Main-Group Clusters

$Sb_8(GaCl_4)_2$: Isolation of a Homopolyatomic Antimony Cation**

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Homopolyatomic species, or clusters, of the majority of the post-transition-group elements are known. However, the bulk part of these are anionic.[1] For the more-electron-rich main-group elements there is a possibility of forming cationic polyatomic species as well. A series of such polycations has been characterized for the halogen and chalcogen groups as well as for cadmium and mercury.[2] Within Groups 15–17, well-characterized polycations have been established for all elements but fluorine, phosphorus, arsenic, and antimony.

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Focusing on Group 15, several bismuth polycations have been synthesized in both the solid state and in solution, for example, Bi_5^{3+}, Bi_8^{2+}, and Bi_9^{5+} as crystalline compounds and Bi_5^{3+} in solution. Based on the general chemical resemblance between antimony and bismuth, it is reasonable to expect that antimony polycations are also stable enough for identification. However, only anionic clusters, such as Sb_7^{3-}[3] and Sb_{11}^{3-},[4] have been characterized, and no more than circumstantial evidence for the existence of antimony polycations has been reported in the literature.

Several synthetic routes have proved useful for preparing main-group clusters in general and bismuth polycations in particular: synthesis in molten salt mixtures,[5] stabilization in superacidic media,[6] and reactions in organic solvents at room temperature.[7] In the search for antimony analogues, the two first methods were employed. Unfortunately, the results from the molten salt mixture were poor, although Corbett and coworkers found evidence of Sb_2I_4, a lower antimony iodide displaying direct Sb–Sb bonding.[8] One serious limitation of this route is the low solubility of antimony metal in liquid SbX_3 or SbX_3–AlX_3 mixtures (X = Cl, Br, I).[9]

The experiments in superacid media had a similar outcome. The only published result is the reaction between Sb metal and AsF_5 to form a compound with the empirical formula $Sb(AsF_6)$. The cation in this compound is suggested to be polymeric $(Sb^+)_n$ owing to the diamagnetic behavior.[10]

No further observations regarding antimony polycations were reported until Ulvenlund et al. described a black product, suggested to be $Sb_5(GaCl_4)_3$, which was obtained from the molten salt system Ga–$SbCl_3$–$GaCl_3$.[11] The proposed composition was based on elemental analysis. No structure determination was performed, but Raman spectroscopy indicated Sb–Sb bonding.

Previously, the same authors had reported a new synthetic route to bismuth polycations: Bi metal could be oxidized by $GaCl_3$ dissolved in benzene, and $Bi_5(GaCl_4)_3$ could be isolated from these solutions.[7] Unfortunately, this method was, in its original form, unsuccessful for the isolation of antimony polycations, since antimony metal cannot be oxidized by either $SbCl_3$ or $GaCl_3$ in benzene.[12] However, Ulvenlund et al. suggested that gallium metal could be used to reduce $SbCl_3$ in a $GaCl_3$–benzene solution.

In summary, it is clear that the overall meager results observed with antimony polycations do not compare at all to the success achieved with bismuth polycation synthesis.

In a modification of the synthetic route based on organic solvents, $SbCl_3$ dissolved in $GaCl_3$–benzene was reduced by a solution of $Ga^+(GaCl_4)^-$ in $GaCl_3$–benzene. Subsequent extraction of the resulting solution with hexane and mesitylene provided black-red crystals of $Sb_8(GaCl_4)_2$ (**1**) together with a black amorphous and a brown polycrystalline phase.[13]

The crystal structure of **1** is shown in Figures 1 and 2. The compound consists of Sb_8^{2+} polycations with square-antiprismatic geometry (D_{4d} symmetry) and tetrahedral tetrachlorogallate anions. The geometry of the polycation is consistent with the Wade rules. These rules were originally formulated for the topology of boranes but can also be applied to naked post-transition-metal clusters.[14] The square-antiprismatic geometry of the polycation is also found for the bismuth

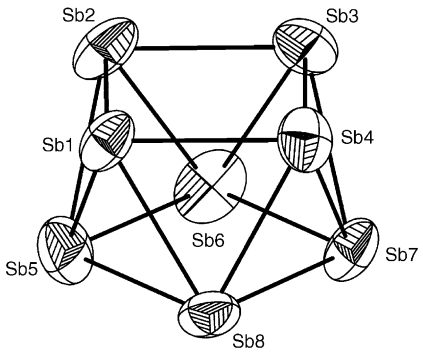

Figure 1. The cation Sb_8^{2+} in the crystal structure of **1**. The thermal ellipsoids are shown at the 70% probability level.

