (deviations of 6 pm at most), the Bi–Se distances are obtained too long by up to 12 pm, which is still acceptable, since one is dealing with relatively weak and long bonds. The computational procedure encounters serious problems to locate Cl and Br, which are most pronounced for **3** with Ag1–Cl1 (Ag2–Cl2) in error by 53 pm (31 pm). The Cl atom in **3** is μ_3-bound to two Bi and one Ag atoms, and the correct position results from a delicate balance of interactions. This is not properly described in the calculations, which move Cl1 towards Bi1 (by 12 pm) and away from Ag1 (by 53 pm) which again may be attributed to difficulties to describe relatively weak bonds. As support for this interpretation we note that the corresponding distances in the monomer, also given in Table 1, are in much better agreement with experimental values for the dimer **3**; even the weak intermolecular interactions effect a considerable shift of Cl1 and Cl2, which obviously occupy a very shallow potential well.

The computed binding energies of **3**, **4** and **5** with respect to the constituting monomers are 0.8, 7.5 and 9.0 kJ/mol, respectively. There are thus neither strong bonds nor electrostatic forces between the monomers, which are held together by weak electrostatic and dispersion interactions. Since the latter are not properly described by DFT calculations, one cannot expect reliable interatomic distances from calculations in this case. The very large deviations in distances between monomer units of up to 185 pm are hence no surprise.

Molecular Electronic Structures

Concerning the electronic structure of **2** one could envisage the ionic limit with PhS^-, Cu^+ and Bi^{2+} (electronegativity according to Allred and Rochow: Bi 1.76, Cu 1.75, S 2.44).[19] This would result in two empty Bi 6p AOs in the planes of the S_4 rings, orthogonal to the Bi–Bi axis; compare the right panel in Figure 2. By virtue of computed charges (Figure 2) this oversimplified picture is clearly not realistic. The charges $Q_{Bi} \approx 0.7$ and $Q_S \approx -0.4$ indicate an electron transfer from PhS^- into the empty 6p AOs of Bi, and also into 4s AOs of Cu. The charge distribution on Bi and S is better described as a 3c-4e bond for either (linear) S–Bi–S moiety, as discussed previously.[1] A simpler rationalization is obtained if one counts electron pairs surrounding the Bi atoms. The total number of electrons on each bismuth atom in the Bi_2^{4+} unit is 12; two electrons from each bond with neighbouring atoms and one lone pair. Such a count for square-pyramidal bismuth is quite common,[20] it also applies to **3**–**5** and provides a unified picture.

Similar geometric and electronic features as in **2** are present in the $[SbBi_3Br_9]^{3-}$ anion of $[Bi_{10}Au_2](SbBi_3Br_9)_2$ re-

Table 1. Selected experimental and calculated (TZVP, Δ deviation from experimental parameters), as explained in text, intramolecular and intermolecular distances [pm] and angles [°] in **3**, **4**, and **5**.

