Finally Fulfilling Wade's Rules: The C_{4v} Symmetric Polycation Bi_{95}^{+} in the Polar Structure of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ $= (\text{Bi}_{95}^{+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$

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**Finally Fulfilling Wade's Rules: The C_{4v} Symmetric
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Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 65th Birthday

Keywords: Bismuth; Cluster compounds; Electron counting rules; Polar structure;
Pseudosymmetry

Running title: The C_{4v} Symmetric Polycation Bi_9^{5+}

Abstract. The bismuth-rich bromidostannate(II) $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24} = (\text{Bi}_9^{5+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$ was crystallized from a melt of Bi, Sn and BiBr_3 . X-ray diffraction on a single-crystal revealed a polar, tetragonal structure (space group $I4cm$, no. 108) with lattice parameters $a = 1323.70(5)$ pm and $c = 1816.86(8)$ pm at 110(5) K. In agreement with Wade's rules and quantum chemical calculations, the homonuclear *nido*-cluster Bi_9^{5+} is a mono-capped square antiprism (point group C_{4v}). The anions of the bromidostannate(II) groups mainly comply with the pseudosymmetry of the space group $I4/mcm$ and thereby affect substantial disorder of the Sn^{II} cations.

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Introduction

Among the post transition metal elements, numerous ligand-free polyhedral clusters — typically polyanions of elements of groups 14 or 15 and polycations of elements of groups 15 or 16 — have been synthesized so far [1]. The formation of deltahedral metal clusters bears great resemblance to the cluster shapes found for boranes and hydroborates. Modifications of Wade's rules, which were originally developed for hydroboranes [2] help to understand the chemical bonding in these clusters [3]. Replacement of n B-H-*exo* bonds by n lone-pairs also results in $2n+m$ skeletal electrons (SE), i.e. the optimal electron count for n -atomic *closo* ($m = 2$), *nido* ($m = 4$), or *arachno* polyhedra ($m = 6$).

In fact these rules proved to be helpful in the interpretation of homoatomic bismuth polycations, where the $6s$ electrons form the lone-pairs and only the $6p$ electrons are used in cluster bonding. Electron count and cluster shape match for Bi_5^+ (*nido*, 14 SE), [4] Bi_5^{3+} (*closo*, 12 SE) [5], Bi_6^{2+} (*nido*, 16 SE) [4, 6], Bi_8^{2+} (*arachno*, 22 SE) [7], and Bi_{10}^{4+} (*arachno*, 26 SE) [8]. Unfortunately, Bi_9^{5+} seemed to be a persistent exception: For a nine-atomic cluster with 22 SE a *nido* cluster with the shape of a mono-capped square antiprism (symmetry C_{4v}) is expected. Instead, in about a dozen characterized compounds the Bi_9^{5+} cluster was always found to have the conformation of a tri-capped trigonal prism [9], which is a *closo* polyhedron. Consequently, discussions about the suitability of the concept arouse. The compound $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24} = (\text{Bi}_9^{5+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$ presented here is the first one featuring a C_{4v} symmetric Bi_9^{5+} cluster and thereby finally fulfills Wade's rules.

Experimental Section

Synthesis

Black square platelets of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ were synthesized by cooling stoichiometric mixtures of Bi (99.5 %, Alfa Aesar, treated with hydrogen at 250 °C in order to remove oxygen impurities), Sn (99.9+ %, Chempur) and BiBr_3 (99 % Riedel-de Haën, sublimated three times from 220 °C to ambient temperature) from 250 to 200 °C within seven days. In humid air, $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ decomposes within weeks. By-products, such as Bi_6Br_7 [9c] and the not yet published compound $\text{Bi}_{37}\text{Sn}_{47}\text{Br}_{117}$, were also observed. The composition of a crystal, which had been previously identified by precession photographs, was checked by semi-quantitative EDX analysis on a scanning electron microscope (CamScan CS 44). The ratio Bi : Sn : Br corresponds within a maximum deviation of 4 At-% with the composition based on the crystal structure refinement. Traces of other elements were not detected.

