mettre en oeuvre et donnent souvent de bons résultats): la densité correspondante est globalement la même, mais avec des variations plus douces.

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Symmetry Rules for the Stereochemistry of the Lone-Pair Electrons in TeX_6^{2-} (X = Cl, Br, I) and the Structures of 1,2-Ethanediammonium Hexachlorotellurate(IV) and 1,2-Ethanediammonium Hexachlorostannate(IV)

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Abstract

The crystal structures of 1,2-ethanediammonium hexachlorotellurate(IV) (1) and 1,2-ethanediammonium hexachlorostannate(IV) (2) were determined by X-ray diffraction. Crystal data: (1) $[C_2H_{10}N_2][TeCl_6]$, $M_r = 402 \cdot 43$, triclinic, $P\bar{1}$, $a = 7 \cdot 156$ (2), $b = 7 \cdot 260$ (2), $c = 7 \cdot 450$ (2) Å, $\alpha = 87 \cdot 931$ (7), $\beta = 64 \cdot 970$ (5), $\gamma = 60 \cdot 12$ (1)°, $V = 296 \cdot 47$ Å³, $Z = 1$, $D_x = 2 \cdot 254$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0 \cdot 7107$ Å, $\mu = 35 \cdot 59$ cm⁻¹, room temperature, $F(000) = 190$, final $R = 0 \cdot 037$ for 1682 reflexions; (2) $[C_2H_{10}N_2][SnCl_6]$, $M_r = 393 \cdot 52$, triclinic, $P\bar{1}$, $a = 7 \cdot 048$ (1), $b = 7 \cdot 128$ (1), $c = 7 \cdot 449$ (1) Å, $\alpha = 88 \cdot 244$ (6), $\beta = 65 \cdot 319$ (7), $\gamma = 60 \cdot 280$ (5)°, $V = 287 \cdot 84$ Å³, $Z = 1$, $D_x = 2 \cdot 27$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0 \cdot 7107$ Å, $\mu = 33 \cdot 18$ cm⁻¹, room temperature, $F(000) = 188$, final $R = 0 \cdot 05$ for 1601 reflexions. The two compounds are isostructural. Only very small distortions from $m\bar{3}m$ symmetry are observed involving the MCl_6 octahedra that occupy the corners of the unit cell [distances: Te–Cl mean $2 \cdot 538$ (2) Å, Sn–Cl mean $2 \cdot 433$ (3) Å]. The cations center the (100) face of the unit cell, giving an NaCl-type arrangement of cations and anions. The results

Table 1. *Experimental information and structure determination details*

	$(enH_2)TeCl_6$	$(enH_2)SnCl_6$
Crystal shape (faces)	{100}, (111), ($1\bar{1}\bar{1}$), ($0\bar{1}1$), ($01\bar{1}$)	
Crystal size (mm)	$0.22 \times 0.34 \times 0.34$	$0.12 \times 0.12 \times 0.2$
Diffractometer	Siemens–Stoe AED2, graphite-monochromated Mo $K\alpha$ radiation	
Determination of cell parameters:		
number of reflexions used (θ range)	35 (3.4–27°)	31 (5.5–22°)
cell parameters at 293 K	$a = 7.156$ (2), $b = 7.260$ (2),	$a = 7.048$ (1), $b = 7.128$ (1),
	$c = 7.450$ (2) Å, $\alpha = 87.931$ (7),	$c = 7.449$ (1) Å, $\alpha = 88.244$ (6),
	$\beta = 64.970$ (5), $\gamma = 60.12$ (1)°	$\beta = 65.319$ (7), $\gamma = 60.280$ (5)°
Intensity data collection:		
max. $\sin\theta/\lambda$ (Å^{-1}), range of h, k, l	0.7041, $\bar{8}$, $\overline{10}$, 0 to 10, 10, 10	0.7042, $\bar{7}$, $\bar{9}$, 0 to 9, 9, 10
scan modes, min. scan angle, max. scan time	Ω, 1·2°, 24 s	
Standard reflexions (intensity variation)	031, 132, $\overline{1}3\bar{2}$, $\overline{1}21$, $0\overline{2}\bar{1}$ (<1%)	$0\bar{2}4$, $00\bar{4}$, 131 (<1%)
Measured reflexions	1808	1720
Unique reflexions	1682	1601
Observed reflexions ($F > 0$)	1682	1601
R_{int}	0.03	0.03
Absorption correction:		
min.–max. transmission	0.31–0.49	0.64–0.69
Structure determination technique	Direct methods, ΔF synthesis	From isotypic structure $(enH_2)TeCl_6$
Structure refinement, based on F:*		
final R, wR (52 parameters), S	0.037, 0.038, 5.84	0.05, 0.046, 5.89
max. final $|\Delta|/\sigma$	0	0
max. and min. $\Delta\rho$ (e Å^{-3})	0.47, −0.31	0.5, −1.29