Intramolecular distances [pm]		**3**	TZVP (Δ)		**4**	TZVP (Δ)		**5**	TZVP (Δ)
Bi1–	Bi2	302.4(9)	307.3 (4.9)		302.9(1)	305.6 (2.7)		302.5(4)	305.3 (2.8)
	Se1	277.7(2)	286.6 (8.9)		276.9(2)	285.2 (8.3)		276.6(8)	285.2 (8.6)
	Se6	278.8(1)	289.8 (11)		279.5(2)	283.9 (4.4)		276.0(8)	282.5 (6.5)
	X1	305.0(3)	293.1 (–11.9)		304.4(4)	303.1 (–1.3)		316.6(8)	321.8 (5.2)
	X3	306.3(3)	296.0 (–10.3)		303.6(5)	296.9 (–6.7)		327.3(1)	315.7 (–13.4)
Bi3–	Bi2	299.9(8)	304.9 (5)		301.3(1)	304.5 (3.2)		302.6(4)	303.7 (1.1)
	Se2	278.2(2)	286.6 (8.4)		274.7(2)	286.4 (11.7)		278.9(8)	286.5 (7.6)
	Se3	279.9(1)	286.3 (6.4)		276.6(2)	286.6 (10)		276.6(9)	286.1 (9.5)
	X1	299.4(3)	297.0 (–2.4)		307.4(4)	296.0 (–11.4)		320.6(1)	313.1 (–7.4)
	X3	305.9(3)	296.9 (–9)		303.2(1)	295.7 (–7.5)		319.5(8)	311.2 (–8.3)
Bi4–	Bi2	302.9(2)	307.1 (4.2)		301.8(1)	305.8 (4)		301.3(4)	305.9 (4.6)
	Se4	277.6(1)	285.5 (7.9)		274.9(2)	285.1 (10.2)		276.2(9)	285.1 (8.9)
	Se5	277.9(2)	287.4 (9.5)		278.5(2)	284.7 (6.2)		274.7(8)	283.5 (8.8)
	X2	301.7(4)	295.6 (–6.1)		307.3(4)	303.2 (–4.1)		322.7(9)	320.2 (–2.5)
	X3	303.4(3)	297.8 (–5.6)		304.9(5)	297.7 (–7.2)		320.3(1)	315.1 (–5.2)
Ag1–	Se1	266.7(1)	266.3 (–0.4)		267.2(2)	270.2 (3)		267.2(9)	273.8 (6.6)
	Se2	263.1(1)	263.0 (–0.1)		268.9(2)	268.6 (–0.3)		270.2(1)	270.0 (–0.2)
	X1	286.6(3)	339.1 (52.5)[a]		279.4(5)	293.4 (14)		288.8(1)	296.7 (7.9)
Ag2–	Se3	267.4(2)	269.2 (1.8)		266.7(2)	272.7 (6)		268.0(1)	273.6 (5.6)
	Se4	266.9(1)	267.0 (0.1)		265.4(2)	268.4 (3)		267.9(1)	269.4 (1.5)
	X2	275.5(3)	306.5 (31)[a]		277.3(5)	291.2 (13.9)		293.1(1)	299.4 (6.3)
Ag3–	Se5	272.4(2)	270.8 (–1.6)		267.0(2)	267.7 (0.7)		270.1(1)	268.6 (–1.5)
	Se6	265.1(2)	269.0 (3.9)		267.4(2)	272.4 (5)		267.5(1)	273.1 (5.6)
	X3	281.3(3)	290.9 (9.6)		281.7(4)	297.6 (15.9)		283.2(1)	303.6 (20.4)
Intermolecular distances [pm]									
Bi2···	Se2′	355.6	416.3 (61)	Se11	371.4	442.1 (70.7)	Se2′	382.9	509.3 (126.4)
	Se3′	360.0	424.4 (64.4)	Se12	363.9	456.0 (92.1)	Se3′	370.3	555.7 (185.4)
Bi6···				Se5	361.6	456.0			
				Se6	368.3	442.1			
Angles [°] (calculated values in square brackets)									
Bi–Bi–Bi		87.5(3)–88.9(3) [86.5–87.6]			89.39(3)–99.91(3) [87.11–89.39]			88.8(3)–92.5(1) [88.8–90.7]	
Se–Bi–Se		93.1(5)–94.1(5) [90.6–93.3]			87.4(1)–94.5(1) [92.1–92.6]			92.8(1)–95.7(2) [92–93]	
Se–Bi–X_{trans}		171.2(1)–176.4(1) [175.2–177.4]			175.7(1)–179.7(1) [172.5–176.8]			175.6(1)–178.8(1) [174–178.1]	
Se–Bi–X_{cis}		83.8(1)–88.6(1) [87.4–89.7]			83.8(1)–91.5(1) [85.7–88.7]			87.4(1)–90.8(2) [85.7–88.9]	
X–Bi–X		91.5(1)–98.3(1) [89.7–94.0]			88.5(1)–94.7(1) [90.1–95.1]			90.53(2)–94.20(2) [89.7–94.4]	
Se–Ag–P		113.3(1)–136.83(1) [105.2–116.4]			92.7(1)–126.8(1) [121.3–132.1]			97.2(1)–127.9(1) [120.3–130.4]	

[a] Calculated distance in monomers: Ag1–Cl1 288.4 pm (Δ = 1.8), Ag3–Cl2 288.9 pm (Δ = 13.9).

