

On the Stereochemistry of the Lone-Pair Electrons in AX₆E-Systems: Dynamically Distorted Anion in (NH₄)₂SeBr₆, Statically Distorted Anion in 1,3-Propanediammonium-Hexabromoselenate(IV) (C₃N₂H₁₂)SeBr₆

Walter Abriel

Institut für Anorganische Chemie und SFB 173 der Universität Hannover,
Callinstraße 9, D-3000 Hannover 1

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Using 293 K diffractometer intensity data, the crystal structures of (NH₄)₂SeBr₆ (**1**) and [H₃N(CH₂)₃NH₃]SeBr₆ (**2**) have been determined by single crystal X-ray technique and refined to a final *R*_w of 0.049 and 0.040, respectively. The dark red crystals of **1** are cubic (space group Fm $\bar{3}$ m) with *a* = 10.478(2) Å and *Z* = 4. This structure contains SeBe₆²⁻ octahedra (point symmetry m $\bar{3}$ m, distance Se–Br: 2.577(2) Å) in an antifluorite type arrangement of cations and anions. In contrast, the SeBr₆²⁻ ion in **2** is statically distorted (approximate point symmetry 3m, distance Se–Br min. 2.547(2), max. 2.595(2) Å). The dark red crystals are orthorhombic (space group Pnma) with *a* = 17.795(3), *b* = 7.5037(6), *c* = 10.476(1) Å and *Z* = 4. The results agree with the rules for the appearance of a static/dynamic stereochemical effect of the lone pair electrons given for TeX₆²⁻ (X = Cl, Br, I) species (W. Abriel, Acta Crystallogr. **B** **42**, 449 (1986)). Consequently these rules can be extended considering SeX₆²⁻ as well. Basic structural data for all compounds containing AX₆²⁻ ions (A = Se, Te; X = Cl, Br, I) known to date are given including the Δ -values (R. D. Shannon, Acta Crystallogr. **A** **32**, 751 (1976)) as a measure for the distortion of the octahedral anion.

Introduction

According to VSEPR theory [1], a distorted coordination is expected for systems of the type AX₆E, which contains six bonding electron pairs and one nonbonding electron pair in the valence shell of the central atom. Therefore the anions TeX₆²⁻ and SeX₆²⁻ (X = Cl, Br, I) were considered to be the most famous exceptions to these rules, because they always showed regular octahedral coordination [2]. The IR-active vibrations T_{1u} (ν_3 and ν_4) of the AX₆²⁻ octahedron (A = Se, Te) are, however, relatively broad which is an indication of vibronic coupling between the ground state (configuration a_{1g}σ*) and the first excited state (configuration a_{1g}σ*, t_{1u}σ*) [3]. Expectations of detecting a “frozen” distorted species by X-ray diffraction or FTIR-spectroscopic techniques down to ca. 10 K were not fulfilled in investigations on compounds A₂TeX₆ (A = Rb, Cs; X = Cl, Br) [4, 5]. As Pearson [6] presumed, the octahedrally enforced, dynamic structure is stabilized by a highly symmetrical crystal field, which, for example, is realized in the simple alkaline-hexahalo-selenates(IV) and -tellurates(IV) by an antifluorite arrangement of cations and anions.

The transition from the dynamically distorted structure of the TeX₆²⁻ ion (mean symmetry m $\bar{3}$ m) to a statically distorted species could be achieved by lowering the symmetry of the crystal field. Structural investigations on Ca(H₂O, HF)₇TeBr₆ [7], [H₃N(CH₂)₃NH₃]TeCl₆ [8], and (Me₄N)₂(CH₃CN)TeCl₆ [9] confirmed this idea by yielding statically distorted TeX₆ octahedra. Consequently symmetry rules for the appearance of a static or dynamic distortion of the TeX₆²⁻ ion could be derived [10]. The responsibility of hydrogen bonding from the cations for the distortions was checked, but a comparison with the corresponding SnX₆²⁻ salts did not yield an evidence for this idea [10].