* $w = 1/\sigma^2(F_o)$, no extinction corrections.

are discussed with a prediction of the appearance of a static stereochemical effect of the lone-pair electrons in the TeX_6^{2-} (X = Cl, Br, I) species (an AX_6E system according to the VSEPR rules).

Introduction

According to VSEPR theory (Gillespie & Nyholm, 1957), a distorted octahedral coordination is expected for systems of the type AX_6E, which contain six bonding electron pairs and one nonbonding electron pair in the valence shell of the central atom. In the case of XeF_6 (Burbank & Jones, 1974) and IF_6^- (Christe, 1972) this can be detected by X-ray diffraction and spectroscopic experiments. However, structural investigations of the analogous TeX_6^{2-} anions (X = Cl, Br, I), containing 14 electron systems, yielded a regular octahedral structure. This was shown by Raman spectroscopy (Adams & Morris, 1967), nuclear quadrupole resonance spectroscopy (Greenwood, 1970), electronic spectra (Couch, Wilkins, Rossman & Gray, 1970) and single-crystal X-ray diffraction work (Brown, 1964). Consequently, Gillespie (1972) classified these systems as exceptions to the VSEPR rule.

The IR-active vibrations T_{1u} (ν_3 and ν_4) of the TeX_6^{2-} octahedron are, however, relatively broad; an indication of vibronic coupling between the ground state and the first excited state (Stufkens, 1970). Expectations of detecting a 'frozen' distorted species by X-ray diffraction techniques at temperatures down to 12 K were not fulfilled in investigations on Rb_2TeBr_6 (Abriel & Ihringer, 1984). As Pearson (1976) presumed, the octahedrally enforced, dynamic structure is stabilized by a highly symmetrical crystal field, which, for example, is realized in the A_2TeX_6 phases (A = K, NH_4, Rb, Cs; X = Cl, Br, I) by an antifluorite arrangement of cations and anions.

The transition from the dynamically distorted structure of the TeX_6^{2-} ion (mean symmetry $m\bar{3}m$) to a statically distorted species could be achieved by lowering the symmetry of the crystal field. A structural investigation on $Ca(H_2O,HF)_7TeBr_6$ (Abriel & Ehrhardt, 1984) confirmed this idea yielding a $2mm$-distorted $TeBr_6$ octahedron. As bivalent (or trivalent) cations should be better able to build a low-symmetry packing (especially when these cations deviate from a spherical shape), a search for further distorted species should be undertaken by structural investigations on these kinds of salts. In order to formulate rules for distortion and its symmetry we need more information from different compounds. A comparison with the analogous SnX_6^{2-} compounds (an AX_6 system with no lone pair of electrons in the valence shell of the central atom) is desirable. These tin systems should give us a standard for discussing atomic distances and angles.

