Cluster Compounds

DOI: 10.1002/anie.200703325

Molecular Structure and Theoretical Studies of $(PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]$**

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Dedicated to Professor Kenneth Wade on the occasion of his 75th birthday

Transition-metal clusters containing main-group elements as bridging ligands have attracted our attention in recent years.[1] In addition to many chalcogenide-bridged coinage-metal clusters, for example, $[Cu_{146}Se_{72}(PPh_3)_{30}]$, $[Ag_{262}S_{100}(StBu)_{62}(dppb)]$ (dppb = bis(diphenylphosphanyl)butane) and $[Ag_{344}S_{124}(StBu)_{96}]$, we have also reported the synthesis and characterization of a number of coinage-metal complexes containing Group 15 elements as ligands.[2] Molecular cluster complexes with bismuth, the heaviest Group 15 element, have also attracted attention recently. In particular, a large variety of bismuth chalcogenide chalcogenolate compounds with bridging oxygen atoms have been synthesized and structurally characterized. Prominent examples for this class of compounds are $[Bi_{22}O_{26}(OSiMe_2tBu)_{14}]$,[3] $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]$[4] (Hsal = salicylic acid), $[Bi_{38}O_{45}(hfac)_{24}]$[5] (Hhfac = hexafluoroacetylacetone) and $[Bi_{50}Na_2O_{64}(OH)_2(OSiMe_3)_{22}]$.[6] Reports on compounds in which bismuth atoms are bridged by sulfur or selenium are scarce. The few examples include bismuth thiolate anions $[Bi_2(SC_6F_5)_7]^-$, $[Bi_2(SC_6F_5)_8]^{2-}$,[7] $[Bi_3(SC_6F_5)_{11}]^{2-}$,[8] and the bismuth selenotate anion $[Bi_4(SePh)_{13}]^-$.[9] In the absence of organic groups, complexes containing bismuth and sulfur, selenium, or tellurium do not tend to form larger oligomeric arrangements. Only from chloroaluminate melts were salts of the cubane cations $[Bi_4E_4]^{4+}$ (E = S, Se,[10] Te[11]) obtained.

In contrast to many examples of heterometallic crystalline phases Bi/E/M (E = chalcogen, M = transition metal), few ternary molecular bismuth complexes are known in which a bismuth and a transition-metal atom are bridged by a chalcogen atom. Examples include $[BiIr_6S_8(Cp^*)_2]Cl$ (Cp^* = η^5-C_5Me_5),[12] $[BiTi_2O(OiPr)_9]$,[13] and $(PPh_4)_3[Bi(WS_4)_3]$.[14] Ternary molecular clusters in which the cluster core consists of transition-metal, chalcogen, and Group 13–15 elements have been the subject of recent investigations, and examples include $[Ga_{10}Cu_{20}Se_{23}Cl_4(PEt_2Ph)_{12}]$, $[In_6Cu_{14}Se_7(SeiPr)_{18}]$,[15] and $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2$.[16] Herein we report synthesis, structure, and theoretical studies of the new ternary bismuth–copper–chalcogenolate anion $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$, which consists of a branched Bi_{10} unit embedded in a $\{Cu_{10}(SPh)_{24}\}$ shell.

$(PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]\cdot 0.5\,DME$ (**1**) was synthesized by heating a suspension of $Bi(SPh)_3$, CuSPh, PPh_4Cl, and $PhSSiMe_3$ in 1,2-dimethoxyethane (DME) at reflux for one hour. From the resulting orange solution, black crystals of **1** formed after several weeks. The analogous compound **1a**, which crystallizes with two equivalents of DME, was obtained at room temperature with the reactants in a different stoichiometric ratio. Compound **1a** contains two molecules of DME as lattice-bound solvent (Scheme 1).

$$2\ Bi(SPh)_3 + 2\ CuSPh + 4\ PhSSiMe_3 \xrightarrow[80\ ^\circ C]{+\ PPh_4Cl} (PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]\cdot 0.5\ DME\ (\mathbf{1})$$

$$10\ Bi(SPh)_3 + 10\ CuSPh + 2\ PhSSiMe_3 \xrightarrow[RT]{+\ PPh_4Cl} (PPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]\cdot 2\ DME\ (\mathbf{1a})$$

Scheme 1. Synthesis of the $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ ion.