An extension of these rules to include the SeX₆²⁻ ion as well should be possible, but there is not much structural information on hexahaloselenates(IV) in the literature. Therefore the present work was performed in order to get high quality structural data for a dynamically and a statically distorted SeBr₆²⁻ ion.

Experimental Procedures and X-Ray Structure Analysis

SeO₂ prepared by oxidation of Se in dry O₂ stream according to Brauer [11]. From the mixed solutions of SeO₂ (excess) and NH₄Br or 1,3-diaminopropane in conc. hydrobromic acid, dark red crystals of

	(NH ₄) ₂ SeBr ₆	(H ₃ N(CH ₂) ₃ NH ₃)SeBr ₆
Crystal shape	cubeoctahedral	irregular
Crystal volume [mm ³]	5.8 × 10 ⁻³	7.1 × 10 ⁻³
Diffractometer	SIEMENS AED2, graphite monochr. MoK _α -rad.	
Determination of cell parameters:		
number of reflexions used (θ -range)	34 (15.6–48°)	43 (18.7–44.5°)
cell parameters at 293 K [Å]	$a = 10.478(2)$	$a = 17.795(3)$ $b = 7.5037(6)$ $c = 10.476(1)$
Space group	Fm $\bar{3}$ m	Pnma
Z	4	4
Calculated density [g cm ⁻³]	3.43	3.01
Intensity data collection:		
max. $\sin \theta/\lambda$ [Å ⁻¹]	0.995	0.595
range of h, k, l	$\bar{2}0, 0, 0$ to $20, 20, 20$	$\bar{2}\bar{1}, 0, \bar{1}\bar{2}$ to $21, 8, 12$
scan mode	Ω	Ω
min. scan angle [°]	1.8	1.4
max. scan time [sec]	41	36
standard reflexions	444, $\bar{4}44, \bar{4}\bar{4}\bar{4}$	723, $\bar{7}2\bar{3}, \bar{7}\bar{2}\bar{3}$
intensity variation	<1%	<1%
measured reflexions	1511	4396
unique reflexions	289	1335
observed reflexions ($F > 3\sigma(F)$)	120	812
R_{int}	0.152	0.098
Absorption correction:		
min.–max. transmission	0.036–0.098	0.054–0.156
μ [cm ⁻¹]	235.9	194.0
Structure determination technique	model from ref. [13]	model from similar (N ₂ C ₃ H ₁₂)SnCl ₆
Structure refinement (based on F):		
R^*, R_w^* ($W = 1/\sigma^2(F_o)$), S^*	0.074, 0.049, 2.22	0.059, 0.040, 2.35
no. of parameters refined	6	70
max. final $ \Delta /\sigma$	0	0
max. and min. $\Delta\rho$ [eÅ ⁻³]	0.37, –0.55	0.48, –0.6

Table I. Experimental information and structure determination details.

* Definition see Acta Crystallogr. B 38, 699 (1982).

(NH₄)₂SeBr₆ (**1**), and (H₃N–C₃H₆–NH₃)SeBr₆ (**2**) precipitate immediately. Recrystallisation in hydrobromic acid and drying over KOH yielded crystals useful for X-ray diffractometry. They were placed in capillaries in order to protect them from moisture.

Details of the X-ray data collection and information on the structure determinations are given in Table I. Atomic scattering factors for neutral atoms were taken from International Tables [12]. The program used was STRUCSY from the diffractometer software package*.

* Additional material to this paper (lists of observed structure factors, anisotropic thermal parameters) can be ordered from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen, FRG. Please quote reference CSD 52303, the name of the author and the title of the paper.