Experimental

Yellow crystals of $(enH_2)TeCl_6$ and colorless crystals of $(enH_2)SnCl_6$ were grown from an equimolar solution of TeO_2 ($SnCl_4$) and ethylendiamine in concentrated HCl. The crystal quality increased when operating with an excess of TeO_2 ($SnCl_4$). The crystals were dried over KOH, and those for use in the diffraction experiment were embedded in glass capillaries in order to protect them from moisture. Details of the X-ray data collection and information on the structure determination are given in Table 1. Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The program used was *STRUCSY* from the diffractometer software package.

Table 2. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²×10⁴); *space group* P1̄ *for both structures*

	x	y	z	U_{eq}*
(enH₂)TeCl₆				
Te	0	0	0	223
Cl(1)	7277 (3)	3764 (2)	2290 (2)	399
Cl(2)	2174 (3)	8526 (3)	2134 (2)	372
Cl(3)	6949 (3)	8960 (2)	2030 (2)	361
N	7993 (10)	6030 (9)	7829 (7)	345
C	8826 (11)	6034 (9)	5631 (8)	336
(enH₂)SnCl₆				
Sn	0	0	0	166
Cl(1)	7335 (3)	3668 (3)	2208 (3)	289
Cl(2)	2112 (3)	8625 (3)	2066 (3)	272
Cl(3)	7066 (3)	8979 (3)	1989 (3)	264
N	7948 (11)	6063 (9)	7839 (8)	239
C	8776 (13)	6061 (11)	5629 (10)	264

* Estimated as ⅓ trace **U**.

Results and discussion

Atomic coordinates are listed in Table 2. Interatomic distances and angles are given in Table 3.* Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of the (enH₂)TeCl₆ crystal structure.

The two compounds are isostructural. The corners of the unit cell are occupied by the octahedral MX_6^{2-} anions ($M = $ Sn, Te), and the center of symmetry in the position $(0\frac{1}{2}\frac{1}{2})$ is the 1̄ center of the cation. An NaCl-type arrangement of the cations and anions is realized, so the idealized 'cubic' lattice parameters of the triclinic subcell for (enH₂)TeCl₆ would, for example, be $a = b = c = 7.29$ Å and $\alpha = 90$, $\beta = \gamma = 60°$. The packing of the anions is almost as close as in the antifluorite compounds A_2MX_6 [Cl–Cl distances between anions in (NH₄)₂TeCl₆ 3·64 Å (Hazell, 1966), in (NH₄)₂SnCl₆ 3·68 Å (Brill, Gearhart & Welsh, 1974)]. Only very small distortions from $m3m$ symmetry are observed for the MX_6 octahedra. It should be noted that this kind of distortion always appears when refining atomic positions with the central atom not occupying a site with full point symmetry (here $m3m$); hence the octahedra found should be quite regular. The mean M–Cl distances agree with the values found by Hazell (1966) and Brill *et al.* (1974). A correction of the M–Cl distances was applied for the apparent bond shortening due to thermal motion (Schomaker & Trueblood, 1968) on the assumption that the rigid MX_6^{2-} ions are librating about their central atom (Table 3). The generalized R index for the agreement of observed and calculated U_{ij} [program *XANADU* by Roberts & Sheldrick (1979)] was 0·04 and 0·027 for the Te and Sn compounds, respectively.

Table 3. *Bond distances* (Å) *and angles* (°)

(enH₂)TeCl₆

		Corrected for thermal motion		
Te–Cl(1)	2·528 (1)	2·539		
Te–Cl(2)	2·531 (3)	2·540		
Te–Cl(3)	2·528 (3)	2·536		
Mean Te–Cl	2·529 (2)	2·538		
N–Cl(1)*	3·43 (1)		Cl(1)–Te–Cl(2)	91·64 (7)
N–Cl(2)*	3·368 (8)		Cl(1)–Te–Cl(3)*	91·69 (7)
N–Cl(3)	3·435 (8)		Cl(2)–Te–Cl(3)*	91·62 (9)
N–C	1·487 (7)		N–C–C*	110·7 (5)
C–C*	1·488 (9)			