Cluster **1** crystallizes in the monoclinic space group $P2_1$ with two independent $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ ions in the asymmetric unit. Compound **1a** crystallizes in the triclinic space group $P\bar{1}$ (Figure 1). Since bond distances between the heavy atoms in **1** and **1a** are almost identical, the following discussion is based on geometric parameters observed in the $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ anion in **1a**. Bi–S distances up to 3.15 Å and Cu–S distances up to 2.80 Å are considered bonding.

The most striking structural motif within the $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ ion is the Bi_{10} unit, which consists of two connected Bi_5 chains with Bi–Bi distances of 3.021(1)–3.079(2) Å. Bond lengths are in the range of Bi–Bi separations reported for the dibismuthines Ph_4Bi_2,[17] $(Me_3Si)_4Bi_2$,[18] $[2\text{-}(Me_3Si)_2CH]_4Bi_2$,[19] and $(2,4,6\text{-}Me_3C_6H_2)_4Bi_2$.[20] The atoms Bi3 and Bi6, through which the two Bi_5 chains are connected, are both in trigonal-

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[**] This work was supported by the DFG (Center for Functional Nanostructures), the Institute of Nanotechnology of the Forschungszentrum Karlsruhe and the Fonds der Chemischen Industrie.

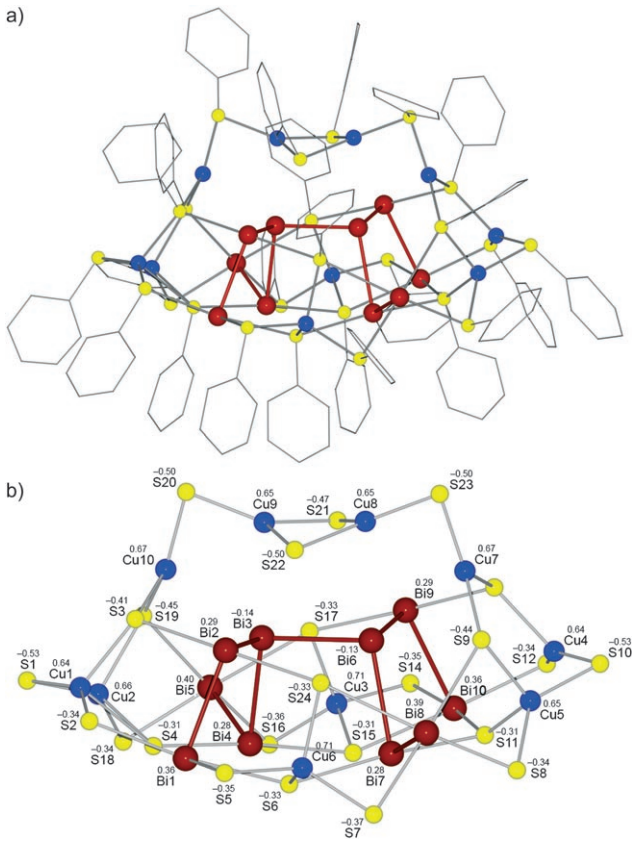
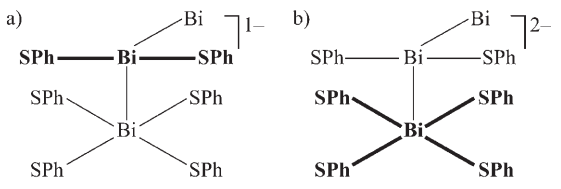