Results

For **1** the K₂PtCl₆ structure type (Fig. 1) was confirmed with the final structural parameters given in Table II; a positional disorder of the NH₄⁺ ion should be assumed. The interatomic distances are given in Table III. A subsequent correction of the positional parameter of the Br atom was applied because of the shortening of the Se–Br bond due to thermal motion [14] on the assumption that the rigid SeBr₆²⁻ ion is librating about the central Se atom. The new corrected atomic distance Se–Br is now 2.577(2) Å. The correctness of the rigid body model can be checked by calculating a generalized R -index for the agreement of observed and calculated U_{ij} (program XANADU [15]: $R_G = 0.004$). The angular displacement of the libration is 3.84° off the center position. As already pointed out [5], this thermal parameters are large enough to mask the small

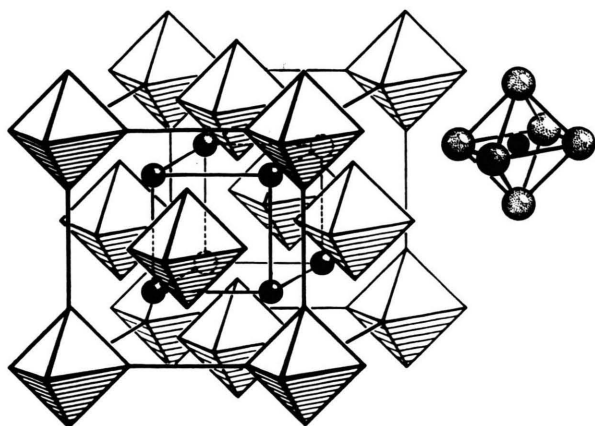


Fig. 1. K_2PtCl_6 structure; small spheres $K(N)$, octahedra $PtCl_6(SeBr_6)$.

Table II. Final structural parameters for $(NH_4)_2SeBr_6$ (293 K) $U = \exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2)]$.

Se in 4(a) (0, 0, 0)	$U_{11} = 0.0210(9) \text{ \AA}^2$
Br in 24(e) (x, 0, 0)	$x = 0.2448(2)$, $U_{11} = 0.0205(8) \text{ \AA}^2$, $U_{22} = U_{33} = 0.0502(9) \text{ \AA}^2$
N in 8(c) (1/4, 1/4, 1/4)	$U_{11} = 0.049(8) \text{ \AA}^2$

dynamic disorder evident from spectroscopic measurements.

The crystal structure of **2** is rather similar to $(H_3N-C_3H_6-NH_3)SnCl_6$; the packing of the cations and anions (Fig. 2) is reminiscent of the NaCl structure type [8]. The final structural parameters are shown in Table IV; the most important interatomic distances and bond angles are given in Table III. In contrast to the $SnCl_6^{2-}$ ion, the $SeBr_6^{2-}$ ion in II is significantly distorted (Fig. 3). There are three shorter (mean 2.549(2) Å) and three longer distances Se–Br (mean 2.593(2) Å); the ion has approximate point symmetry $3m$. The atom C(2) of the cation shows a positional disorder similar to that detected in $(H_3N-C_3H_6-NH_3)SnCl_6$. All non-hydrogen atoms of the cation lie on the mirror plane, except this C(2) atom. If the C(2) atom is required to lie on the mirror plane the bond lengths and angles are not chemically reasonable. A ΔF synthesis confirmed this disorder.

As previously pointed out [8, 10], the twelve-electron system SnX_6^{2-} (X = halogen) represents a

Table III. Interatomic distances (Å) and angles (°).

1. $(NH_4)_2SeBr_6$			
Se–Br (6×)	2.565(2)	Br–Br (4×)	3.628(2)*
N–Br (12×)	3.705(2)	Br–Br (4×)	3.781(2)**
2. $(H_3N-C_2H_6-NH_3)SeBr_6$			
Anion			
Se–Br(1)	2.590(3)		
–Br(2)	2.550(3)		
–Br(3) (2×)	2.595(2)		
–Br(4) (2×)	2.547(2)		
Br(1)–Se–Br(4)	89.9(1)	Br(1)–Se–Br(3)	90.4(1)
Br(1)–Se–Br(2)	179(2)	Br(2)–Se–Br(3)	90.9(1)
Br(3)–Se–Br(3)	90.1(1)	Br(3)–Se–Br(4)	88.6(1)
Br(4)–Se–Br(4)	92.6(1)		
Cation			
N(1)–C(1)	1.49(3)	N(1)–C(1)–C(2)	120(2)
N(2)–C(3)	1.57(3)	C(1)–C(2)–C(3)	123(3)
C(1)–C(2)	1.47(3)	C(2)–C(3)–N(2)	117(2)
C(2)–C(3)	1.42(3)		
Contacts cation–anion			
N(1)–Br(3) (2×)	3.52(1)		
N(1)–Br(4) (2×)	3.56(2)		
N(1)–Br(4) (2×)	3.56(2)		
N(2)–Br(3) (2×)	3.46(2)		
N(2)–Br(3) (2×)	3.49(2)		