cently published by Wahl, Kloo, and Ruck.[21] These authors propose a 3c-2e bond for Br–Bi–Br (and a 4c-4e bond between Sb and Bi), which is incompatible with the computed NPA atomic charges of 1.0 for Bi and –0.46 to –0.50 for Br; a 3c-2e bond would invariably lead to a positive charge on the Br atom. The same geometric situation around the bismuth atom is present in previously synthesized compounds BiI and BiBr with one-dimensional $^{1}_{\infty}[Bi_4X_4]$ (X = Br,[22] I[23]) units and also in $RhBi_7Br_8$.[24] For $RhBi_7Br_8$ we have checked by DFT calculations that one finds 3c-4e bonds as indicated by the atomic charges.

We finally consider the electronic structure of the Bi_4 moiety in **3**–**5**. The apical atom Bi2 (compare Figure 5) is covalently bonded to the terminal Bi atoms (Bi1, Bi3, Bi4), in agreement with a virtually vanishing charge on the Bi2 atom. For the "terminal" atoms one finds the same situation as for Bi1 and Bi2 in **2** (Figure 2): the two empty 6p AOs in a purely ionic model (leading to an atomic charge of +2) are partially filled by a delocalization of electrons of the four ions surrounding the Bi atom in a nearly square-planar configuration. This state of affair is succinctly described as 3c-4e bond, as for **2**. The resulting charge of the Bi atom of about +0.7 is actually close to that found in **2** and in $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$,[1] it is also close to the one reported by Ruck et al. for $[Bi_{10}Au_2](SbBi_3Br_9)_2$.

Conclusions

We have described preparations, structures and results of DFT calculations of new bismuth/transition metal chalcogenolate cluster complexes. A comparison of experimental and calculated bond lengths shows virtually perfect agreement for **2**, whereas a more diverse picture is found for **3**–**5**. DFT calculations still give reliable results (deviations of up to 6 pm) for short bonds, but fail badly to yield a proper description of intermolecular interactions between constituting monomers in these cases. This confirms the common knowledge that dispersion interactions are not properly included in DFT functionals.

The most interesting feature of **2**–**5** is the presence of a $–BiE_{4–n}X_n$ (E = S, Se; X = Cl, Br) moiety with an almost square-planar conformation of Bi. The formal charge, Bi^{2+}, is considerably reduced by transfer of electrons from E or X into empty 6p orbitals of Bi, which shows analogies with 3c-4e bonds. This type of geometric and electronic structures was found recently in $[Bi_2(O_2CCF_3)_4]$,[25] $[BiPh\{OP(NMe_2)_3\}_4]^{2+}$,[26] $(PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]$,[1] or $[Bi_{10}Au_2](SbBi_3Br_9)_2$.[21] Compunds **2**–**5** enlarge the known family of compounds showing this feature, which may be quite common.

Experimental Section

General: Investigations were performed under exclusion of water and oxygen under purified N_2. 1,2-Dimethoxyethane (dme), hexane and thf were dried with sodium/benzophenone and were distilled under nitrogen. CuCl was washed with HCl, CH_3OH, and diethyl ether to remove traces of $CuCl_2$, and then dried under vacuum. AgS*t*Bu,[27] $S(Ph)SiMe_3$ and $Se(Ph)SiMe_3$ were prepared according to literature procedures.[28]

1: CuCl (0.1 g, 1.01 mmol), $BiBr_3$ (0.16 g, 0.34 mmol) and PPh_3 (0.53 g, 2.02 mmol) were dissolved in thf (15 mL). After 30 min, $S(Ph)SiMe_3$ (0.37 mL, 2.02 mmol) was added to yield a red solution. After 3–4 d, red crystals of $[BiCu_2(SPh)_3Br_2(PPh_3)_3]$ (**1**) were isolated at –40 °C, which decomposed at room temperature. Yield: 0.33 g (0.204 mmol, 60%). $C_{72}H_{60}BiBr_2Cu_2P_3S_3$ (1610.25): calcd. C 53.71, H 3.76; found C 53.73, H 3.78. ^1H NMR (400.1 MHz, 25 °C, C_6D_6): δ = 7.66 (d, 18 H), 7.40 (m, 6 H), 7.16 (m, 9 H), 6.91 (m, 27 H) ppm. ^{31}P NMR (400.1 MHz, 25 °C, C_6D_6): δ = –4.30, 24.99 ppm. UV/Vis (MeCN): λ_{max} (ε) = 390 (1.26×10^4), 234 (60.6×10^4) nm. IR (KBr): $\tilde{\nu}$ = 520.86 (s), 693.15 (s), 742.58 (s), 847.35 (w), 910.94 (w), 998.05 (w), 1024.10 (m), 1069.24 (m), 1094.46 (m), 1157.68 (w), 1182.93 (w), 1307.12 (w), 1433.51 (s), 1477.20 (s), 1573.13 (m), 1821.0 (w), 1897.01 (w), 1964.99 (w), 2861.0 (w), 3050.88 (m) cm^{-1}.

