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**Finally Fulfilling Wade's Rules: The  $C_{4v}$  Symmetric Polycation  $Bi_{95}^+$  in the Polar Structure of  $Bi_{18}Sn_7Br_{24} = (Bi_{95}^+)_2[Sn_7Br_{24}^{10-}]$**

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**Finally Fulfilling Wade's Rules: The  $C_{4v}$  Symmetric  
Polycation  $\text{Bi}_9^{5+}$   
in the Polar Structure of  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24} = (\text{Bi}_9^{5+})_2[\text{Sn}_7\text{Br}_{24}^{10-}]$**

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



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9 **Bernhard Wahl<sup>[a]</sup> and Michael Ruck<sup>\*,[a]</sup>**  
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14 *Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 65<sup>th</sup> Birthday*  
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19 **Keywords:** Bismuth; Cluster compounds; Electron counting rules; Polar structure;

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21 Pseudosymmetry  
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23  
24 **Running title:** The  $C_{4v}$  Symmetric Polycation  $\text{Bi}_9^{5+}$   
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28  
29 **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  
30 crystallized from a melt of Bi, Sn and  $\text{BiBr}_3$ . X-ray diffraction on a single-crystal revealed a  
31 polar, tetragonal structure (space group  $I4cm$ , no. 108) with lattice parameters  $a = 1323.70(5)$   
32 pm and  $c = 1816.86(8)$  pm at 110(5) K. In agreement with Wade's rules and quantum  
33 chemical calculations, the homonuclear *nido*-cluster  $\text{Bi}_9^{5+}$  is a mono-capped square antiprism  
34 (point group  $C_{4v}$ ). The anions of the bromidostannate(II) groups mainly comply with the  
35 pseudosymmetry of the space group  $I4/mcm$  and thereby affect substantial disorder of the  $\text{Sn}^{\text{II}}$   
36 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  $\text{Bi}_5^+$  (*nido*, 14 SE), [4]  $\text{Bi}_5^{3+}$  (*closo*, 12 SE) [5],  $\text{Bi}_6^{2+}$  (*nido*, 16 SE) [4, 6],  $\text{Bi}_8^{2+}$  (*arachno*, 22 SE) [7], and  $\text{Bi}_{10}^{4+}$  (*arachno*, 26 SE) [8]. Unfortunately,  $\text{Bi}_9^{5+}$  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  $\text{Bi}_9^{5+}$  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 arose. 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  $\text{Bi}_9^{5+}$  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  $\text{BiBr}_3$  (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  $\text{Bi}_6\text{Br}_7$  [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  $\text{MoK}_\alpha$  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

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3 isotropic, Sn3 atoms with equal anisotropic displacement parameters. The examined crystal  
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5 was an inversion twin with the domain ratio of 0.463:0.537(9). Twin refinements in the  
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7 maximal translationengleiche subgroups *Iba2* and *Fmm2* as well as in *Cc* did not result in  
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9 ordered structure models. For visualization of the structure, the program Diamond was used  
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11 [12].  
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14  
15  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ ,  $M_m = 6510.31 \text{ g mol}^{-1}$ , tetragonal, *I4cm* (no. 108),  $T = 110(5) \text{ K}$ ,  $a =$   
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17  $1323.70(5) \text{ pm}$ ,  $c = 1816.86(8) \text{ pm}$ ,  $V = 3183.5(2) \cdot 10^6 \text{ pm}^3$ , ( $T = 293(1) \text{ K}$ :  $a = 1332.7(2)$   
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19  $\text{pm}$ ,  $c = 1842.9(4) \text{ pm}$ ,  $V = 3273(2) \cdot 10^6 \text{ pm}^3$ ),  $Z = 2$ ,  $\rho_{\text{calc}} = 6.792 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 67.3$   
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21  $\text{mm}^{-1}$ ,  $2\theta_{\text{max}} = 56.1^\circ$ ,  $-17 \leq h, k \leq 17$ ,  $-23 \leq l \leq 23$ , 12961 measured reflections, 2024 unique  
22  
23 reflections,  $R_{\text{int}} = 0.045$ ,  $R_\sigma = 0.022$ , 78 parameters, 1 restraint, extinction parameter  $x = 5(1) \cdot$   
24  
25  $10^{-5}$ ,  $R_1(1976 F_o > 4\sigma(F_o)) = 0.027$ ,  $R_1(\text{all } F_o) = 0.028$ ,  $wR_2(\text{all } F_o^2) = 0.058$ ,  $Goof = 1.07$ ,  
26  
27 residual electron density  $+1.56/-1.40 \text{ e} \cdot 10^{-6} \text{ pm}^{-3}$ . Atomic parameters are listed in Table 1,  
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29 selected interatomic distances are gathered in Table 2. Further data, in the form of a CIF, have  
30  
31 been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-  
32  
33 Leopoldshafen, Germany (E-mail address: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)), as supplementary  
34  
35 material no. CSD-420786, and can be obtained by contacting the FIZ quoting the article  
36  
37 details and the CSD number.  
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### 45 ***Quantum Chemical Calculations***