* Within anion; ** between anions.

Table IV. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$), estimated as $1/3$ trace U , for $(H_3N-C_3H_6-NH_3)SeBr_6$ (293 K).

Atom	x	y	z	U_{eq}
Se	8536(1)	2500	3290(2)	277
Br(1)	9947(1)	2500	2684(3)	475
Br(2)	7136(1)	2500	3809(3)	454
Br(3)	8778(1)	4948(2)	4990(1)	396
Br(4)	8296(1)	4954(2)	1659(1)	405
N(1)	7754(8)	2500	8906(18)	360
N(2)	27(9)	2500	6870(20)	554
C(1)	8466(12)	2500	8165(26)	808
C(2)	–5833(13)	1924(32)	–3775(26)	350
C(3)	9886(11)	2500	8350(23)	506

standard for allowed deviation from octahedral $m\bar{3}m$ symmetry. Compared with other tin compounds, this deviation is rather large in $(H_3N-C_3H_6-NH_3)SnCl_6$ [8], but it can be rationalized by packing arguments. In the isostructural Se-compound (**2**) this deviation is more than twice as large as in the Sn compound (*cf.* below).

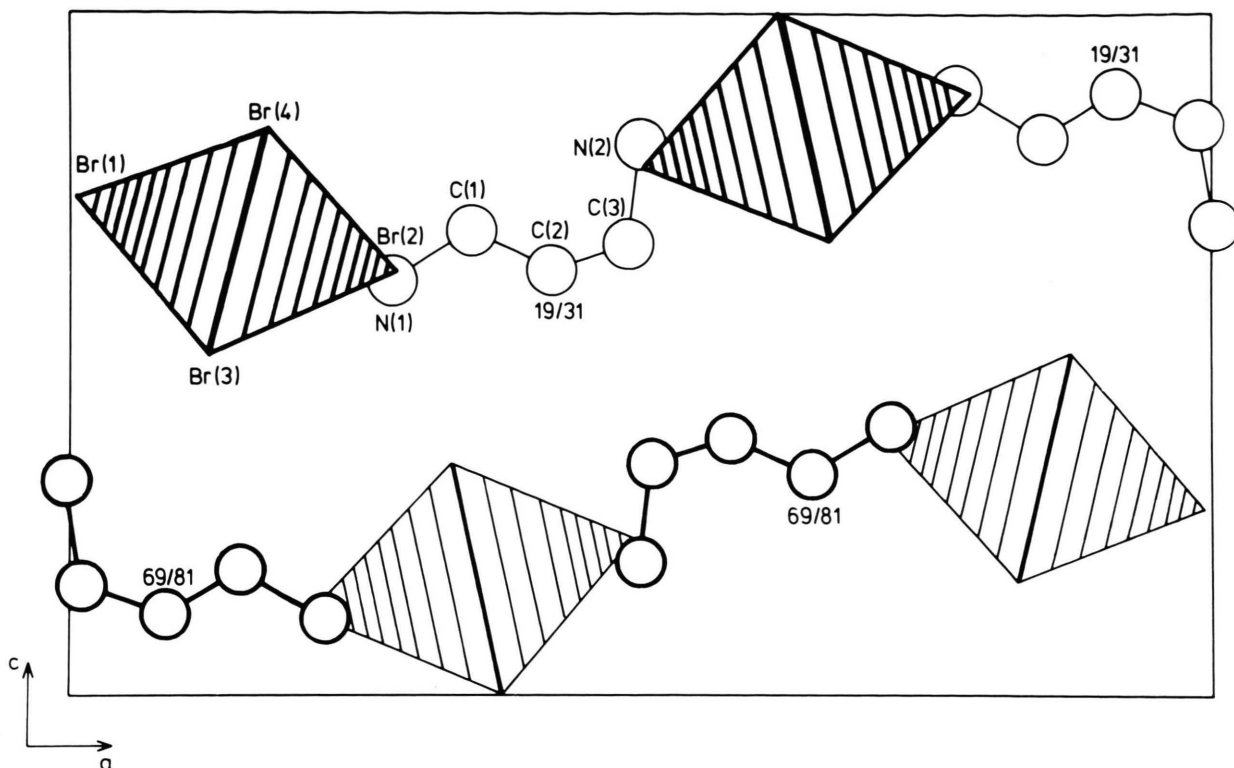


Fig. 2. Projection of the structure of **2** on (010), the content of one unit cell is shown. Different heights of the ions (center of gravity) are given by different strokes: thin $y = 1/4$, thick $y = 3/4$. The atom C(2) shows a positional disorder (heights in 1/100 of the b axis).

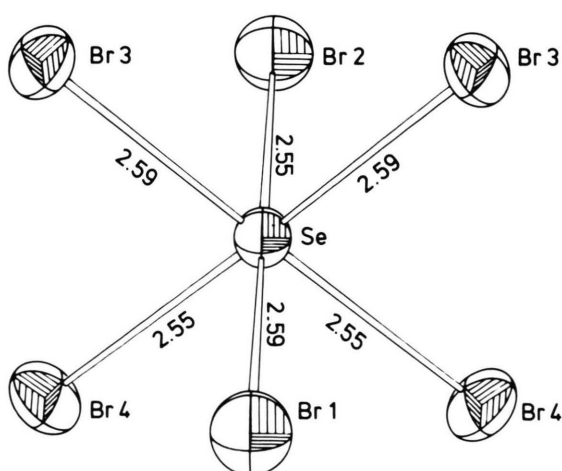


Fig. 3. ORTEP plot (50% probability) of the SeBr_6^{2-} ion in **2**; distances are given in Å.

Extended Symmetry Rules for the Stereochemistry of the Lone-Pair-Electrons in AX_6E Systems

According to Shannon [16] octahedral distortion can be defined by the quantity $\Delta = 1/6 \sum [(R_i - \bar{R})/\bar{R}]^2$ where \bar{R} = average bond length and R_i = an individual bond length. Table V lists the Δ -values for all structure types found in the literature considering hexahalo-selenates(IV) and -tellurates(IV)*. For comparison, some SnCl_6^{2-} salts are also included. In most cases, only one representative for the isotypes of one structure type is given.

All average bond lengths \bar{R} for one anion species show rather similar values even when calculated from the strongly distorted octahedra (TeCl_6^{2-} : mean 2.538 Å from all examples). The SnCl_6^{2-} ion is octahedrally enforced by an AX_6 electron configuration of the valence shell of the central atom. With a

* The search was assisted by computational methods [17, 18]. Only high quality data were admitted.

Table V. Complete listing of structure types containing AX_6^{2-} ions ($A = \text{Se}, \text{Te}$) with Δ -values as a measure for distortion of the octahedron; SnCl_6^{2-} salts as standard (see text).