Cl–Cl distances Within anion		Between anions		
Cl(1)–Cl(3)*	3·522 (3)	Cl(1)–Cl(2)	3·613 (3)	
Cl(1)–Cl(2)*	3·526 (3)	Cl(1)–Cl(3)	3·664 (2)	
Cl(1)–Cl(3)	3·628 (3)	Cl(1)–Cl(1)*	3·707 (2)	
Cl(1)–Cl(2)	3·628 (3)	Cl(2)–Cl(3)	3·554 (5)	
Cl(2)–Cl(3)*	3·526 (2)	Cl(2)–Cl(2)*	3·909 (2)	
Cl(2)–Cl(3)	3·627 (5)	Cl(3)–Cl(3)*	3·935 (2)	

(enH₂)SnCl₆

		Corrected for thermal motion		
Sn–Cl(1)	2·425 (2)	2·433		
Sn–Cl(2)	2·433 (3)	2·439		
Sn–Cl(3)	2·422 (3)	2·428		
Mean Sn–Cl	2·427 (3)	2·433		
N–Cl(1)*	3·41 (1)		Cl(1)–Sn–Cl(2)	90·93 (8)
N–Cl(2)*	3·361 (8)		Cl(1)–Sn–Cl(3)	90·83 (9)
N–Cl(3)	3·431 (8)		Cl(2)–Sn–Cl(3)	91·0 (1)
N–C	1·499 (9)		N–C–C*	110·0 (6)
C–C*	1·51 (1)			

Cl–Cl distances Within anion		Between anions		
Cl(1)–Cl(3)*	3·403 (4)	Cl(1)–Cl(2)	3·668 (4)	
Cl(1)–Cl(2)*	3·407 (4)	Cl(1)–Cl(3)	3·697 (3)	
Cl(1)–Cl(3)	3·453 (4)	Cl(1)–Cl(1)*	3·820 (3)	
Cl(1)–Cl(2)	3·463 (3)	Cl(2)–Cl(3)	3·600 (6)	
Cl(2)–Cl(3)*	3·403 (3)	Cl(2)–Cl(2)*	3·960 (3)	
Cl(2)–Cl(3)	3·463 (6)	Cl(3)–Cl(3)*	4·001 (3)	

* Atomic position derived by 1̄ symmetry operation.

Prediction of the appearance of a static stereochemical effect of the lone-pair electrons in TeX_6^{2-} anions ($X = $ Cl, Br, I)

At first sight the structural results of the (enH₂)MCl₆ compounds ($M = $ Te, Sn) are not surprising; a nondistorted TeCl₆²⁻ octahedron is expected because this seems to be the normal case (see *Introduction*). However, the results of this investigation, when compared with structural data from some other compounds, give an insight into the lone-pair problem.

What causes stereochemical activity or nonactivity of the lone-pair electrons in TeX_6^{2-} species? According to Rosso, Valle & Calogero (1980) and Dahan & Lefèbvre-Soubeyran (1976a, b), the N–H–Cl and N–H–Br hydrogen bonds in protonated amines, amides or amino acids weaken the Te–X bonds with a resultant distortion of the TeX₆ octahedron. The distortions observed by these authors are significant {in [(MeHN)₂CS]₂TeCl₆, Te–Cl min. 2·420 (3), max. 2·740 (3) Å; in [(CONH₂)₂(CH₂)₂]₂H₂TeBr₆, Te–Br min. 2·642 (3), max. 2·798 (3) Å}. In contrast, the

Table 4. *Comparison of* N–X ($X = Cl$, Br) *distances* (*see text*)