X-ray Crystallography

A suitable single-crystal was selected by Buerger precession photographs (Zr-filtered Mo radiation). Intensity data were collected at 110(5) K on an imaging plate diffractometer IPDS-II (Stoe) with graphite-monochromatized MoK_α radiation. The microscopic description of the shape of the crystal was optimized on the basis of sets of equivalent reflections in the Laue class $4/mmm$ [10a]. Numerical absorption corrections were applied to the data [10b]. The structure was solved with direct methods in the polar space group $I4cm$ (no. 108) and refined using anisotropic displacement parameters for Bi and Br atoms [11]. The occupancy of the position Sn1 refined to 25 % and was then fixed, while anisotropic displacement parameters were introduced. For the in total fully occupied atoms Sn2 and Sn3 a split model was introduced. In the course of refinement the majority positions Sn2A, Sn2B, and Sn3A proved to have the same occupancy. Correspondingly also the minority positions Sn2C, Sn2D, and Sn3B were refined with a common occupation factor. Sn2 atoms were refined with equal

isotropic, Sn3 atoms with equal anisotropic displacement parameters. The examined crystal was an inversion twin with the domain ratio of 0.463:0.537(9). Twin refinements in the maximal translationengleiche subgroups *Iba*2 and *Fmm*2 as well as in *Cc* did not result in ordered structure models. For visualization of the structure, the program Diamond was used [12].

$\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$, $M_{\text{m}} = 6510.31 \text{ g mol}^{-1}$, tetragonal, *I4cm* (no. 108), $T = 110(5) \text{ K}$, $a = 1323.70(5) \text{ pm}$, $c = 1816.86(8) \text{ pm}$, $V = 3183.5(2) \cdot 10^6 \text{ pm}^3$, ($T = 293(1) \text{ K}$: $a = 1332.7(2) \text{ pm}$, $c = 1842.9(4) \text{ pm}$, $V = 3273(2) \cdot 10^6 \text{ pm}^3$), $Z = 2$, $\rho_{\text{calc}} = 6.792 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 67.3 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 56.1^\circ$, $-17 \leq h, k \leq 17$, $-23 \leq l \leq 23$, 12961 measured reflections, 2024 unique reflections, $R_{\text{int}} = 0.045$, $R_{\sigma} = 0.022$, 78 parameters, 1 restraint, extinction parameter $x = 5(1) \cdot 10^{-5}$, $R_1(1976 F_o > 4\sigma(F_o)) = 0.027$, $R_1(\text{all } F_o) = 0.028$, $wR_2(\text{all } F_o^2) = 0.058$, $\text{Goof} = 1.07$, residual electron density $+1.56/-1.40 \text{ e} \cdot 10^{-6} \text{ pm}^{-3}$. Atomic parameters are listed in Table 1, selected interatomic distances are gathered in Table 2. Further data, in the form of a CIF, have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (E-mail address: crysdata@fiz-karlsruhe.de), as supplementary material no. CSD-420786, and can be obtained by contacting the FIZ quoting the article details and the CSD number.

Quantum Chemical Calculations

The atomic parameters of the C_{4v} and the D_{3h} symmetric polycations were optimized in DFT-B3LYP [13] or in MP2 calculations using the program Gaussian03 [14] along with an aug-cc-pVTZ basis set [15]. The inner electrons of Bi were replaced using the core potentials ECP-MDF60 [16]. The second derivative matrix of the B3LYP calculation was used in order to evaluate the nature of the stationary points. In case of D_{3h} symmetry, the negative frequencies that convert the cluster into the C_{4v} conformation are observed.