Compound	Space group	Point symmetry for Te, Se, Sn	R_1 max. [\AA]	R_1 min. [\AA]	\bar{R} [\AA]	$\Delta \cdot 10^5$	References
$(\text{NH}_4)_2\text{SnCl}_6$	$\text{Fm}\bar{3}\text{m}$	$\text{m}\bar{3}\text{m}$	2.421(1)	2.421(1)	2.421	0	19
$(\text{N}(\text{C}_2\text{H}_5)_4)_2\text{SnCl}_6$	$\text{C}2/\text{c}$	$\bar{1}$	2.435(2)	2.410(2)	2.422	1.78	20
$(\text{N}_2\text{C}_3\text{H}_{12})\text{SnCl}_6$	Pnma	m	2.453(2)	2.416(4)	2.438	3.29	8
$(n\text{-Pr}_3\text{NH})_2\text{SnCl}_6$	$\text{C}2/\text{c}$	1	2.44(1)	2.39(1)	2.42	5.73	21
$(\text{Me}_4\text{N})_2\text{TeCl}_6$	$\text{Fd}\bar{3}\text{c}$	$\bar{3}$	2.538(5)	2.538(5)	2.538	0	9
$(\text{NHMe}_3)_2\text{TeCl}_6$	$\text{Pa}\bar{3}$	$\bar{3}$	2.536(1)	2.536(1)	2.536	0	22
$(\text{enH}_2)\text{TeCl}_6$	$\text{P}\bar{1}$	$\bar{1}$	2.536(3)	2.540(3)	2.538	0.05	10
$\text{C}_{24}\text{H}_{34}\text{N}_4\text{O}_2\text{S}_2\text{TeCl}_6$	$\text{P}2_1/\text{n}$	$\bar{1}$	2.542(2)	2.528(2)	2.535	0.51	23
$(\text{C}_8\text{H}_{12}\text{N})_2\text{TeCl}_6$	$\text{P}\bar{1}$	$\bar{1}$	2.542(3)	2.520(2)	2.531	1.26	24
$((\text{C}_6\text{H}_5)_4\text{As})_2\text{TeCl}_6$	$\text{P}\bar{1}$	$\bar{1}$	2.548(3)	2.518(3)	2.537	2.75	25
$\text{HT-Rb}_2\text{TeBr}_6$	$\text{Fm}\bar{3}\text{m}$	$\text{m}\bar{3}\text{m}$	2.704(3)	2.704(3)	2.704	0	4
$\text{LT-Rb}_2\text{TeBr}_6$	$\text{I}4/\text{m}$	$4/\text{m}$	2.702(5)	2.685(7)	2.696	0.89	4
$(\text{C}_4\text{NO}_2\text{H}_{10})_2\text{TeBr}_6$	$\text{P}2_1/\text{c}$	$\bar{1}$	2.695(3)	2.689(3)	2.693	0.11	26
K_2TeBr_6 (293 K)	$\text{P}2_1/\text{n}$	$\bar{1}$	2.698(6)	2.687(6)	2.693	0.28	27
$(\text{Na}(\text{H}_2\text{O})_3)_2\text{TeBr}_6$	$\text{C}2/\text{m}$	$2/\text{m}$	2.706(1)	2.684(2)	2.699	1.48	28
$(\text{NHMe}_3)_2\text{TeI}_6$	$\text{Pa}\bar{3}$	$\bar{3}$	2.952(2)	2.952(2)	2.952	0	29
Rb_2TeI_6 (293 K)	$\text{P}4/\text{mnc}$	$4/\text{m}$	2.948(2)	2.946(2)	2.947	0.01	30
$(\text{C}_6\text{H}_{14}\text{NO}_2)_2\text{TeI}_6$	$\text{P}\bar{1}$	$\bar{1}$	2.950(1)	2.943(1)	2.947	0.10	31
$(\text{TeC}_3\text{H}_6\text{N}_2\text{S})_4\text{TeCl}_6$	$\text{C}222_1$	2	2.546(3)	2.508(4)	2.530	2.86	32
$(\text{N}_2\text{C}_3\text{H}_{12})\text{TeCl}_6$	Pnma	m	2.672(1)	2.426(1)	2.541	68.4	8
$\text{C}_{10}\text{H}_{24}\text{N}_4\text{S}_2\text{TeCl}_6$	$\text{P}2_1/\text{a}$	1	2.725(3)	2.451(3)	2.546	126.44	33
$((\text{MeHN})_2\text{CS})_2\text{TeCl}_6$	$\text{Pna}2_1$	1	2.740(3)	2.420(3)	2.551	186.53	34
$(\text{C}_4\text{H}_8\text{N}_2\text{O}_2\text{H})_2\text{TeBr}_6$	$\text{C}2/\text{c}$	2	2.798(3)	2.642(3)	2.713	56.44	35
$\text{Ca}(\text{H}_2\text{O} \cdot \text{HF})_7\text{TeBr}_6$	$\text{I}4_1\text{md}$	2mm	2.84(1)	2.58(1)	2.70	157.29	7
$(\text{NH}_4)_2\text{SeCl}_6$	$\text{Fm}\bar{3}\text{m}$	$\text{m}\bar{3}\text{m}$	2.411(1)	2.411(1)	2.411	0	36
$(\text{NH}_4)_2\text{SeBr}_6$	$\text{Fm}\bar{3}\text{m}$	$\text{m}\bar{3}\text{m}$	2.577(2)	2.577(2)	2.577	0	this work
$(\text{N}_2\text{C}_3\text{H}_{12})\text{SeBr}_6$	Pnma	m	2.595(2)	2.547(2)	2.571	7.83	this work

