part et d'autre des bases du prisme. Chaque atome de soufre équatorial S(3) est sensiblement dans le plan de la face S(1)S(4)S(4), l'angle des plans S(1)S(4)S(4) et S(3)S(4)S(4) valant 176,6 (3)°. Ainsi le polyèdre de coordination de l'atome Tl(3) peut être décrit comme un quasi-dodécaèdre.

Dans la direction **c**, il n'y a pas enchaînement de dodécaèdres [TlS_{11}] mais alternance de dodécaèdres [TlS_{11}] et de groupements [Ga_3S_{10}] (Fig. 2).

La grande longueur des distances Tl—S (de 3,315 à 3,668 Å) s'explique par la coordinence élevée du thallium monovalent. Ces distances sont en bon accord avec la longueur des rayons ioniques de Tl^+ en fonction du nombre de coordination, déterminée par Shannon (1976): la somme des rayons ioniques donne une distance Tl—S de 3,43 Å pour la coordinence 8 et de 3,54 Å pour la coordinence 12. Les moyennes des distances interatomiques observées ici pour la coordinence 9 sont: Tl(1)—S = 3,485 Å, Tl(2)—S = 3,408 Å, et pour la coordinence 11: Tl(3)—S = 3,563 Å (Tableau 2).

Cette structure peut être décrite comme étant formée de trois types de groupements atomiques, disposés en colonne parallèlement à la direction [001]:

(1) sur l'axe sénaire des colonnes de prismes 'tricapés' [TlS_9] qui, mettant en commun leurs bases, forment un enchaînement [TlS_6]$_n$;

(2) sur l'un des axes ternaires des groupements plans de trois tétraèdres [$GaOS_3$] qui forment une chaîne [Ga_3OS_6]$_n$;

(3) sur l'autre axe ternaire, des groupements alternés de trois tétraèdres [GaS_4] et de dodécaèdres [TlS_{11}] formant un ensemble [Ga_3TlS_{13}]$_n$.

Si l'on s'en tient uniquement au réseau formé par les tétraèdres de gallium, les colonnes [Ga_3OS_6]$_n$ disposées le long de l'un des axes ternaires sont unies les unes aux autres par des ponts [Ga_3S_{10}] situés sur le second axe ternaire. L'ensemble forme un réseau tridimensionnel dont les liaisons sont certainement fortement covalentes. Au sein de cet assemblage le thallium est reçu comme un hôte qui échange avec lui des liaisons ioniques. Cette description ne signifie pas que le squelette $Ga_9S_{13}O_2$ puisse exister en dehors de la présence de l'ion Tl^+.

Tableau 2. *Distances interatomiques en* Å

Les écarts types, compte tenu des erreurs sur les paramètres de la maille, sont entre parenthèses.

Tl(1)—S(4)	3,494 (6) ×6	Ga(1)—O	1,894 (3)
Tl(1)—S(2)	3,497 (9) ×3	Ga(1)—S(3)	2,244 (6)
		Ga(1)—S(4)	2,247 (5)
Tl(2)—S(3)	3,348 (9) ×3	Ga(1)—S(2)	2,346 (5)
Tl(2)—S(4)	3,451 (6) ×6		
		Ga(2)—S(4)	2,237 (6) ×2
Tl(3)—S(3)	3,315 (9) ×3	Ga(2)—S(1)	2,291 (4)
Tl(3)—S(4)	3,668 (6) ×6	Ga(2)—S(2)	2,30 (1)
Tl(3)—S(1)	3,717 (2) ×2		

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Structure of Ammonium Hexachloroselenate(IV)

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Abstract. $(NH_4)_2SeCl_6$, $M_r = 327{\cdot}76$, cubic, $Fm\bar{3}m$, $a = 9{\cdot}9616\ (5)$ Å, $V = 998{\cdot}52$ Å^3, $Z = 4$, $D_x = 2{\cdot}202$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, $\mu = 51{\cdot}52$ cm^{-1}, $F(000) = 632$, room temperature, final $R = 0{\cdot}056$ for 311 unique reflexions. The title compound has an antifluorite-type arrangement of NH_4^+ cations and octahedral $SeCl_6^{2-}$ anions. The NH_4^+ ion is disordered. The Cl-atom positional parameters are corrected

assuming that the rigid $SeCl_6$ group is librating about the central Se atom. The corrected Se—Cl bond length is 2·411 (1) Å.