Figure 1. a) Molecular structure of the $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ anion of **1a** in the crystal (Bi red, Cu blue, S yellow). b) The core of the $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ anion (without C and H atoms). Calculated partial charges are above the atom labels. Selected bond lengths [Å] and angles [°]: Bi1-Bi2 3.052(1), Bi2-Bi3 3.027(1), Bi3-Bi6 3.021(1), Bi3-Bi4 3.043(1), Bi4-Bi5 3.062(1), Bi6-Bi9 3.036(1), Bi6-Bi7 3.047(1), Bi7-Bi8 3.067(1), Bi9-Bi10 3.079(2), Bi-S 2.659(4)–3.106(3), Cu-S 2.212(5)–2.455(5); Bi3-Bi2-Bi1 101.51(3), Bi6-Bi3-Bi2 91.53(3), Bi6-Bi3-Bi4 100.74(3), Bi2-Bi3-Bi4 103.34(3), Bi3-Bi4-Bi5 84.32(3), Bi3-Bi6-Bi9 91.75(3), Bi3-Bi6-Bi7 101.61(4), Bi9-Bi6-Bi7 103.83(3), Bi6-Bi7-Bi8 85.59(3).

pyramidal environments in which the corners are occupied by Bi atoms. The coordination environment of the remaining eight Bi atoms is displayed in Scheme 2.

The ten Bi and ten Cu atoms are μ_2-, μ_3,- or μ_4-bridged by 24 S atoms of SPh groups. S1, S10, S20, and S23 coordinate in μ_2-mode to two Cu atoms. S2, S5, S7, S8, S12, S14, S16, and S18 each bridge a Bi and a Cu atom. Bi1, Bi4, Cu1, and Cu2 are connected by μ_4-S4. Atoms S6, S11, S15, S17, and S24 each coordinate two Bi atoms and one Cu atom in μ_3-mode, while S3, S9, S13, and S19 bridge two Cu atoms and one Bi atom.



Scheme 2. Three-center, four-electron bonds (shown in bold type) in the $[(Bi)_2\mathbf{Bi(SPh)_2}]^-$ (a) and $[(Bi)\mathbf{Bi(SPh)_4}]^{2-}$ (b) fragments.

Cu1, Cu2, Cu3, Cu5, and Cu6 are surrounded by S atoms of SPh ligands in a distorted tetrahedral fashion; the distorted trigonal-planar coordination spheres of Cu4, Cu7, Cu8, Cu9, and Cu10 are formed by three S atoms of SPh ligands. The sum of the S-Cu-S bond angles around these atoms amounts to 356–360°, thus indicating that no additional bonding interactions to neighboring atoms Bi3 and Bi6 (Bi–Cu: 3.109(2)–3.199(2) Å) and Bi10 (Bi10–Cu4: 3.653(1) Å) are present. The previously reported covalent Bi–Cu bond in $[(Me_3Si)_2BiCu(PMe_3)_3]$ (2.744(1) Å) is much shorter.[21]

Assuming Cu^+ and SPh^- in this description of the bonding situation implies a $[Bi_{10}]^{12+}$ fragment. Terminal atoms of the Bi_{10} unit (Bi1, Bi2, Bi8, Bi10) are assigned the formal oxidation number +II. Bi2, Bi4, Bi7, and Bi9 are each bound to two Bi atoms and are assigned the oxidation number +I. Bi3 and Bi6 are neutral. This range of oxidation states is not unusual in bismuth chemistry; the formation of homonuclear polycations is characteristic for of bismuth in low oxidation states. In bismuth subhalides, for example, Bi_6Cl_7[22] and Bi_6Br_7[23] ($BiCl_{1.167}$ and $BiBr_{1.167}$) contain $[Bi_9]^{5+}$ polycations surrounded by halobismuthate(III) ions. Further examples are the $[Bi_8]^{2+}$ cation (square antiprism) in $Bi_8(AlCl_4)_2$[24] and the $[Bi_5]^{3+}$ cation (trigonal bipyramid) in $Bi_5(MCl_4)_3$ (M = Al,[25] Ga[26]). The bonding within these ploycations can be rationalized by the Wade rules.[27] For $[Bi_{10}]^{12+}$, however, $18 = 2n-2$ framework bonding electrons would be obtained, for which the Wade rules cannot be applied. The small number of framework bonding electrons would suggest a cage architecture, for example, a bicapped square antiprism, which would be unstable because of the high charge.

