Cluster Compounds

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The Molecular Cluster $[Bi_{10}Au_2](SbBi_3Br_9)_2$**

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Heavy p-block elements, especially indium, tin, tellurium, and bismuth, tend to form subvalent compounds, in which the cations have oxidation numbers lower than expected from the $8-N$ rule. Often this is achieved by formation of homonuclear clusters. Especially the heavy elements of group 15 show a structural variety of homonuclear polycationic cages, such as Bi_9^{5+},[1] Bi_8^{2+},[1e,j,2] Bi_6^{2+},[3] Bi_5^{3+},[2a,d,e,4] Bi_5^{+},[3] and Sb_8^{2+}.[2e,5] Moreover heteropolycations like $[Bi_4E_4]^{4+}$[6] (E = S, Se, Te) have been synthesized.

Herein we present a novel compound containing a heteroatomic gold–bismuth polycation, namely, the quaternary subbromide $[Bi_{10}Au_2](SbBi_3Br_9)_2$ (**1**), which was obtained by cooling a melt of the metals and $BiBr_3$. Beside $[Bi_7RhBr_8]$[7] it is the second molecular cluster in the group of bismuth subhalides.[8] Crystal structure determination by X-ray diffraction on a pseudomerohedrally twinned crystal revealed a rhombohedral packing of dumbbell-shaped molecular clusters, each composed of a central $[Bi_{10}Au_2]$ heteroicosahedron, embraced by two $(SbBi_3Br_9)$ hemispheres (Figure 1).

The molecule shows a unique combination of remarkable structural and bonding features: The bimetallic polycation $[Bi_{10}Au_2]^{6+}$, one of the largest empty single-shell metal clusters, involves significant bismuth–gold interactions. Furthermore, the molecule has a rare interpnicogen covalent bond between bismuth and antimony, as well as a complex donor–acceptor bond between the anionic caps and the polycation. The constitution of the molecule can be rationalized in terms of an uncommon combination of known structural motives. To minimize controversy, we emphasize that the "ionic model" developed below is a consequence of electron-counting rules and arguments based on chemical analogy.

As the central $[Bi_{10}Au_2]$ heteroicosahedron is a heavy analogue of (1,12)-dicarba-*closo*-dodecaborane,[9] counting electrons according to the rules of Wade and Mingos[10] can give a first idea about chemical bonding. As a *closo* cluster with 12 vertices, the icosahedron would require $2\times12+2=26$ skeletal electrons (SE). Each of the bismuth atoms contributes three electrons to chemical bonding, which implies that the 6s electrons are not accessible due to their relativistic stabilization. With each of the gold atoms contributing one valence electron, a total of 32 SE would be achieved. To meet the optimum number of 26 SE, a formal charge of +6 must be assumed.

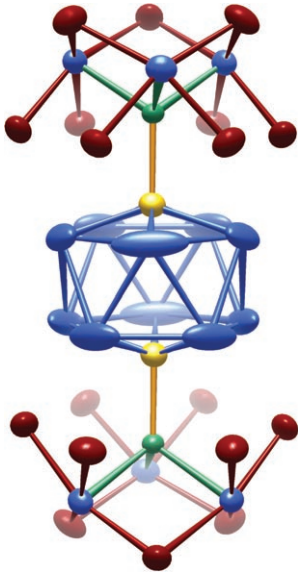

Figure 1. The $[Bi_{10}Au_2](SbBi_3Br_9)_2$ molecule. Thermal ellipsoids represent 90% probability at 293(2) K. Bi blue, Au yellow, Sb green, and Br dark red.

In the bismuth part of the heteroicosahedron, the pentagonal antiprism $[Bi_{10}]^{4+}$ can be identified, which has been predicted by ab initio calculations at the Hartree–Fock and density functional levels.[11] This polycation was found as a metal-centered cluster $[Pd@Bi_{10}]^{4+}$ in the compounds $Bi_{14}PdBr_{16}$[12] and $Bi_{16}PdCl_{22}$.[13] With 26 SE the Archimedean antiprism $[Bi_{10}]^{4+}$ is formally an *arachno* cluster in the Wade–Mingos classification. From this point of view the heteropolycation $[Bi_{10}Au_2]^{6+}$ can be interpreted as a $[Bi_{10}]^{4+}$ polycation capped by two Au^+ cations.