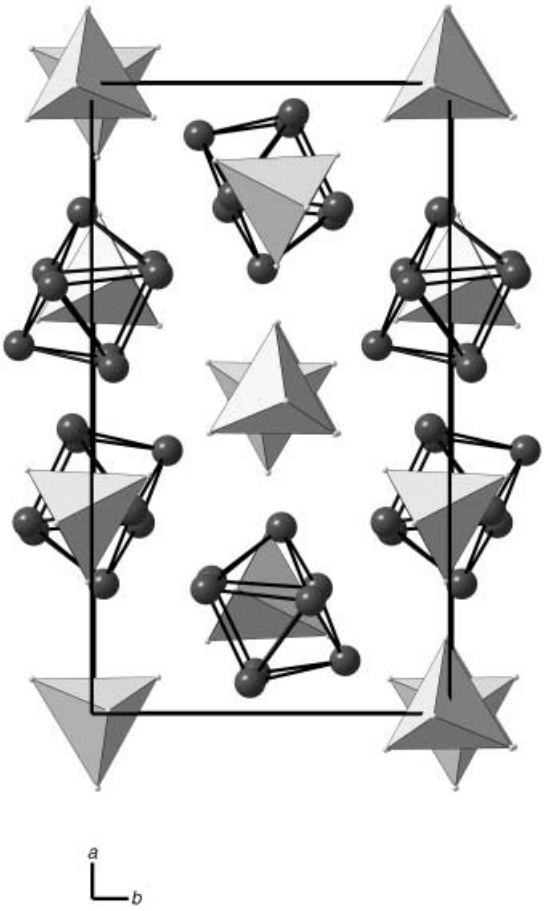

Figure 2. The unit cell of **1** as viewed along the crystallographic *c* axis.

analogue $Bi_8(AlCl_4)_2$.[15] The Sb–Sb bond lengths in the Sb_8^{2+} polycation are summarized in Table 1, together with corresponding values for Bi_8^{2+}. The closest Sb–Cl bond length in **1** is 343.3 pm; thus, the interaction between cation and anion may be considered to be predominantly electrostatic.

The data in Table 1 demonstrate that there is one important difference between the geometry of Bi_8^{2+} in $Bi_8(AlCl_4)_2$ and that of Sb_8^{2+} in **1**: the atom–atom distances between the Sb_4 squares of the Sb_8^{2+} cation are 3.3% longer than those within. In the bismuth cluster cation, on the other hand, the bonds between the two squares are only marginally

Table 1: Summary of the interatomic bond lengths in the polycations Sb_8^{2+} and Bi_8^{2+}.

Compound	Space group	Intrasquare distance [pm] (average [pm])	Intersquare distance [pm] (average [pm])	Intersquare distance / Intrasquare distance
$Sb_8(GaCl_4)_2$	$Pna2_1$	284.9–288.8 (286.9)	294.0–299.5 (296.5)	1.0331
Sb_8^{2+} (calcd)	–	295.1 (295.1)	304.1 (304.1)	1.0305
$Bi_8(AlCl_4)_2$[15b]	$P6_3/m$	307.8–309.8 (308.6)	309.2–312.3 (311.0)	1.0078
$Bi_8(GaCl_4)_2$[16]	$P6_3$	307.1–312.3 (308.8)	306.7–312.3 (310.0)	1.0038

longer than those within the squares. This difference may indicate a lower degree of delocalization in the individual squares of the Sb cluster. This hypothesis may be investigated by theoretical calculations from which the electron localization function (ELF) in Sb_8^{2+} and Bi_8^{2+} can be evaluated.[17] However, ELF data display no significant difference in bonding between the two polycations; for both, the intrasquare interactions are of localized character while the intersquare ones are more delocalized. The calculated intersquare/intra-square distance ratio for Bi_8^{2+} is 1.0248, that is, significantly larger than the ratio observed in the crystal structures. Thus, the differences in bond lengths may originate from differences in the interactions between cations and anions or between neighboring cluster cations in the crystal structures. For the related cation $Bi_4Te_4^{4+}$,[18] the ELF results indicate an apparent localized character for all bonds, reflecting the fact that this cation has two more bonding cluster electrons than Sb_8^{2+}.

Raman spectra from a single crystal of **1** in the region of 120–500 cm^{-1} revealed four Raman-active vibration modes (Table 2). The band at 343 cm^{-1} is recognized as the symmetric stretch mode of the $GaCl_4^-$ anion.[19] A second band of this anion should be present at 158 cm^{-1}, but owing to the very strong band at 180 cm^{-1}, attributable to the polycation, this weak band may be hidden. The positions of the bands assigned to the polycation are in good agreement with the calculated values, and there is almost total agreement between the bands of the Sb_8^{2+} polycation reported herein and those attributed to the proposed Sb_5^{3+} cation in reference [11]. Therefore, it is reasonable to assume that the cationic parts of the products are identical.

Table 2: Observed and calculated Raman bands ($\geq$120 cm^{-1}) of **1** and their assignments.