In an attempt to understand the bonding in **1**, DFT calculations were performed; phenyl groups were replaced with methyl groups. The calculations were performed with TURBOMOLE[28] and the BP86[29]/SV(P)[30] functional using the RIJ approximation.[31] The geometry optimization was performed using analytical gradients with redundant internal coordinates.[32] This approach resulted in a calculated structure for **1** in which bond distances (Bi–Bi and Bi–S) differ by less than 8 pm from the X-ray structure of **1**. Atomic charges were obtained by the NPA method (natural population analysis) of Weinhold and co-workers.[33] Resulting net charges are displayed in Figure 1 and give a clear picture [Eq. (1); Q_X = partial charge of atom X].

$$Q_S \approx -0.3 \text{ to } -0.5,\ Q_{Cu} \approx +0.65,\ Q_{Bi} = -0.14 \text{ to } +0.39 \qquad (1)$$

The results rule out a mere ionic description of the bonding in **1**, which was also not expected because of the small difference in electronegativity ($\Delta EN < 0.7$). Only Cu atoms could be described as Cu^+, but only with partial occupation of 4s (and 4p) atomic orbitals. The bonding situation of the Bi atoms could be described as follows: Bi3 and Bi6 are each bound to three Bi atoms and carry a small negative charge ($Q_{Bi} \approx -0.1$). Bi2, Bi4, Bi7, and Bi9 each form bonds to two Bi atoms and exhibit a calculated partial charge of +0.3. These Bi atoms are also each linearly coordinated by two SPh groups, thus resulting in a three-center, four-electron bond (Scheme 2). Terminal Bi atoms of the Bi_{10} unit (Bi1, Bi5, Bi8, Bi10; $Q_{Bi} \approx +0.4$) are surrounded by four SPh groups in

square-planar fashion, thus forming two three-center, four-electron bonds, as in XeF_4.

Within the Bi_{10} unit, Bi atoms that are bonded to one or two other Bi atoms form three-center, four-electron bonds to saturate empty valences. In the model, the electron distribution for such a bond is 1.5:1:1.5.[34] The net charges of components in Scheme 2 are −0.5 for SPh ligands and 0 for Bi atoms, which is close to calculated NPA charges. Assuming that bismuth atoms are all in the formal oxidation state 0, $30 = 2n + 10$ framework bonding electrons are obtained for the neutral Bi_{10} unit. According to the Wade rules, this situation would be a *klado* case, for which a branched chain would be expected, similar to **1**, BiBr, and BiI.[23] This reasoning, however, could only be applied to an isolated Bi_{10} cluster. Bi–S distances of 2.659(4)–3.106(3) Å indicate that the case here is different. The mechanism that gave rise to the surprising formation of **1** is unclear. At present, the synthesis of further examples of this class of compounds is being explored.

Experimentelles

Investigations were performed under exclusion of water and oxygen in an atmospere of purified N_2. DME was dried over Na/benzophenone. CuSPh and $PhSSiMe_3$ were prepared according to published procedures.[35]

$Bi(SPh)_3$: $Bi(OOCCH_3)_3$ (1.32 g, 3.42 mmol) was dissolved in EtOH (135 mL), stirred, and heated to reflux. HSPh (1.08 mL, 10.2 mmol) was added, resulting in a yellow solution; the reaction mixture was stirred and heated for another 30 min. Slow cooling to room temperature produced orange crystals of $Bi(SPh)_3$. Yield: 1.60 g (87 %). Elemental analysis calcd (%) for $C_{18}H_{15}BiS_3$ (536.48): C 40.30, H 2.82; found: C 40.17, H 2.82.

1: $PhSSiMe_3$ (0.11 mL, 0.59 mmol) was added slowly to a yellow suspension of $Bi(SPh)_3$ (160 mg, 0.29 mmol), CuSPh (50 mg, 0.29 mmol), and PPh_4Cl (65 mg, 0.14 mmol) in DME (15 mL) to yield a dark orange solution. This solution was heated at reflux for 30 min. A yellow precipitate was filtered off using a G4 glass filter. After 3–4 weeks, black crystals of **1** were isolated from the filtrate.