Although the crystallographic symmetry of the $[Bi_{10}Au_2]$ icosahedron is only a center of inversion, the point group symmetry D_{5d}, corresponding to a semiregular (Archimedean) polyhedron, is almost fulfilled. The bond angles in the five-membered rings of bismuth atoms are $108\pm1°$, the rotation angle between the two pentagons is about 36°, and the maximum deviation from planarity is less than 1 pm. The interatomic distances within the five-membered ring (321 to 325 pm) and between the two pentagons (318 to 322 pm) are in the same range and agree very well with the calculated (DFT-B3LYP) distances of 324 pm within and 322 pm between the rings.[11] In the palladium-centered cluster all distances between neighboring bismuth atoms are about 6 pm shorter. Capping of the Bi_{10} antiprisms with two gold atoms

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results in bismuth–gold distances of 288 ± 1 pm, which are much shorter than reported in the intermetallic compound Au_2Bi ($MgCu_2$ structure type).[14] However, evaluation of this bond length is quite difficult, since in Au_2Bi the coordination is completely different, all other intermetallic compounds with significant bismuth–gold interactions are poorly characterized, and recent efforts to establish a donor–acceptor bond between bismuth and gold failed.[15]

Table 1: Natural charges of **1** and the approximants.

Atom	$[Bi_{10}]^{4+}$	$[Bi_{10}Au_2I_2]^{4+}$	$[(SbBi_3Br_9)I]^{2-}$	$(SbBi_3Br_9)^{3-}$	$[Bi_{10}Au_2](SbBi_3Br_9)_2$
$Bi_{cluster}$	0.4	0.41	–	–	0.27 to 0.30
Au	–	0.16	–	–	0.23
Sb	–	–	0.16	−0.23	−0.39
Bi_{cap}	–	–	0.98	0.88	1.0
Br	–	–	−0.53, −0.57	−0.59, −0.60	−0.46 to −0.50
I	–	−0.20	−0.23	–	–

The $(SbBi_3Br_9)^{3-}$ ligands satisfy the coordinative saturation of the two capping gold atoms. The interaction between antimony and gold can be classified according to Lewis as a donor–acceptor bond. Correspondingly, the $[Au^I(Sb^0R_3)]^{2-}$ fragment with $R = Bi^{II}Br_{2/1}Br_{2/2}$ is a complex analogue of cations $[Au^I(E^0R_3)]^+$ with E = P, As, Sb and R = alkyl or aryl.[16]

In the bromobismuthate(II) caps of the molecule each of the bismuth atoms is linked to two terminal bromine atoms at a distance of 283 ± 5 pm, whereas the distances to the two μ_2-bridging bromine atoms are 301 ± 9 pm. The $(SbBi_3Br_9)^{3-}$ hemisphere (Figure 2) with approximate C_{3v} symmetry topologically resembles a section of a hypothetical cuboctahedral

Figure 2. The $(SbBi_3Br_9)^{3-}$ hemisphere of $[Bi_{10}Au_2](SbBi_3Br_9)_2$ (middle), its relation to a hypothetical $[SbBi_6Br_{12}]$ cuboctahedron (left), and a representative section of the BiBr structure (right).

cluster $[SbBi_6Br_{12}]^{3+}$. However, it is more appropriate to compare the $(SbBi_3Br_9)^{3-}$ fragment with the structure of BiBr ($= Bi^0Bi^{II}Br_{4/2}$).[1d] In both compounds the outer Bi^{II} atom has square-planar coordination of four bromine anions and is perpendicularly bonded to a central Bi^0 (299 pm) or Sb^0 (291 ± 1 pm) atom. Since the electronegativities of bismuth and antimony[17] are almost equal, the Bi–Sb bond can be regarded as homopolar covalent. Such direct interactions between the heavier elements of group 15 are very rare. Based on spectroscopic data, single bonds in $Pr_2BiSbMe_2$ and $Me_2BiSbMe_2$[18] as well as a double bond in BbtSbBiBbt (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl)[19] have been postulated. Weak interactions exist in the intermetallic compound Ba_2BiSb_2[20] with a Bi–Sb distance of 322 pm. The observed distance of 291 pm in **1** should be regarded as equivalent to a covalent single bond.