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48 The atomic parameters of the  $C_{4v}$  and the  $D_{3h}$  symmetric polycations were optimized in DFT-  
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50 B3LYP [13] or in MP2 calculations using the program Gaussian03 [14] along with an aug-cc-  
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52 pVTZ basis set [15]. The inner electrons of Bi were replaced using the core potentials ECP-  
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54 MDF60 [16]. The second derivative matrix of the B3LYP calculation was used in order to  
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56 evaluate the nature of the stationary points. In case of  $D_{3h}$  symmetry, the negative frequencies  
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58 that convert the cluster into the  $C_{4v}$  conformation are observed.  
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**Table 1.** Wyckoff positions, occupancies, coordinates and (equivalent) isotropic displacement parameters of the atoms in  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$  at 110(5) K.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

atom	W. p.	occup.	$x$	$y$	$z$	$U_{\text{eq}}, U_{\text{iso}}$
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  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$  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 <sup>ii, iii</sup>	308.51(6)	Sn1–	Br3 <sup>i, v</sup>	257.1(3)
	Bi2	312.47(6)		Br2	262.3(5)
	Bi2 <sup>ii</sup>	312.80(7)		Br1	271.3(5)
Bi2–	Bi3	309.63(7)	Sn2A–	Br5	272.9(3)
	Bi1	312.47(6)		Br2 <sup>ii, vi</sup>	295.5(2)
	Bi1 <sup>iii</sup>	312.80(7)		Br3 <sup>i, v</sup>	297.3(2)
	Bi2 <sup>ii, iii</sup>	342.38(6)	Sn2B–	Br3 <sup>i, v</sup>	267.4(2)
Bi3–	Bi2 <sup>i, ii, iii, iv</sup>	309.63(7)		Br5	280.4(4)
				Br2 <sup>ii, vi</sup>	328.0(3)
			Sn2C–	Br3 <sup>i, v</sup>	256(3)
				Br4	325(6)
Sn3A–	Br1 <sup>ii, vi</sup>	273.1(2)		Br5	334(7)
	Br4 <sup>i, vii</sup>	298.7(2)	Sn2D–	Br1 <sup>ii, vi</sup>	283(4)
Sn3B–	Br2 <sup>viii, ix</sup>	281(2)		Br4	288(4)
	Br5 <sup>x, xi</sup>	301.4(8)		Br3 <sup>i, v</sup>	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  $\text{BiBr}_3$ . X-ray diffraction on a single-crystal at 110 K revealed a tetragonal structure with polycations  $\text{Bi}_9^{5+}$  that are separated by bromidostannate(II) groups (Figure 1).

With the caps of all antiprismatic  $\text{Bi}_9^{5+}$  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  $\text{Sn}^{\text{II}}$  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  $\text{Sn}^{\text{II}}$  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

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3 resolved static displacements misleadingly affect unusually short Sn1–Br distances. The  
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5 [Sn1Br<sub>4</sub>]-tetrahedron shares one edge and one corner with the pairs of edge-sharing  $\psi^1$ -  
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7 octahedra around Sn2 (Figures 3 and 4). The fourth corner of the [Sn1Br<sub>4</sub>]-tetrahedron forms  
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9 the connection to the  $\psi^2$ -octahedron around Sn3. Taking the longer distances ( $d(\text{Sn–Br}) > 360$   
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11 pm) into account, the coordination of Sn3 is extended to [4+2], the coordination of Sn2 to  
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13 [5+2], and the previously isolated bromidostannate(II) groups appear to be linked into an open  
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15 three-dimensional network.  
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### 22 *The Issue of Cluster Shape*