Table 1. Wyckoff positions, occupancies, coordinates and (equivalent) isotropic displacement parameters of the atoms in Bi₁₈Sn₇Br₂₄ at 110(5) K. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

atom	W. p.	occup.	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} , U_{iso}
Bi1	16 <i>d</i>	1	0.15370(3)	0.05946(3)	−0.08667(3)	272(1)
Bi2	16 <i>d</i>	1	0.07418(4)	0.16718(3)	0.05498(3)	265(1)
Bi3	4 <i>a</i>	1	0	0	0.16122(5)	265(2)
Sn1	8 <i>c</i>	0.25	0.2063(2)	0.2937(2)	0.2495(3)	232(9)
Sn2A	8 <i>c</i>	0.905(3)	0.4078(1)	0.0922(1)	0.2128(1)	157(4)
Sn2B	8 <i>c</i>	0.905(3)	0.3881(1)	0.1119(1)	0.2253(2)	157(4)
Sn2C	8 <i>c</i>	0.095(3)	0.382(3)	0.118(3)	0.257(4)	157(4)
Sn2D	8 <i>c</i>	0.095(3)	0.409(2)	0.091(2)	0.288(3)	157(4)
Sn3A	4 <i>b</i>	0.905(3)	1/2	0	0.46058(9)	215(4)
Sn3B	4 <i>b</i>	0.095(3)	1/2	0	0.539(2)	215(4)
Br1	8 <i>c</i>	1	0.10255(8)	0.39745(8)	0.35370(9)	204(3)
Br2	8 <i>c</i>	1	0.10986(9)	0.39014(9)	0.14478(9)	208(3)
Br3	16 <i>d</i>	1	0.18967(9)	0.1002(1)	0.25134(7)	302(3)
Br4	8 <i>c</i>	1	0.34302(8)	0.15698(8)	0.4312(1)	227(3)
Br5	8 <i>c</i>	1	0.34350(9)	0.15650(9)	0.0779(1)	239(3)

Table 2. Selected interatomic distances (in pm) in Bi₁₈Sn₇Br₂₄ at 110(5) K. Symmetry codes: (i): *x*, *y*, *z*; (ii): *y*, −*x*, *z*; (iii): −*y*, *x*, *z*; (iv): −*x*, −*y*, *z*; (v): 1/2−*y*, 1/2−*x*, *z*; (vi): 1−*y*, *x*, *z*; (vii): 1−*x*, −*y*, *z*; (viii): 1/2+*x*, *y*−1/2, 1/2+*z*; (ix): 1/2−*x*, 1/2−*y*, 1/2+*z*; (x): 1/2−*y*, *x*−1/2, 1/2+*z*; (xi): 1/2+*y*, 1/2−*x*, 1/2+*z*.

Bi1–	Bi1 ^{ii, iii}	308.51(6)	Sn1–	Br3 ^{i, v}	257.1(3)
	Bi2	312.47(6)		Br2	262.3(5)
	Bi2 ⁱⁱ	312.80(7)		Br1	271.3(5)
Bi2–	Bi3	309.63(7)	Sn2A–	Br5	272.9(3)
	Bi1	312.47(6)		Br2 ^{ii, vi}	295.5(2)
	Bi1 ⁱⁱⁱ	312.80(7)		Br3 ^{i, v}	297.3(2)
	Bi2 ^{ii, iii}	342.38(6)	Sn2B–	Br3 ^{i, v}	267.4(2)
Bi3–	Bi2 ^{i, ii, iii, iv}	309.63(7)		Br5	280.4(4)
				Br2 ^{ii, vi}	328.0(3)
			Sn2C–	Br3 ^{i, v}	256(3)
				Br4	325(6)
Sn3A–	Br1 ^{ii, vi}	273.1(2)		Br5	334(7)
	Br4 ^{i, vii}	298.7(2)	Sn2D–	Br1 ^{ii, vi}	283(4)
Sn3B–	Br2 ^{viii, ix}	281(2)		Br4	288(4)
	Br5 ^{x, xi}	301.4(8)		Br3 ^{i, v}	299(4)

Results and Discussion

The Crystal Structure

The bismuth-rich bromidostannate(II) $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24} = (\text{Bi}_9^{5+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$ was crystallized from a melt of Bi, Sn and BiBr_3 . X-ray diffraction on a single-crystal at 110 K revealed a tetragonal structure with polycations Bi_9^{5+} that are separated by bromidostannate(II) groups (Figure 1).