	Space group	Point symmetry for Te/Sn	Nearest N–X contact (Å)	CN for first coordination sphere	Mean distance N–X (Å) for this coordination	Reference
$(H_3N-C_2H_4-NH_3)TeCl_6$	$P\bar{1}$	$\bar{1}$	3·368 (8)	3	3·411 (8)	This work
$(H_3N-C_2H_4-NH_3)SnCl_6$	$P\bar{1}$	$\bar{1}$	3·361 (8)	3	3·401 (9)	This work
$(H_3N-C_3H_6-NH_3)TeCl_6^*$	Pnma	m	3·201 (6) [N(2)] 3·359 (6) [N(1)]	4 3	3·242 (6) 3·376 (6)	Abriel & Friedrich (1985)
$(H_3N-C_3H_6-NH_3)SnCl_6$	Pnma	m	3·442 (8) [N(1)] 3·393 (7) [N(2)]	6 4	3·460 (7) 3·397 (7)	Abriel & Friedrich (1985)
$[(MeHN)_2CS]_2TeCl_6^*$	$Pna2_1$	1	3·20[N(2)]	1	—	Rosso, Valle & Calogero (1980)
NH_4Cl	$Pm\bar{3}m$		3·36	8		Greenberg & Walden (1940)
NH_4Cl	$Fm\bar{3}m$		3·27	6		Bartlett & Langmuir (1921)
$(C_2H_5-CHNH_3-COOH)_2TeBr_6$	$P2_1/c$	$\bar{1}$	3·41 (2)	3	3·46 (2)	Dahan & Lefèbvre-Soubeyran (1976a)
$[(CONH_2)_2(CH_2)_2]_2H_2TeBr_6^*$	C2/c	2	3·47 [N(1)] 3·44 [N(4)]	2 1	3·485	Dhan & Lefèbvre-Soubeyran (1976b)
NH_4Br	$Pm\bar{3}m$		3·515	8		Weigle & Saini (1936)
NH_4Br	$Fm\bar{3}m$		3·455	6		Bartlett & Langmuir (1921)

* Distorted MX_6 octahedron.

anion distortion in $Ca(H_2O, HF)_7TeBr_6$ (Abriel & Ehrhardt, 1984) and in $(H_3N-C_3H_6-NH_3)TeCl_6$ (Abriel & Friedrich, 1985) was explained by packing and symmetry arguments [Te–Br min. 2·58 (1), max. 2·843 (9) Å; Te–Cl min. 2·426 (1), max. 2·672 (1) Å].
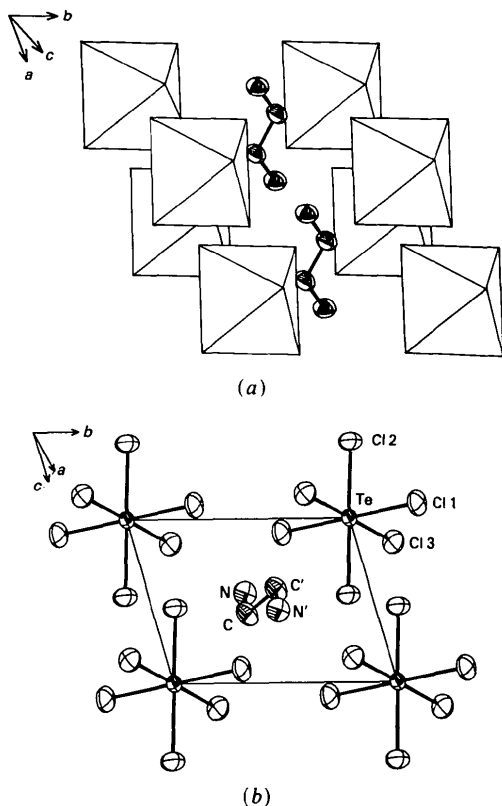

(a)

(b)

Fig. 1. (a) Array of octahedral anions and ethylenediammonium cations in the crystal structure of $(enH_2)TeCl_6$, and (b) the (100) layer of this structure with thermal ellipsoids based on 50% probability.

At this stage there are two questions: If the hydrogen-bonding idea is correct this must be a general rule (is it?) and if hydrogen bonding is the cause for distortion this should also be observed when considering SnX_6^{2-} anions ($X = Cl$, Br, I) (will it be?).