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24 For Sn<sub>9</sub><sup>4-</sup>, the question of *nido* or *closo* cluster has been controversially discussed for a long  
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26 time [17]. Since the constitution of Bi<sub>9</sub><sup>5+</sup> is equal to E<sub>9</sub><sup>4-</sup> (E = Ge, Sn, Pb), this discussion can  
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28 be applied to all isoelectronic clusters. Yet for M<sub>9</sub> clusters in general, and especially observed  
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30 for Sn<sub>9</sub><sup>4-</sup> [18], the difference between cluster conformations with C<sub>4v</sub> or D<sub>3h</sub> symmetry is  
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32 admittedly small. The conversion from one to the other in solution takes place very fast, and  
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34 even in solid state large displacement ellipsoids are observed in most cases, making a  
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36 distinction between both conformers based on diffraction data difficult. This is not surprising  
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38 since for Sn<sub>9</sub><sup>4-</sup> the difference in energy is less than 5 kJ/mol [18]. Therefore Kloo et al.  
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40 suggested that this question — *nido* or *closo* cluster / C<sub>4v</sub> or D<sub>3h</sub> symmetry — is actually not  
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42 up for discussion.  
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49 For nine-atomic bismuth polyhedra things are quite similar. However, all Bi<sub>9</sub><sup>5+</sup> clusters  
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51 analyzed so far exhibit more or less D<sub>3h</sub> symmetry. This can be exemplified regarding the  
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53 parameters *e* (meaning edge lengths *e*<sub>1</sub> to *e*<sub>6</sub> of the equilateral triangles of the prism), *h*<sub>*i*</sub>  
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55 (heights *h*<sub>1</sub> = *h*<sub>2</sub> = *h*<sub>3</sub> for an ideal prism), and  $\alpha_i$  (angles  $\alpha_1 = \alpha_2 = \alpha_3$  for an ideal prism), see  
56  
57 Figure 5 and literature [9c, 17] for comparison. As shown in Table 3 these are roughly  
58  
59 fulfilled in all cases. For the family of compounds Bi(Bi<sub>9</sub>)[MX<sub>6</sub>]<sub>3</sub> (M = Zr, Hf, Nb; X = Cl, Br)  
60

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  $\alpha$  (see Figure 5 for their definition) of previously characterized compounds containing the  $\text{Bi}_9^{5+}$  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 $\text{Bi}_9^{5+}$	$D_{3h}$	319 pm	373 pm	18.3°
$\text{Bi}_6\text{Br}_7$ [8c]	$C_s$	316 (2×) / 332 / 326 (2×) / 318 pm	372 (2×) / 392 pm	23.6 (2×) / 17.5°
$\text{Bi}_6\text{Cl}_7$ [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 $\text{Bi}_9^{5+}$	$C_{4v}$	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  $\alpha_1$  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  $\text{Bi}_9^{5+}$  polycation. The displacement ellipsoids at 110(5) K do neither suggest a marked librational movement nor hint to a conversion into the