With the caps of all antiprismatic Bi_9^{5+} clusters pointing in the same direction the crystal structure has a polar axis (space group $I4cm$). Beyond the crystallographic C_4 symmetry, the polycation shows only marginal deviations from the point group C_{4v} (equiv. $4mm$). The observed interatomic distances ($d(\text{Bi}-\text{Bi}) > 308$ pm) in the cluster agree quite well with those from the MP2 calculation (Tables 2 and 3). In a shell with Bi–Br distances between 328 pm and 359 pm, 24 Br atoms surround each polycation (Figure 2). This cage of anions around the center of the polycation in $00z$ (Wyckoff site $4a$ in $I4cm$) exhibits the pseudosymmetry D_4 , which corresponds to the point symmetry 422 of Wyckoff site $4a$ in the space group $I4/mcm$. The proximity of the coordinates of Br1 and Br2 (resp. of Br3 and Br4) to the symmetry relation $x, y, \frac{1}{2}-z$ can clearly be seen in Table 1.

The Br atoms belong to the bromidostannate(II) part of the structure ($d(\text{Sn}-\text{Br}) \geq 256$ pm), which is subject to substantial disorder of the Sn^{II} cations (Figure 3). This disorder seems to be caused by the pseudosymmetry: The Sn3 atom occupies two positions ($A : B \approx 10 : 1$) that would be equivalent in the space group $I4/mcm$ ($4b, \bar{4}2m$). In the case of an occupation of the Sn3A position, the Sn2A and Sn2B sites are favorable. The alternative is the combination of Sn3B with Sn2C and Sn2D. The coordinating Br anions react on the particular occupancies of the Sn^{II} cations by small shifts, which are included in the displacement factors. The same holds for the tetrahedrally coordinated Sn1 cation sites, of which only one out of four is occupied (Remark: There is no analytical evidence nor chemical significance (average charge +0.5) for full occupancy by a lighter atom, e. g. Si from the silica ampoule). The not

resolved static displacements misleadingly affect unusually short Sn1–Br distances. The [Sn1Br₄]-tetrahedron shares one edge and one corner with the pairs of edge-sharing ψ^1 -octahedra around Sn2 (Figures 3 and 4). The fourth corner of the [Sn1Br₄]-tetrahedron forms the connection to the ψ^2 -octahedron around Sn3. Taking the longer distances ($d(\text{Sn–Br}) > 360$ pm) into account, the coordination of Sn3 is extended to [4+2], the coordination of Sn2 to [5+2], and the previously isolated bromidostannate(II) groups appear to be linked into an open three-dimensional network.

The Issue of Cluster Shape

For Sn₉^{4−}, the question of *nido* or *closo* cluster has been controversially discussed for a long time [17]. Since the constitution of Bi₉⁵⁺ is equal to E₉^{4−} (E = Ge, Sn, Pb), this discussion can be applied to all isoelectronic clusters. Yet for M₉ clusters in general, and especially observed for Sn₉^{4−} [18], the difference between cluster conformations with C_{4v} or D_{3h} symmetry is admittedly small. The conversion from one to the other in solution takes place very fast, and even in solid state large displacement ellipsoids are observed in most cases, making a distinction between both conformers based on diffraction data difficult. This is not surprising since for Sn₉^{4−} the difference in energy is less than 5 kJ/mol [18]. Therefore Kloo et al. suggested that this question — *nido* or *closo* cluster / C_{4v} or D_{3h} symmetry — is actually not up for discussion.