The formal charge assignment based on chemical analogies was validated by quantum chemical calculations on a series of less complex model systems (see Table 1) in order to analyze the chemical bonding in the whole molecule within a quasi-isolobal[23] approach.

Molecular orbitals of the bimetallic cluster in **1** with similar densities and energies can be obtained by replacing the $(SbBi_3Br_9)$ caps by a simple model which can coordinate to the cluster with a p-like lone pair. The iodide ion is a suitable approximant forming a hypothetical $\{[Bi_{10}](AuI)_2\}^{4+}$ entity (Figure 3). On linking the isolated and rather simple

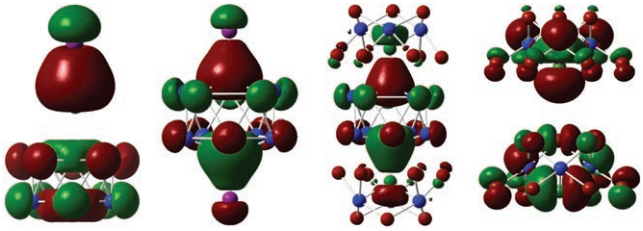

Figure 3. Molecular orbitals of AuI (HOMO−2), $[Bi_{10}]^{4+}$ (HOMO), $\{[Bi_{10}](AuI)_2\}^{4+}$ (HOMO−17), $[Bi_{10}Au_2](SbBi_3Br_9)_2$ (HOMO−71) and $(SbBi_3Br_9)^{3-}$ (HOMO−2 and HOMO).

molecules $[Bi_{10}]^{4+}$ and AuI together, only the bonding, p-type molecular orbitals of $[Bi_{10}]^{4+}$ fulfilling the fivefold symmetry combine with the two bonding molecular orbitals of AuI (combinations of I 5p and Au 6s/5d_{z^2}), whereas the others remain almost unchanged and are distinctly located on the respective molecular components.

The HOMO−2 orbital (Figure 3) of the outer $(SbBi_3Br_9)^{3-}$ fragment in **1** also exhibits more or less the character of a p donor and thus emphasizes its analogy to I^-. Saturation of the dangling bond by formal addition of I^+ to the isolated hemisphere to give $(Bi_3Br_9Sb)I^{2-}$ results in related orbital contributions as far as the Bi–Br and Bi–Sb interactions are concerned. In the latter, similar to the molecule of **1**, four almost nonbonding combinations of s-type orbitals from Sb and Bi, six bonding MOs between Bi and Br, and two bonding p-type MOs between Sb and Bi (HOMO, Figure 3) are identified. In simple terms, this could be described as 3c–2e bonds between Bi and Br and a 4c–4e bond between Sb and Bi.

In the molecule $[Bi_{10}Au_2](SbBi_3Br_9)_2$, some of the molecular orbitals almost exactly correspond to those of the chosen approximants by being localized on the particular modules in a similar way. Yet some of them, especially those originating from additional interactions between the "lone pairs" of the Br atoms and the $[Bi_{10}]^{4+}$ cluster, are delocalized over the entire molecule. Some hints to such interactions are also given by the comparatively short intramolecular (≥ 326 pm) and intermolecular distances (≥ 330 pm), between bismuth atoms of the antiprism and bromine atoms. Additionally, the

lowered natural charges[24] of the bismuth atoms in the cluster indicate charge transfer from the Br atoms to the cluster and underline their stabilizing function, in which they act as brackets. Furthermore, the natural charges support the chemical analogy between parts of the molecule of **1** and the approximants (Table 1). The above-mentioned interactions result in charge transfer to Au and charges of about ± 0; this is a slight deviation from the simplistic discussion of the ionic model above. A detailed discussion of the chemical bonding will be given elsewhere.[25]

Comparison of **1** with a selection of adequate but simple models gives a rational description of the chemical bonding in the complex, capped $[Bi_{10}]^{4+}$ cluster. So far, the existence of the molecule seems to be restricted to the solid state. Although we do not have high expectations concerning molecular solubility, stabilization of fragments such as the $[Au_2Bi_{10}]$ icosahedron in solution might be a challenge for future work.