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3  $D_{3h}$  conformation. As the according parameters clearly confirm (Table 3), the  $\text{Bi}_9^{5+}$  cluster in  
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5  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$  almost matches point group  $C_{4v}$  and thereby ideal *nido* conformation.  
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8 The performed quantum chemical calculations (MP2 / B3LYP) with aug-cc-pVTZ  
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10 [15] basis sets and the ECP-MDF-60 [16] for  $\text{Bi}_9^{5+}$  show a slightly higher energetic stability  
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12 for the  $C_{4v}$  symmetric cluster ( $\Delta E = -3.3 / -2.7$  kJ/mol). In B3LYP no imaginary frequencies  
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14 were observed for  $C_{4v}$  symmetry, while for  $D_{3h}$  the imaginary frequencies already indicate the  
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16 conversion. These results of calculations conducted on a higher level of theory are in  
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18 accordance with literature [19], but using only LANL-2DZ+PP basis sets  $D_{3h}$  seems to be  
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20 stable in a MP2 calculation [20]. Anyway, all investigations confirm the low energy barrier  
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22 between both conformations, and the comparatively small frequencies, which were obtained  
23  
24 for the vibrations of the clusters, also point out that the potential energy hyper-surface is  
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26 rather flat. Thus, the discussion is similar to the  $\text{Sn}_9^{4-}$  case [18].  
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31 Regarding the centers of gravity of the atom positions, still there has to be a reason  
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33 why in all known cases (approx.)  $D_{3h}$  symmetric  $\text{Bi}_9^{5+}$  clusters are observed, the compound  
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35 presented here being the only exception up to now, while for  $E_9^{4-}$  in contrast (approx.)  $C_{4v}$   
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37 symmetry seems to be preferred [18]. In this regard, a closer look also has to be taken at van  
38  
39 der Waals radii of both cluster metals as well as the packing of clusters and counter ions in the  
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41 crystal structures, and especially at nature, charge and distance of coordinating atoms in the  
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43 immediate vicinity of the clusters. But this is a rather delicate issue, because differences are  
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45 mostly quite small and the influence of different packing or effects of charge distribution etc.  
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47 can hardly be evaluated reasonably. So it can simply be stated that a tri-capped trigonal prism  
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49 ( $D_{3h}$ ) provides a more homogenous (spherical) contact surface whereas a mono-capped square  
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51 antiprism ( $C_{4v}$ ) due to the single cap offers one more outstanding part, which might be of  
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53 importance here. Furthermore, in the majority of reported compounds with  $E_9^{4-}$  clusters the  
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55 interactions with the counter ions are weaker and more diffuse, especially when the cations  
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57 are encased by cryptands.  
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3 On the side of the anionic structure part,  $\text{Sn}^{\text{II}}$  is, compared to the halogenidometallates  
4 with  $\text{Bi}^{\text{III}}$ ,  $\text{Zr}^{\text{IV}}$ ,  $\text{Hf}^{\text{IV}}$ , or  $\text{Nb}^{\text{V}}$ , a weaker Lewis acid and favors smaller coordination numbers  
5 for the cations. Furthermore the lone-pair of  $\text{Sn}^{\text{II}}$  is often found to be stereochemically active,  
6 which results in a hemispherical primary coordination (cf. Sn2 or Sn3). The polarizability and  
7 the flexibility of the bromidostannate(II) groups might be advantageous for the formation of  
8  $\text{Bi}_9^{5+}$  in the electronically (slightly) favorable  $C_{4v}$  symmetry. Unfortunately this structural  
9 flexibility goes along with crystallographic problems [21]. In the not yet published compound  
10  $\text{Bi}_{37}\text{Sn}_{47}\text{Br}_{117} = (\text{Bi}_9^{5+})_4[\text{BiSn}_{47}\text{Br}_{117}^{20-}]$ , which also contains  $C_{4v}$  symmetric  $\text{Bi}_9^{5+}$  polycations  
11 (space group  $Pm\bar{m}n$ ,  $a = 3121.6(1)$ ,  $b = 2136.1(1)$ ,  $c = 1908.3(1)$  pm at 110(5) K,  $Z = 2$ ) we  
12 found similar disorder of the bromidostannate(II) network.  
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## 31 Conclusions