Wavenumber [cm^{-1}]	Calcd wavenumber [cm^{-1}]	Calcd relative intensity [%]	"$Sb_5(GaCl_4)_3$"[11] [cm^{-1}]	Assignment
343, m				$GaCl_4^-$
180, s	170	100	183, s	Sb_8^{2+}
171, sh	160	4	174, sh	Sb_8^{2+}
135, sh	130	10	133, sh	Sb_8^{2+}

Energy-dispersive X-ray analysis on crystals of **1** confirms a high antimony content of 44 atom %, which is very close to the theoretical value of 44.4 %. The analysis also shows that no other elements (except Sb, Ga, and Cl) are present.

In conclusion, this work describes the first isolated homopolyatomic antimony cation. The structure has been determined by single-crystal X-ray diffraction, and can be described as consisting of an Sb_8^{2+} polycation with a square antiprismatic shape and two $GaCl_4^-$ counterions. The structure and electronic properties of the cation are similar to those of the previously known Bi_8^{2+} cation. The interaction between the cluster cation and surrounding anions is likely to be predominantly electrostatic, based on the long Sb–Cl distances observed.

Experimental Section

General: $GaCl_3$ (Aldrich, anhydrous, 99.99 %), $SbCl_3$ (Alfa, anhydrous, 99.999 %), and gallium metal (Alfa, 99.999 %) were used as received. Benzene (Fluka, 99.5 %), hexane (Merck, 99 %), and mesitylene (Janssen, 99 %) were dried over molecular sieves. Owing to the air and moisture sensitivity of the reactants and products, all synthetic work was performed in a glovebox under an inert atmosphere of nitrogen (< 1 ppm H_2O and O_2). The synthetic route used for **1** was originally developed and optimized to produce high-quality crystals of bismuth polycations.[16]

1: Gallium metal (0.2 g, 3 mmol) was added to $GaCl_3$ (1.32 g, 7.5 mmol) in benzene (2 mL). After 24 h, undissolved gallium metal was removed, and the solution was added to a mixture formed by adding $SbCl_3$ (0.25 g, 1.1 mmol) to a solution of $GaCl_3$ (1.32 g, 7.5 mmol) in benzene (2 mL). The resulting reaction mixture was left overnight. During this time, a black amorphous precipitate formed, and the solution turned light brown in color. The solution, together with the amorphous material, was extracted with hexane (2 mL), which led to a reduction in the volume of the brown solution. The hexane phase was removed and mesitylene (2 mL) was carefully added on top of the brown solution. The tube was again left overnight. The mesitylene fraction was then removed, and new mesitylene was added and this time thoroughly mixed with the brown solution by shaking the tube. A brown precipitate formed immediately. The solid phases were washed several times in benzene before drying by evaporation at room temperature. Small, black-red crystals were formed together with a brown powder (probably consisting of small crystals of **1** mixed with $GaCl_3$) and an uncharacterized, black, amorphous material.

Raman spectroscopy: The Raman spectrum of **1** was obtained using a Renishaw System 1000 spectrometer, equipped with a DMLM Leica microscope and a 25-mW He–Ne laser (633 nm).

Elemental analysis: Energy dispersive X-ray analysis was performed on a JEOL JSM-820 scanning electron microscope. Six points on two different crystals were investigated. Observed average contents (standard deviations): Sb 44(3) atom %, Ga 17(3) atom %, Cl 39(1) atom %; calculated values for **1**: Sb 44.4 %, Ga 11.1 %, Cl 44.4 %.

Quantum chemistry calculations: Ab initio calculations were performed, using the hybrid density function B3LYP, for the Sb_8^{2+} cation with Gaussian98 to evaluate the vibrational spectrum.[20] Calculations were also carried out for Bi_8^{2+} and $Bi_4Te_4^{4+}$ to compare their electronic properties. The Stuttgart quasi-relativistic effective core potentials and valence basis sets,[21] with one polarization

function added, were used for all atom types. The electron localization functions were calculated with the ToPMoD package.[22]

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[13] Crystal structure determination of **1**: orthorhombic, space group $Pna2_1$, $a = 1754.9$ (1), $b = 991.73(9)$, $c = 1285.8(1)$ pm, $V = 2237.8(2) \times 10^6$ pm^3, $\rho_{calcd} = 4.15$ g cm^{-3}; $2\theta_{max} = 55.0$, $Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, $T = 299$ K. The diffraction data were collected on a Bruker-Nonius KappaCCD diffractometer. All atoms were refined using anisotropic temperature parameters. Numerical absorption corrections were applied. The structure was solved with SHELXS97 and refined against F^2 using SHELXL97. Final R values: $R_1 = 0.0286$, $wR_2 = 0.0646$; GOF = 1.088 for 4569 unique reflections and 163 parameters; Flack parameter $x = 0.03(2)$; min./max. residual electron density 0.88/ −0.84. 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 number CSD-413577.

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