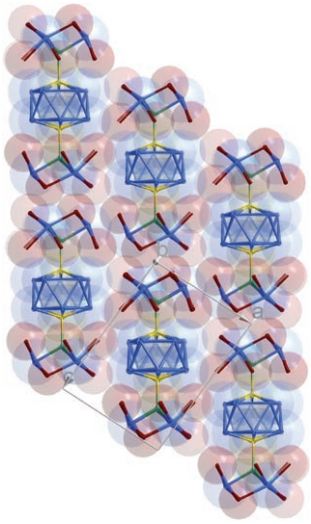

Figure 4. Section parallel to (010) through the packing of molecules in the crystal structure of **1**.

Experimental Section

Synthesis: Black crystals of **1** were synthesized in high yield in fused silica ampoules ($V \approx 17\ cm^3$) from a mixture of Bi (99.5%, Alfa Aesar, treated with hydrogen at 250°C to remove oxygen impurities), Au (99.9+%, Chempur), $BiBr_3$ (99%, Riedel-de Haën, sublimed three times from 220°C to ambient temperature) and Sb (99.9%, Alfa Aesar) in the target composition and a total amount of about 1 g. The ampoules were rapidly heated to 360°C, cooled to 200°C over 24 h, left at this temperature for about seven days, and finally quenched to ambient temperature. In the powder diffraction pattern of the reaction product no byproducts could be detected. However, traces of $BiBr_3$ were found in the coolest part of the ampoule. Crystals of higher quality can be obtained by adding a 10% excess of Sb and $BiBr_3$. The needle-shaped crystals are almost unaffected by moisture and air, although decomposition is observed after several months. Thermal decomposition under equilibrium pressure starts at 311(5)°C. Semiquantitative energy-dispersive X-ray analysis (EDX) of single crystals of **1** was performed on a scanning electron microscope (type CamScan CS 44). In excellent agreement with the proposed sum formula, it revealed the presence of the elements bismuth, gold, antimony and bromine in average ratios of about 41:5:6:48.

The X-ray crystal structure determination of **1** (Figure 4) was hindered by some crystallographic peculiarities. The symmetries of the heteroicosahedron and the anionic part are incompatible. The $[Bi_{10}Au_2]$ part of the structure almost fulfils the noncrystallographic D_{5d} symmetry, whereas the point group of the combined $(SbBi_3Br_9)$ caps is D_{3d}. For the whole molecule, their common subgroup, the C_{2h} symmetry, is nearly maintained, although in the crystal structure only the center of inversion remains. The discrepancy between the D_{3d} pseudosymmetry of the molecule and the actual symmetry of the crystal structure causes crystallographic problems: All crystals checked suggest a rhombohedral cell with lattice parameters of about $a = 1530$ pm and $c = 1760$ pm with weak superstructure reflections that seem to double the a and b axes. In fact, the additional reflections are due to a lower point group symmetry (monoclinic), as well as a loss of translational symmetry (primitive cell) accompanied by pseudomerohedral twinning along the pseudothreefold axis. Finally, the structure was refined in the space group $P2_1/c$. The twinning was handled by using the reflection data in the HKLF5 format of the SHELX97[21] program. At ambient temperature the thermal ellipsoids of the bismuth atoms in the icosahedron still indicate either a static or a dynamic disorder. Therefore, additional datasets were recorded at 200 and 110 K. From linear extrapolation of the mean-square displacements to absolute zero it can be deduced that the effect is caused by thermal libration of the $[Bi_{10}Au_2]$ cage around its pseudofivefold axis.

The diffraction data were collected on an imaging plate diffraction system IPDS-II (Stoe). Based on an optimized crystal description numerical absorption corrections were applied.[22] The structure was solved and refined against F_o^2 with the SHELX97 program package.[21] All atoms were refined with anisotropic displacement parameters.