2: The reaction of $[BiCu_2Br_2(SPh)_3(PPh_3)_3]$ (**1**) (0.24 g, 0.15 mmol) with NaSPh (0.39 g, 0.29 mmol) in a mixture of thf (5 mL) and hexane (10 mL) yielded very small black crystals of $[Bi_2Cu_4(SPh)_8(PPh_3)_4]$ (**2**). Yield: approx. 30%.

3: dme (15 mL) was added to $BiCl_3$ (0.16 g, 0.51 mmol), AgS*t*Bu (0.07 g, 0.38 mmol) and PPh_3 (0.10 g, 0.38 mmol) to give a white suspension. After 1 h of stirring, $Se(Ph)SiMe_3$ (0.19 mL) was added to give a brown solution and a brown precipitate. After 1 d, deep red crystals of **3** had grown, which decomposed at room temperature. Yield: approx. 50%.

4: $BiCl_3$ (0.18 g, 0.57 mmol) and AgS*t*Bu (0.11 g, 0.57 mmol) were suspended in dme (15 mL). While stirring the mixture, PPh*i*Pr_2 (0.11 mL,0.57 mmol) and $Se(Ph)SiMe_3$ (0.40 mL, 1.71 mmol) were added to give a brown solution. Black, needle-like crystals of **4** grew over several days. Yield: approx. 40%.

5: $BiBr_3$ (0.36 g, 0.80 mmol) and AgS*t*Bu (0.12 g, 0.60 mmol) were suspended in dme (15 mL), and PPh^iPr_2 (0.12 mL, 0.60 mmol) was added to the yellowish suspension. After 1 h of stirring, $Se(Ph)SiMe_3$ (0.28 mL, 1.2 mmol) was added to give a deep red solution. Very small black, needle-like crystals of **5** grew over several days at –20 °C. Yield: approx. 20%.

Table 2. Crystallographic data for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{72}H_{60}BiBr_2Cu_2P_3S_3\cdot 4C_4H_8O$	$C_{120}H_{100}Bi_4Cu_4P_4S_8\cdot 2C_4H_8O$	$C_{90}H_{75}Ag_3Bi_4Cl_3P_3Se_6\cdot 2C_4H_{10}O_2$	$C_{90}H_{75}Ag_3Bi_4Cl_3P_3Se_6\cdot Bi(SePh)_3\cdot C_4H_{10}O_2$	$C_{90}H_{75}Ag_3Bi_4Br_3P_3Se_6\cdot Bi(SePh)_3\cdot C_4H_{10}O_2$
Formula mass	1610.25	3012.59	2989.15	2989.15	3685.63
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a [Å]	13.922(4)	25.007(5)	14.722(3)	21.456(4)	18.242(1)
b [Å]	17.247(6)	13.701(3)	19.135(4)	47.493(10)	18.649(1)
c [Å]	19.721(7)	39.732(8)	19.648(4)	21.550(4)	20.078(1)
α [°]	69.16(3)	90	108.85(3)	90	115.37(2)
β [°]	69.97(3)	107.59(3)	109.41(3)	100.79(3)	110.85(2)
γ [°]	82.89(3)	90	97.47(3)	90	98.51(2)
V [Å]	4157.8(2)	12977.1(1)	4762.4(16)	21572.1(7)	5391.1(3)
Z	2	4	2	4	2
$\rho_{calcd.}$ [$g\,cm^{-3}$]	1.517	1.398	2.179	2.410	2.270
μ(Mo-K_α) [mm^{-1}]	3.761	3.570	10.443	13.806	12.900
F(000)	1912	5448	2915	14228	3408
T [K]	150(2)	120(2)	123(2)	120(2)	180(2)
$2\theta_{max}$ [°]	2.52–54.26	3.02–52.40	2.60–52.02	2.60–54.34	3.78–54.64
Messured reflexions	20432	34392	24870	74885	38371
Unique reflexions	14845	21581	16649	36495	19793
Refined parameters	828	683	1026	1017	1042
R_{int}	0.0967	0.1379	0.0434	0.0847	0.0605
Residual electron density [$e\,Å^{-3}$]	1.336/–1.964	1.511/–2.059	2.305/–1.562	4.858/–3.371	1.460/–2.917
R_1 [$I > 2\sigma(I)$][a]	0.0684 (0.1676)	0.1009 (0.2339)	0.0479 (0.1006)	0.0715 (0.1916)	0.0407 (0.0954)
wR_2 (all data)[b]	0.1361 (0.1722)	0.1981 (0.2886)	0.0734 (0.1126)	0.1140 (0.2254)	0.0556 (0.1010)