1a: $Bi(SPh)_3$ (360 mg, 0.67 mmol), CuSPh (115 mg, 0.67 mmol), and PPh_4Cl (25 mg, 0.07 mmol) were suspended in DME (20 mL) and dissolved by addition of $PhSSiMe_3$ (0.02 mL, 0.13 mmol) and stirring for one hour. The yellow precipitate was separated using a G4 glass filter, and the orange filtrate was stored at −20 °C. After several days, black crystals of **1a** were isolated. Yield: 37 % (based on Bi). Elemental analysis calcd (%) for $C_{192}H_{160}Bi_{10}Cu_{10}P_2S_{24}$ (6013.6): C 38.31, H 2.68; found: C 37.84, H 2.69.

Crystal structure determination: The data were collected on a Stoe-IPDS-II diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data).[36–39] Bi, Cu, and S atoms were refined with anisotropic temperature factors. C atoms were refined with isotropic temperature factors. CCDC-655311 (**1**) and 655312 (**1a**) 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.

Received: July 24, 2007
Published online: September 21, 2007

Keywords: bismuth · cluster compounds · copper · density functional calculations · sulfur

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[37] Crystal data for **1**: $C_{192}H_{160}Bi_{10}Cu_{10}P_2S_{24}\cdot 0.5\,C_4H_{10}O_2$; monoclinic, space group $P2_1$ (no. 4); $Z=4$; $a=22.945(5)$, $b=29.199(6)$, $c=32.953(7)$ Å; $\beta=101.18(3)°$; $V=21\,659(7)$ Å; $T=150(2)$ K; $F(000)=11\,484$; $\rho_{calcd}=1.861$ g cm^{-3}; $\mu(Mo_{K\alpha})=9.341$ mm^{-1}; 110 050 reflections measured; 63 307 independent reflections; $R_{(int)}=0.0925$, 2330 parameters; $R_1=0.0720$ [$I>2\sigma(I)$]; $wR_2=0.1652$ (all data); max residual electron density 2.592 e Å^{-3}. The structure was refined as a racemic twin. Phenyl groups C169–C186, C367–C372, and C379–C378 were refined as rigid hexagons using AFIX 66.

[38] Crystal data for **1a**: $C_{192}H_{160}Bi_{10}Cu_{10}P_2S_{24}\cdot 2\,C_4H_{10}O_2$; triclinic space group $P\bar{1}$ (no. 2); $Z=2$; $a=19.656(4)$, $b=20.397(4)$, $c=35.243(7)$ Å; $\alpha=74.89(3)$, $\beta=74.58(3)$, $\gamma=79.91(3)°$, $V=13\,065(5)$ Å; $T=150(2)$ K; $F(000)=5924$; $\rho_{calcd}=1.577$ g cm^{-3}; $\mu(Mo_{K\alpha})=7.745$ mm^{-1}, 93 659 measured reflections; 47 862 independent reflections; $R_{(int)}=0.0909$, 1236 parameters; $R_1=0.0903$ [$I>2\sigma(I)$]; $wR_2=0.2625$ (all data); max residual electron density 5.090 e Å^{-3}. The large residual electron density is located 0.884 Å from Bi9. An empirical absorption correction was performed (Habitus) but did not give improved refinement results. Phenyl groups C55–C60, C79–C84, and C145–C150 were refined as rigid hexagons. The phenyl group C151–C156 was disordered.

[39] The $[Bi_{10}Cu_{10}(SPh)_{24}]^{2-}$ anion was also obtained with $(AsPh_4)^+$ as counterion. Poor-quality crystals of $(AsPh_4)_2[Bi_{10}Cu_{10}(SPh)_{24}]\cdot Bi(SPh)_3\cdot 4\,THF$ were refined to $R_1=0.1217$. The cell constants are $a=19.144(4)$, $b=23.319(5)$, $c=28.595(6)$ Å; $\alpha=92.54(3)$, $\beta=103.40(3)$, $\gamma=95.44(3)°$; $V=12\,332(4)$ Å.