Decabismuth digold bis[tris(tribromobismuthyl)stibane]; monoclinic, space group $P12_1/c1$ (No. 14), $2\theta_{max} = 56°$, $Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, $T_{max}/T_{min} = 0.185/0.018$. Relative contributions of the twin domains: 7:2:1. At 293(2) K: $a = 1063.99(5)$, $b = 1532.24(5)$, $c = 1471.08(7)$ pm, $\beta = 93.346(4)°$, $V = 2394.2(2) \times 10^6\ pm^3$, $\rho_{calcd} = 7.518\ g\,cm^{-3}$, absorption coefficient $\mu = 80.8\ mm^{-1}$. Final R values: $R_1\ [F_o > 4\sigma(F_o)] = 0.050$, wR_2 (all F_o^2) $= 0.066$; GoF $= 0.975$ for 21677 unique reflections and 175 parameters; min./max. residual electron density $-5.01/+4.46\ e \times 10^{-6}\ pm^{-3}$. At 200(5) K: $a = 1062.02(8)$, $b = 1528.61(8)$, $c = 1466.7(1)$ pm, $\beta = 93.459(6)°$, $V = 2376.7(3) \times 10^6\ pm^3$, $\rho_{calcd} = 7.573\ g\,cm^{-3}$, absorption coefficient $\mu = 81.4\ mm^{-1}$. Final R values: $R_1\ [F_o > 4\sigma(F_o)] = 0.058$, wR_2 (all F_o^2) $= 0.081$; GoF $= 1.326$ for 20463 unique reflections and 175 parameters; min./max. residual electron density $-4.52/+4.16\ e \times 10^{-6}\ pm^{-3}$. At 110(5) K: $a = 1059.70(7)$, $b = 1526.69(6)$, $c = 1464.24(8)$ pm, $\beta = 93.544(5)°$, $V = 2364.4(2) \times 10^6\ pm^3$, $\rho_{calcd} = 7.612\ g\,cm^{-3}$, absorption coefficient $\mu = 81.8\ mm^{-1}$. Final R values: $R_1\ [F_o > 4\sigma(F_o)] = 0.048$, wR_2 (all F_o^2) $= 0.064$; GoF $= 1.213$ for 20892 unique reflections and 175 parameters; min./max. residual electron density $-3.54/+4.33\ e \times 10^{-6}\ pm^{-3}$.

Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-416285 (293 K), CSD-416286 (200 K), and CSD-416287 (110 K).

Quantum chemical calculations: All calculations were performed with the program suite Gaussian 03.[26] The hybrid DFT calculations were carried out with the B3LYP functional.[27] The atomic parameters of the approximants $[Bi_{10}]^{4+}$ (symmetry D_{5d}), $[Bi_{10}Au_2I_2]^{4+}$ (D_{5d}), AuI ($C_{\infty v}$), $(Bi_3Br_9Sb)^{3-}$ (C_{3v}), and $(Bi_3Br_9Sb)I^{2-}$ (C_{3v}) were optimized with cc-pVDZ basis sets for all atoms.[28] The inner electrons of the heavy atoms were replaced with the quasirelativistic effective core potentials MDF60 for Bi and Au, MDF28 for Sb and I, and MDF10 for Br.[28c,29] The second-derivative matrix (Hessian) was used to evaluate the nature of the stationary points. No negative eigenvalues were observed.

In a second step the density was recalculated with the optimized parameters by using cc-pVTZ basis sets.[28] Since optimization of the whole molecule leads to a deviation from planarity of the Bi_5 rings, to bromine atoms that seem to be more attached to the cluster, and therefore to a differently shaped molecule, the coordinates from the crystal structure were used for the calculation with cc-pVTZ basis sets. In any case, the distortion of the molecule also underlines the interaction between bromine atoms of neighboring molecules and the Bi_{10} antiprisms, but this minor defect of the model was taken into account. For the comparison of the orbital energies and to acquire a physical meaning in case of the anionic species, the charges were compensated by the COSMO model ($\varepsilon = 78.39$).[30]

The charges were obtained by natural population analysis with the NBO 3.0 program.[24] The molecular orbitals were visualized by the program Gauss View 3.0.[31] The molecular orbitals are attached to the Supporting Information.

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