For nine-atomic bismuth polyhedra things are quite similar. However, all Bi₉⁵⁺ clusters analyzed so far exhibit more or less D_{3h} symmetry. This can be exemplified regarding the parameters e (meaning edge lengths e_1 to e_6 of the equilateral triangles of the prism), h_i (heights $h_1 = h_2 = h_3$ for an ideal prism), and α_i (angles $\alpha_1 = \alpha_2 = \alpha_3$ for an ideal prism), see Figure 5 and literature [9c, 17] for comparison. As shown in Table 3 these are roughly fulfilled in all cases. For the family of compounds Bi(Bi₉)[MX₆]₃ (M = Zr, Hf, Nb; X = Cl, Br)

in particular, the deviation of the C_{3h} symmetric polyhedra from D_{3h} is very small [9]. Anyway, this approach does not consider the thermal movement of the cluster atoms.

Table 3. Characteristic parameters d , e , h and α (see Figure 5 for their definition) of previously characterized compounds containing the Bi_9^{5+} cluster and those of the one presented here, as well as optimized parameters (MP2 calculation, aug-cc-pVTZ basis sets) of both ideal clusters in D_{3h} and C_{4v} .

compound	symmetry	e	$h_1 / h_2 / h_3$	$\alpha_1 / \alpha_2 / \alpha_3$
calculated Bi_9^{5+}	D_{3h}	319 pm	373 pm	18.3°
Bi_6Br_7 [8c]	C_s	316 (2×) / 332 / 326 (2×) / 318 pm	372 (2×) / 392 pm	23.6 (2×) / 17.5°
Bi_6Cl_7 [8a]	C_s	317 (2×) / 328 / 322 (2×) / 320 pm	371 (2×) / 396 pm	23.8 (2×) / 16.2°
$\text{Bi}_{14}\text{Ag}_3\text{Br}_{21}$ [8k]	C_s	326 (2×) / 315 / 326 (2×) / 315 pm	375 (2×) / 357 pm	18.2 (2×) / 25.8°
$\text{Bi}_{37}\text{InBr}_{48}$ [8h]	C_1	314 / 328 / 327 / 314 / 329 / 328 pm	404 / 383 / 341 pm	13.6 / 18.2 / 29.6°
$\text{Bi}_{10}\text{Zr}_3\text{Br}_{18}$ [8f]	C_{3h}	325 pm	380 pm	22.5°
$\text{Bi}_{10}\text{Zr}_3\text{Cl}_{18}$ [8g]	C_{3h}	325 pm	374 pm	22.1°
$\text{Bi}_{10}\text{Hf}_3\text{Cl}_{18}$ [8e]	C_{3h}	324 pm	374 pm	22.2°
$\text{Bi}_{10}\text{Nb}_3\text{Cl}_{18}$ [7c]	C_{3h}	324 pm	374 pm	22.0°
compound	symmetry	d_1 / d_2	d_3 / d_4	
calculated Bi_9^{5+}	C_{4v}	447 pm	482 pm	
$\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$	C_4	436 / 436 pm	484 / 484 pm	

For a cluster with C_{4v} symmetry, the diagonals d_1 and d_2 as well as d_3 and d_4 of the squares have to be equal, and each two segments must enclose 90°. Further on, ideally these squares are staggered by a rotation through 45° and the single cap is situated above the center of one square. A $D_{3h} \rightarrow C_{4v}$ transformation is achieved by minimizing α_1 to 0° (still leaving $\alpha_2 = \alpha_3$), increasing h_1 to obtain d_1 (so that eventually $d_1 = d_2$), and changing h_2 and h_3 and those e parameters in-between to produce the square where $d_3 = d_4$.

In $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ the atoms Bi1 (Wyckoff position 4a, site symmetry 4..), Bi2 and Bi3 (both 16d, 1) generate the C_4 symmetric Bi_9^{5+} polycation. The displacement ellipsoids at 110(5) K do neither suggest a marked librational movement nor hint to a conversion into the

D_{3h} conformation. As the according parameters clearly confirm (Table 3), the Bi_9^{5+} cluster in $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ almost matches point group C_{4v} and thereby ideal *nido* conformation.