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34 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  
35 a Lewis acid has been expanded by the embedding into a matrix of halogenidostannate(II)  
36 anions. For the first time a  $C_{4v}$  symmetric  $\text{Bi}_9^{5+}$  polycation that is conform to the predictions  
37 of Wade's rules and to quantum chemical calculations is reported.  
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3 **Figure 1.** Crystal structure of  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ . Partially occupied positions Sn2B, Sn2C, Sn2D,  
4 and Sn3B are omitted. Only one out of four shown tetrahedrally coordinated Sn1 positions is  
5 occupied. The coordination polyhedra for Sn are restricted to bonds shorter than 300 pm. The  
6 ellipsoids represent 95 % probability at 110 K.  
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13 **Figure 2.** The  $C_{4v}$  symmetric  $\text{Bi}_9^{5+}$  polycation in its  $D_4$  symmetric surrounding of 24 Br  
14 atoms. The ellipsoids represent 95 % probability at 110 K.  
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22 **Figure 3.** Disorder in the bromidostannate(II) matrix of  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ . The most probable  
23 combination of occupancies (Sn2A, Sn2B, Sn3A) is emphasized. Sn–Br bonds shorter than  
24 300 pm are drawn with solid lines; broken lines indicate distances longer than 360 pm. The  
25 ellipsoids represent 95 % probability at 110 K.  
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33 **Figure 4.** Bromidostannate(II) matrix in the crystal structure of  $\text{Bi}_{18}\text{Sn}_7\text{Br}_{24}$ . Partially  
34 occupied positions Sn2B, Sn2C, Sn2D, and Sn3B are omitted. Only one out of four shown  
35 tetrahedrally coordinated Sn1 positions is occupied. Sn–Br bonds shorter than 300 pm are  
36 drawn with solid lines; broken lines indicate distances longer than 360 pm. The ellipsoids  
37 represent 95 % probability at 110 K.  
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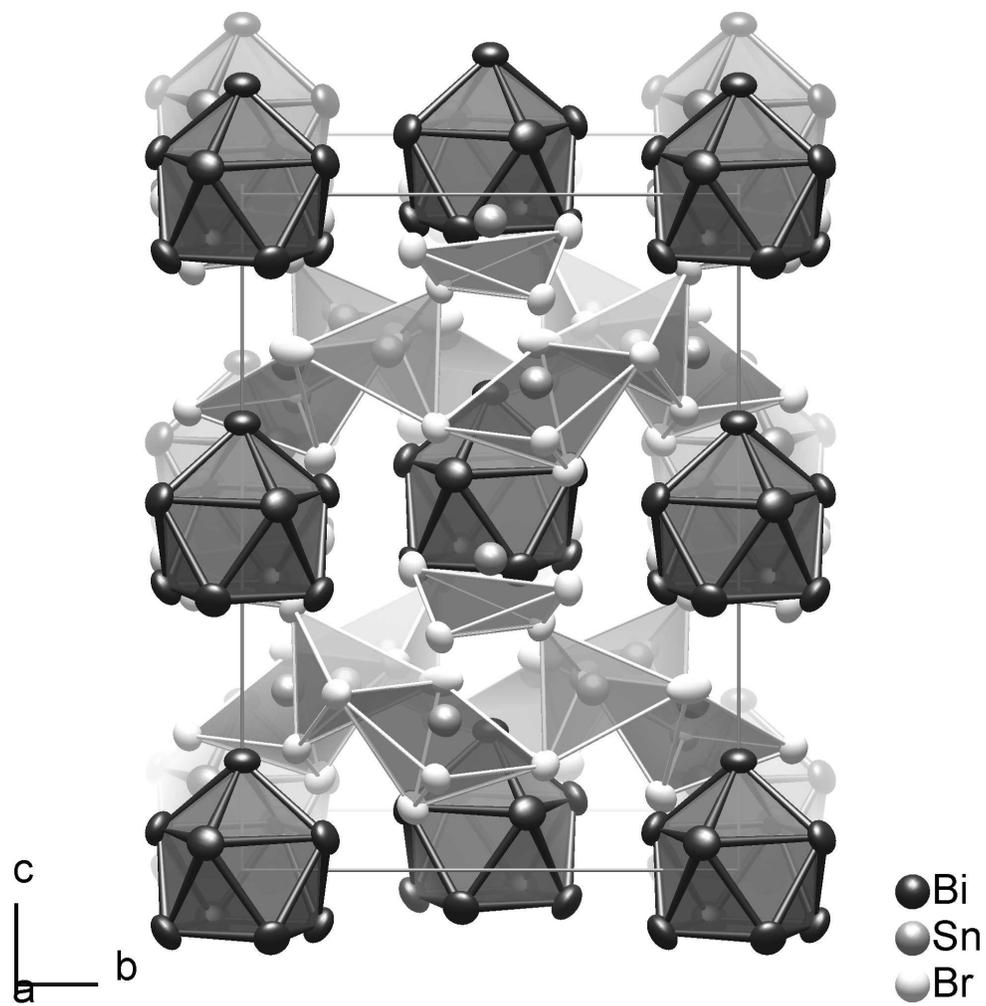
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48 **Figure 5.** The  $\text{Bi}_9^{5+}$  polycation in the two favored symmetries  $D_{3h}$  and  $C_{4v}$  (atomic parameters  
49 taken from quantum chemical calculations). Letters  $d$ ,  $e$ ,  $h$  and  $\alpha$  denote characteristic  
50 geometrical parameters (see Table 3):  
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55  $e \dots$  edge length of the equilateral triangles of the trigonal prism.  
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58  $h_i \dots$  heights of the trigonal prism, with  $h_1 = h_2 = h_3$ .  
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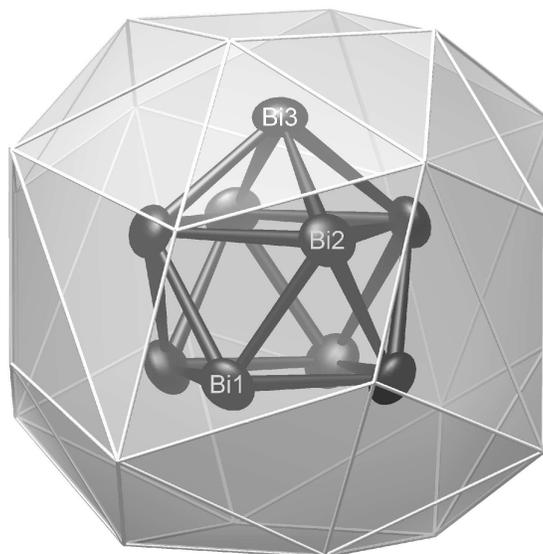
60  $\alpha_i \dots$  dihedral angles, with  $\alpha_1 = \alpha_2 = \alpha_3$ . Only  $\alpha_1$  is shown for the sake of clearness.