Table 4 shows a comparison of some compounds with MX_6^{2-} anions ($M = Sn$, Te; $X = Cl$, Br) and cations containing N–H functions, with the following results:

(a) There is no distortion of SnX_6^{2-} anions (none were found in the literature).

(b) TeX_6^{2-} anions may either show distortion or have a regular octahedral shape.

Consequently, the neighborhood of a more or less acid N–H function is not the decisive factor for distortion. Looking at the point symmetry of the Te atoms, the existence of a center of symmetry always produces a nondistorted anion, or, distortion is allowed only with the Te atom in a noncentrosymmetric point symmetry group (the SnX_6^{2-} octahedra do not distort anyway). As the distorted species show an increasing ionic character of the longer Te–X bonds, these more polarized halogen ligands are able to form hydrogen-bridged connections to neighboring N atoms. Here, we find N–Cl distances of about 3·2 Å, denoted as N–H–Cl contacts listed by Wells (1984). The values of nonbonding N–Cl distances may be obtained from the corresponding data on NH_4Cl/NH_4Br. In particular, the $Fm\bar{3}m$ high-temperature phase with a rotating cation should be free of hydrogen bonding. The following rules ensue:

(a) Packing of cations and anions fixes the point symmetry of the Te atom.

(b) With a center of symmetry for this Te position a nondistorted TeX_6^{2-} ion results. Only small deviations from ideal $m\bar{3}m$ symmetry (of the same order of magnitude as in SnX_6^{2-} ions) will be allowed when

the point group is of lower symmetry than $m\bar{3}m$. The octahedrally enforced dynamic structure is stabilized by this crystal field.

(c) With a noncentrosymmetric point symmetry for the Te atom the TeX_6^{2-} group will be statically distorted. According to Pearson (1976) the resulting symmetry must be $4mm$, $2mm$ or $3m$, displaying the three orientations of one component of the T_{1u} deformation vibration of the octahedron.

Symmetry rule (c) is obeyed resulting in a $2mm$ distortion in most cases known to date. An irregular distortion found in [(MeHN)$_2$CS]$_2$TeCl$_6$ (Rosso, Valle & Calogero, 1980) should be regarded with care because no significance test for the noncentrosymmetric space group is given for this structural refinement. At least for TeI_6^{2-} the known structures show a center of symmetry for the Te position exclusively, e.g., Rb$_2$TeI$_6$ (Abriel, 1982). With a knowledge of the above symmetry rules, we shall find a suitable cation for building a salt with a statically distorted anion.

The rules given above should also be useful when considering compounds containing SeX_6^{2-} ($X = $ Cl, Br). Most recently we found the first distorted species in [H$_3$N(CH$_2$)$_3$NH$_3$]SeBr$_6$ with approximate point symmetry $3m$ for the anion (Abriel, 1986).

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Structures of Diisothiocyanatotetrakis(1-phenyl-1-ethylamine)nickel(II): Enclathration of Organic Guests with Host Isomerization

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Abstract

Host complexes of Ni(NCS)$_2$(1-phenyl-1-ethylamine)$_4$, prepared from racemic and enantiomerically pure amine and its clathrates with sec-butylbenzene and o-xylene have been examined by X-ray diffraction: (a) $\frac{1}{2}$\{[Ni(NCS)$_2$\{(R)-1-phenyl-1-ethylamine\}$_2$\{(S)-1-phenyl-1-ethylamine\}$_2$]-[Ni(NCS)$_2$\{(R)-1-phenyl-1-ethylamine\}$_4$]\}, $\frac{1}{2}$\{[Ni(C$_8$H$_{11}$N)$_4$(NCS)$_2$].[Ni(C$_8$H$_{11}$N)$_4$(NCS)$_2$]\}, $M_r = 659 \cdot 59$, orthorhombic, $P2_12_12$, $a = 15 \cdot 543$ (2), $b = 15 \cdot 300$ (4), $c = 14 \cdot 75$ (3) Å, $U = 3507$ (7) Å^3, $Z = 4$, $D_x = 1 \cdot 25$

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