The performed quantum chemical calculations (MP2 / B3LYP) with aug-cc-pVTZ [15] basis sets and the ECP-MDF-60 [16] for Bi_9^{5+} show a slightly higher energetic stability for the C_{4v} symmetric cluster ($\Delta E = -3.3 / -2.7$ kJ/mol). In B3LYP no imaginary frequencies were observed for C_{4v} symmetry, while for D_{3h} the imaginary frequencies already indicate the conversion. These results of calculations conducted on a higher level of theory are in accordance with literature [19], but using only LANL-2DZ+PP basis sets D_{3h} seems to be stable in a MP2 calculation [20]. Anyway, all investigations confirm the low energy barrier between both conformations, and the comparatively small frequencies, which were obtained for the vibrations of the clusters, also point out that the potential energy hyper-surface is rather flat. Thus, the discussion is similar to the Sn_9^{4+} case [18].

Regarding the centers of gravity of the atom positions, still there has to be a reason why in all known cases (approx.) D_{3h} symmetric Bi_9^{5+} clusters are observed, the compound presented here being the only exception up to now, while for E_9^{4+} in contrast (approx.) C_{4v} symmetry seems to be preferred [18]. In this regard, a closer look also has to be taken at van der Waals radii of both cluster metals as well as the packing of clusters and counter ions in the crystal structures, and especially at nature, charge and distance of coordinating atoms in the immediate vicinity of the clusters. But this is a rather delicate issue, because differences are mostly quite small and the influence of different packing or effects of charge distribution etc. can hardly be evaluated reasonably. So it can simply be stated that a tri-capped trigonal prism (D_{3h}) provides a more homogenous (spherical) contact surface whereas a mono-capped square antiprism (C_{4v}) due to the single cap offers one more outstanding part, which might be of importance here. Furthermore, in the majority of reported compounds with E_9^{4+} clusters the interactions with the counter ions are weaker and more diffuse, especially when the cations are encased by cryptands.

On the side of the anionic structure part, Sn^{II} is, compared to the halogenidometallates with Bi^{III} , Zr^{IV} , Hf^{IV} , or Nb^{V} , a weaker Lewis acid and favors smaller coordination numbers for the cations. Furthermore the lone-pair of Sn^{II} is often found to be stereochemically active, which results in a hemispherical primary coordination (cf. Sn^{II} or Sn^{III}). The polarizability and the flexibility of the bromidostannate(II) groups might be advantageous for the formation of Bi_9^{5+} in the electronically (slightly) favorable C_{4v} symmetry. Unfortunately this structural flexibility goes along with crystallographic problems [21]. In the not yet published compound $\text{Bi}_{37}\text{Sn}_{47}\text{Br}_{117} = (\text{Bi}_9^{5+})_4[\text{BiSn}_{47}\text{Br}_{117}^{20-}]$, which also contains C_{4v} symmetric Bi_9^{5+} polycations (space group $Pmmn$, $a = 3121.6(1)$, $b = 2136.1(1)$, $c = 1908.3(1)$ pm at 110(5) K, $Z = 2$) we found similar disorder of the bromidostannate(II) network.

Conclusions

With $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24} = (\text{Bi}_9^{5+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$ the series of bismuth polycations that are stabilized by a Lewis acid has been expanded by the embedding into a matrix of halogenidostannate(II) anions. For the first time a C_{4v} symmetric Bi_9^{5+} polycation that is conform to the predictions of Wade's rules and to quantum chemical calculations is reported.