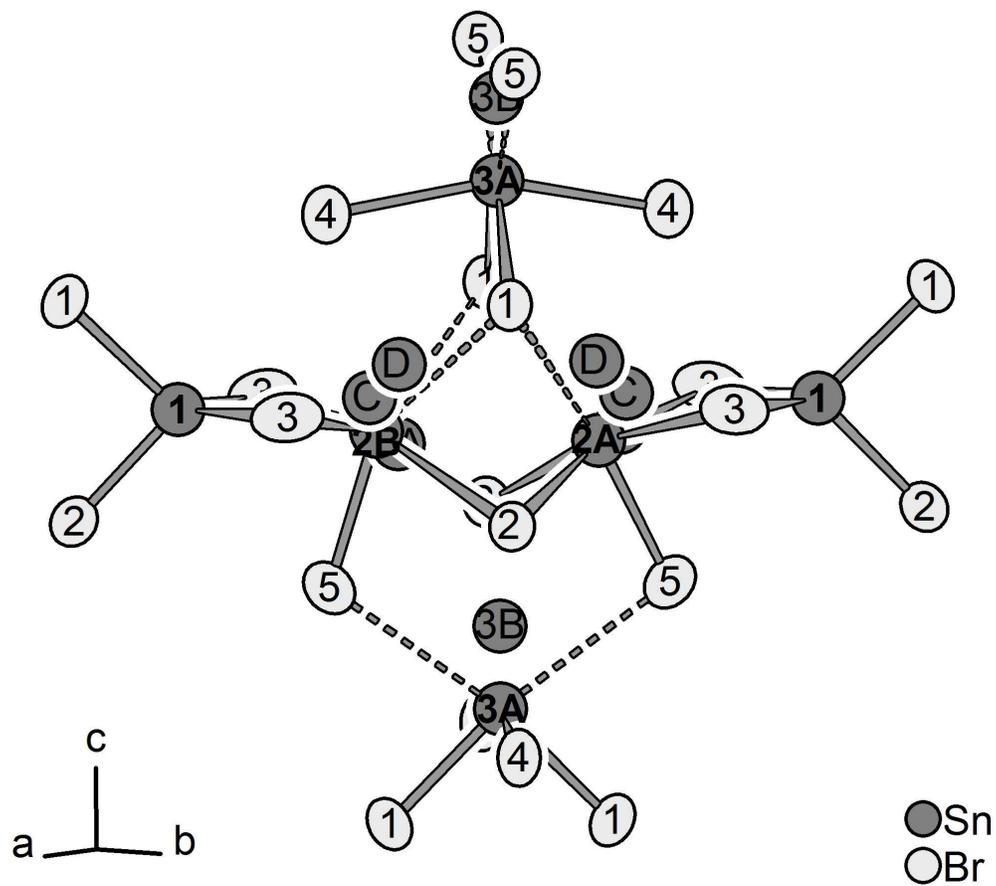
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3  $d_i \dots$  diagonals of the antiprism squares, with  $d_1 = d_2$  and  $d_3 = d_4$  and each two enclosing an  
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5 angle of  $90^\circ$ . The angle of tilt between both squares amounts to  $45^\circ$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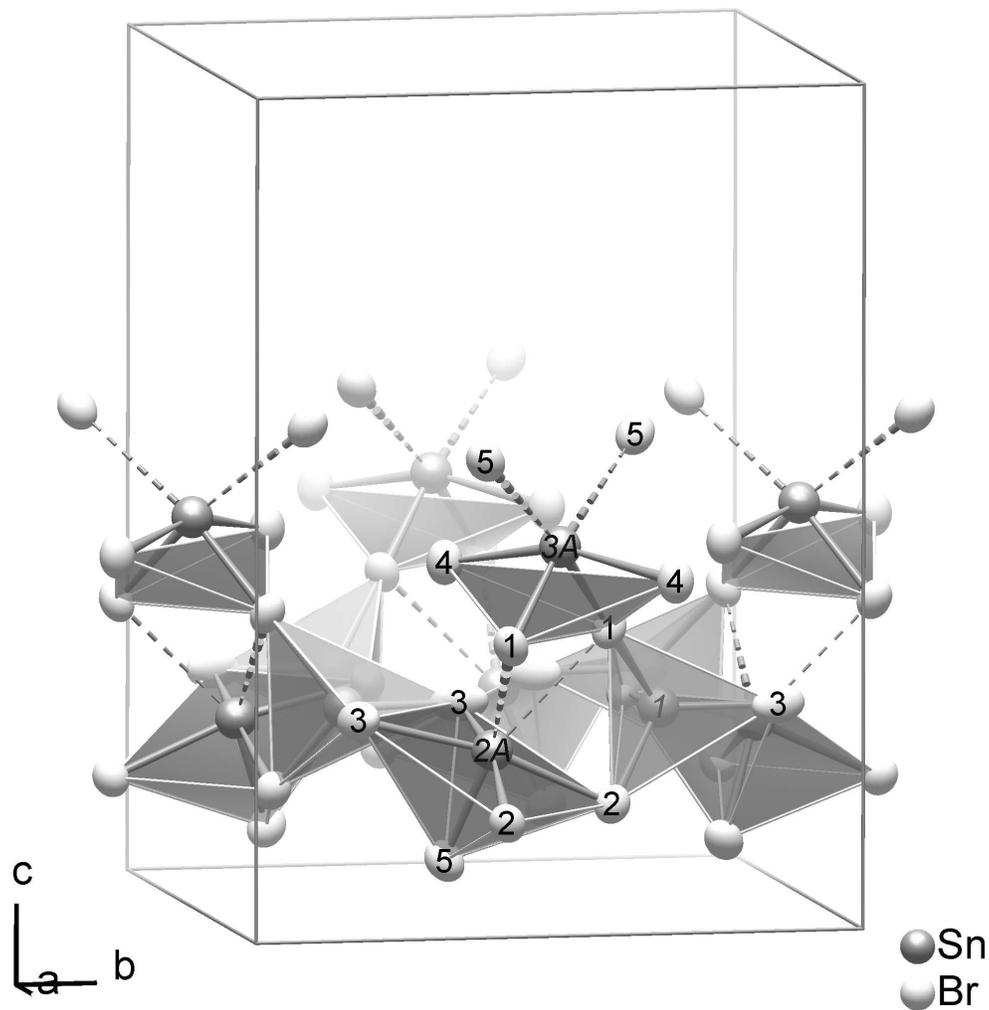
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