maximum distortion of $\Delta = 5.73 \cdot 10^{-5}$ calculated for $(n\text{-Pr}_3\text{NH})_2\text{SnCl}_6$ this anion should still be regarded as a regular octahedron. The deviations are due to packing effects. Consequently, Δ -values within this order of magnitude calculated from TeX_6^{2-} and SeX_6^{2-} data should point out a regular octahedron as well.

The crystallographic point symmetry for the AX_6^{2-} ion ($A = \text{Se}, \text{Te}$) is decisive for the stereochemical effect of the lone pair electrons. The following rules apply:

1. With at least a center of symmetry ($\bar{1}$), a statically undistorted ion results. Small deviations from ideal $\text{m}\bar{3}\text{m}$ symmetry will be allowed when the centrosymmetrical point group is of lower symmetry than $\text{m}\bar{3}\text{m}$ (standard SnX_6^{2-} , cf. above). The octahedrally enforced dynamic structure is stabilised by this crystal field (weak pseudo-Jahn-Teller effect, cf. [37]).

2. If the crystallographic site symmetry of the AX_6^{2-} ion does not include an inversion center, a statically distorted ion results. The symmetry should preferably be 4mm , 2mm or 3m due to the three orientations of one component of the T_{1u} deformation vibration of the octahedron. A change of bond angles ($\neq 90^\circ$) is not necessarily connected with this symmetry reduction (strong pseudo-Jahn-Teller effect, cf. [37]).

The Δ -values for species associated with rule #1 show a maximum ($2.75 \cdot 10^{-5}$) for $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{TeCl}_6$; the average value for all these "undistorted" octahedra is $<1 \cdot 10^{-5}$, the deviation from $\text{m}\bar{3}\text{m}$ symmetry being much less than observed for SnX_6^{2-} . Among the Te compounds, $(\text{TeC}_3\text{H}_6\text{N}_2\text{S})_4\text{TeCl}_6$ seems to contradict rule #2. Its rather small Δ ($2.86 \cdot 10^{-5}$) is an exception, but the "regular" octahedral shape should be due to the high pseudo-symmetry of the ion packing (the positional param-

eters of Te are very close to special points, cf. ref. [32]).

(H₃N–C₃H₆–NH₃)SeBr₆ is the first example with a statically distorted SeX₆²⁻ group. In contrast to the Δ -values calculated for the distorted TeX₆²⁻ species, the Δ -value $7.83 \cdot 10^{-5}$ seems to be rather low. Its 3m distortion is the first example among all the AX₆E-systems quoted here. Consequently the symmetry predictions of rule #2 are proved with at least one example for each kind of distortion (4mm distortion in (Me₄N)₂(CH₃CN)TeCl₆ [9], 2mm distortion in most other cases).

The symmetry rules given above should be applicable to systems like SbX₆³⁻ or BiX₆³⁻ (X = halogen) as well. In order to prove this, corresponding preparative and crystallographic work is in progress.

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