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References

- [1] R. B. King, P. von R. Schleyer, G. Linti, H. Schnöckel, W. Uhl, N. Wiberg, P. P. Power, I. Krossing, W. S. Scheldrick, in: *Molecular Clusters of the Main Group Elements*, M. Driess, H. Nöth (eds), Wiley-VCH, Weinheim 2004.
- [2] a) K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, 18, 1; b) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, 17, 311.
- [3] M. Ruck, *Angew. Chem.* **2001**, 113, 1222; *Angew. Chem. Int. Ed.* **2001**, 40, 1182.
- [4] a) M. Ruck, *Z. Anorg. Allg. Chem.* **1998**, 624, 521; b) M. Ruck, S. Hampel, *Polyhedron* **2002**, 21, 651.
- [5] a) J. D. Corbett, *Inorg. Chem.* **1968**, 7, 198; b) B. Krebs, M. Mummert, C. Brendel, *J. Less-Common Met.* **1986**, 116, 159; c) S. Ulvenlund, K. Ståhl, L. Bengtsson-Kloo, *Inorg. Chem.* **1996**, 35, 223; d) M. Lindsjö, A. Fischer, L. Kloo, *Eur. J. Inorg. Chem.* **2005**, 670; e) A. N. Kuznetsov, B. A. Popovkin, K. Ståhl, M. Lindsjö, L. Kloo, *Eur. J. Inorg. Chem.* **2005**, 4907; f) M. Ruck, F. Steden, *Z. Anorg. Allg. Chem.* **2007**, 633, 1556.
- [6] S. Hampel, M. Ruck, *Z. Anorg. Allg. Chem.* **2006**, 632, 1150.
- [7] a) R. M. Friedman, J. D. Corbett, *Inorg. Chim. Acta* **1973**, 7, 525; b) B. Krebs, M. Hücke, C. J. Brendel, *Angew. Chem.* **1982**, 94, 453; *Angew. Chem. Int. Ed.* **1982**, 21, 445; c) J. Beck, T. Hilbert, *Eur. J. Inorg. Chem.* **2004**, 2019; d) A. N. Kuznetsov, B. A. Popovkin, *Z. Anorg. Allg. Chem.* **2002**, 628, 2179.

- [8] a) M. Ruck, V. Dubenskyy, T. Söhnel, *Angew. Chem.* **2003**, *115*, 3086; *Angew. Chem. Int. Ed.* **2003**, *42*, 2978; b) M. Ruck, V. Dubenskyy, T. Söhnel, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2458; c) B. Wahl, L. Kloo, M. Ruck, *Angew. Chem.* **2008**, *120*, 3996; *Angew. Chem. Int. Ed.* **2008**, *47*, 3932; d) B. Wahl, M. Ruck, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2267; e) B. Wahl, M. Erbe, A. Gerisch, L. Kloo, M. Ruck, *Z. Anorg. Allg. Chem.* **2009**, *635*, 743.
- [9] a) A. Hershaft, J. D. Corbett, *Inorg. Chem.* **1963**, *2*, 979; b) A. Hershaft, J. D. Corbett, *J. Chem. Phys.* **1962**, *36*, 551; c) H. von Benda, A. Simon, W. Bauhofer, *Z. Anorg. Allg. Chem.* **1978**, *438*, 53; d) J. Beck, C. J. Brendel, L. Bengtsson-Kloo, B. Krebs, M. Mummert, A. Stankowski, S. Ulvenlund, *Chem. Ber.* **1996**, *129*, 1219; e) R. M. Friedman, J. D. Corbett, *Inorg. Chem.* **1973**, *12*, 1134; f) A. N. Kuznetsov, A. V. Shevel'kov, S. I. Troyanov, B. A. Popovkin, *Zh. Neorg. Khim.* **1996**, *41*, 958; *Russ. J. Inorg. Chem.* **1996**, *41*, 920; g) A. N. Kuznetsov, A. V. Shevel'kov, B. A. Popovkin, *Koord. Khim.* **1998**, *24*, 919; *Russ. J. Coord. Chem.* **1998**, *24*, 861; h) M. Ruck, V. Dubenskyy, *Z. Anorg. Allg. Chem.* **2003**, *629*, 375; i) A. N. Kuznetsov, P. I. Naumenko, B. A. Popovkin, L. Kloo, *Russ. Chem. Bull.* **2003**, *52*, 2100; j) S. Hampel, P. Schmidt, M. Ruck, *Z. Anorg. Allg. Chem.* **2005**, *631*, 272; k) B. Wahl, M. Ruck, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2873.
- [10] a) X-SHAPE 1.06, *Crystal Optimisation for Numerical Absorption Correction Program*, Stoe & Cie GmbH, Darmstadt 1999; b) X-RED32 1.01, *Data Reduction Program*, Stoe & Cie GmbH, Darmstadt 2001.
- [11] a) G. M. Sheldrick, *SHELX97, Programs for crystal structure determination*, Univ. of Göttingen, 1997; b) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
- [12] K. Brandenburg, *Diamond 3.2, Crystal and Molecular Structure Visualization*, Crystal Impact GbR, Bonn 2009.