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Compounds **2**–**5** could not be isolated without an insoluble precipitate. Therefore, no further analytical methods were applied.

Crystallography: Crystals suitable for single-crystal X-ray diffraction were taken directly from the reaction solution of the compounds and then selected in perfluoroalkylether oil. Single-crystal X-ray diffraction data of **1**–**5** (Table 2) were collected by using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) with a STOE IPDS II (Imaging Plate Diffraction System) equipped with a Schneider rotating anode. The structures were solved with the direct-methods program SHELXS of the SHELXTL PC suite of programs, and were refined with the use of the full-matrix least-squares program SHELXL.[29] Molecular diagrams were prepared by using DIAMOND 3.1.[30] All Bi, Cu, Ag, S, Se, Cl, Br, P, and C atoms of the cluster molecules were refined with anisotropic displacement parameters, whereas O and C atoms of the solvent molecules were refined isotropically. Phenyl groups C151–C156, and C157–C162 of **4** were refined as rigid hexagons by using AFIX 66. A $Bi(SePh)_3$ molecule in **4** was disordered and could not be refined completely. Crystals of **1** and **2** scattered only to a 2θ angle of 40°; these crystals obviously lose the embedded solvent molecules (slow decomposition at room temperature); therefore, the decay correction for data sets of **1** and **2** was applied. For all data sets a numerical absorption correction was applied.[31] CCDC-689594 (**1**), -689595 (**2**), -689596 (**3**), -689597 (**4**), and -689598 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations: Molecular electronic structure calculations were carried out with TURBOMOLE[32] to shed light on some unusual features of **2**–**5**: chemical bonding around the central Bi_2 unit in **2**, the Bi_4 moiety in **3**–**5**, and the type of interaction between the monomers in **3**–**5**. The system size in these compounds, up to 356 atoms, left non-hybrid DFT procedures as the only reasonable choice, and we chose the BP86 functional,[33a] which has proved reliable in previous similar treatments.[1] To be on the safe side we used an extended def2-TZVP basis[34b] for heavier atoms, only for the Ph groups the smaller SV(P) basis[33a] was selected. We applied the m4 multiple grid for numerical evaluations of the exchange–correlation term[32b,34] and the efficient MARI-J technique (multipole accelerated resolution of identity approximation for the inter-electronic Coulomb term *J*).[35] All structure parameters were optimized in C_1 symmetry for **2** and C_i for **3**–**5** by means of analytical gradients using redundant internal coordinates.[36] X-ray geometries served as a start where possible, only a few H atoms of Ph had to be assigned proper positions by hand. For the comparison of measured and computed bond lengths one has to keep in mind that the best agreement (deviations up to about 5 pm) is typically found for relatively strong and short bonds, deviations up to 10 pm are to be expected for weak bonds. Even larger discrepancies arise in the absence of direct bonding, that is, if weak electrostatic and dispersion interactions are decisive, since DFT methods do not account reliably for London forces. Molecular electronic atom charges are discussed in terms of NPA (natural population analysis).[37]

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