- [13] a) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [14] *Gaussian 03*, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [15] K. A. Peterson, *J. Chem. Phys.* **2003**, 119, 11099.
- [16] B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, 113, 2563.
- [17] T. F. Fässler, *Coord. Chem. Rev.* **2001**, 215, 347.
- [18] J. Rosdahl, T. F. Fässler, L. Kloo, *Eur. J. Inorg. Chem.* **2005**, 2888.
- [19] A. N. Kuznetsov, L. Kloo, M. Lindsjö, J. Rosdahl, H. Stoll, *Chem. Eur. J.* **2001**, 7, 2821.
- [20] G. Day, R. Glaser, N. Shimomura, A. Takamuku, K. Ichikawa, *Chem. Eur. J.* **2000**, 6, 1078.
- [21] M. Ruck, *Z. Kristallogr.* **2000**, 215, 148.

Figure 1. Crystal structure of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$. Partially occupied positions Sn2B, Sn2C, Sn2D, and Sn3B are omitted. Only one out of four shown tetrahedrally coordinated Sn1 positions is occupied. The coordination polyhedra for Sn are restricted to bonds shorter than 300 pm. The ellipsoids represent 95 % probability at 110 K.

Figure 2. The C_{4v} symmetric Bi_9^{5+} polycation in its D_4 symmetric surrounding of 24 Br atoms. The ellipsoids represent 95 % probability at 110 K.

Figure 3. Disorder in the bromidostannate(II) matrix of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$. The most probable combination of occupancies (Sn2A, Sn2B, Sn3A) is emphasized. Sn–Br bonds shorter than 300 pm are drawn with solid lines; broken lines indicate distances longer than 360 pm. The ellipsoids represent 95 % probability at 110 K.

Figure 4. Bromidostannate(II) matrix in the crystal structure of $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$. Partially occupied positions Sn2B, Sn2C, Sn2D, and Sn3B are omitted. Only one out of four shown tetrahedrally coordinated Sn1 positions is occupied. Sn–Br bonds shorter than 300 pm are drawn with solid lines; broken lines indicate distances longer than 360 pm. The ellipsoids represent 95 % probability at 110 K.

Figure 5. The Bi_9^{5+} polycation in the two favored symmetries D_{3h} and C_{4v} (atomic parameters taken from quantum chemical calculations). Letters d , e , h and α denote characteristic geometrical parameters (see Table 3):

$e \dots$ edge length of the equilateral triangles of the trigonal prism.

$h_i \dots$ heights of the trigonal prism, with $h_1 = h_2 = h_3$.

$\alpha_i \dots$ dihedral angles, with $\alpha_1 = \alpha_2 = \alpha_3$. Only α_1 is shown for the sake of clearness.

$d_i \dots$ diagonals of the antiprism squares, with $d_1 = d_2$ and $d_3 = d_4$ and each two enclosing an angle of 90° . The angle of tilt between both squares amounts to 45° , the capping atom is situated above the center of the square.

531x562mm (96 x 96 DPI)

531x500mm (96 x 96 DPI)

531x562mm (96 x 96 DPI)