Introduction. The most famous exceptions to the electron-pair repulsion rules (VSEPR; Gillespie & Nyholm, 1957) seem to be the anions TeX_6^{2-} (X = Cl, Br, I) and SeX_6^{2-} (X = Cl, Br). The first structural investigations yielded a regular octahedral coordination although a distorted octahedron with the lone-pair electrons pointing to the seventh position was expected (a survey is given by Abriel, 1986). However, from our recent work there is evidence of compounds with distorted TeX_6^{2-} anions (Abriel & Ehrhardt, 1984; Abriel & Friedrich, 1985). Consequently, symmetry rules for the stereochemistry of the lone-pair electrons in TeX_6^{2-} ions could be given (Abriel, 1986) considering the static distortion (with possible point symmetry *4mm*, *2mm* or *3m*) and the dynamically distorted case (with mean point symmetry $m\bar{3}m$). It should be pointed out that this fluctuating structure model is evident from spectroscopic measurements only (Abriel & Zehnder, 1986).

Subsequent investigations should answer the question whether these symmetry rules found for the TeX_6^{2-} system can be applied to anions SeX_6^{2-} as well. Structural data about hexahalogenoselenates(IV) known to date are very rare. For the $SeCl_6^{2-}$ group there is only one report by Engel (1935) concerning compounds A_2SeCl_6 (A = NH_4, Rb, Cs). A more recent investigation on $H_2SeBr_6(H_2O)_8$ was reported by Krebs & Hein (1979). So we need more structural data from compounds with dynamically distorted and statically distorted (are there any?) SeX_6^{2-} ions. In order to obtain high-accuracy data from the $SeCl_6^{2-}$ group in a high-symmetry crystal field the present work was carried out.

Experimental. SeO_2 prepared by oxidation of Se in dry O_2 stream according to Brauer (1975). From the mixed solutions of SeO_2 (excess) and NH_4Cl in conc. HCl, bright yellow crystals grew within several days using a desiccator filled with conc. H_2SO_4 as water absorber (additionally a weak vacuum was applied). As the crystals of the hexachloroselenate(IV) are very sensitive to moisture, but can be stored under dry HCl, the experimental set-up fulfilled these requirements. During manipulation the crystals were protected by 2-propanol.

Octahedral single crystal (volume $8{\cdot}37 \times 10^{-3}$ mm³, faces {111}) embedded in glass capillary. Quality of crystal checked by precession photographs (Mo $K\alpha$), Laue group $m\bar{3}m$ confirmed. X-ray data collection with Siemens–Stoe AED2 using graphite-monochromatized Mo $K\alpha$ radiation. Cell parameter determined from 32 reflexions in θ range 8·2–31°. Intensity data collection: max. $\sin\theta/\lambda = 1{\cdot}0765$ Å^{-1}, range of h,k,l $\overline{20},\overline{20},\overline{20}$ to 20,20,12 in Ω-scan mode (min. scan angle 1·2°, max. scan time 36 s). Reflexions 444, $\bar{4}4\bar{4}$ and $4\bar{4}4$ used for standard intensity measurements, intensity variation less than 0·7%. 8980 measured reflexions yielded 311 unique reflexions with $F \geq 0$ ($R_{\rm int} = 0{\cdot}072$). Numerical absorption correction, min./max. transmission of 0·298/0·488. Structure model given by Engel (1935). Structural refinement on F with 311 reflexions: without extinction correction $R = 0{\cdot}07$, $wR = 0{\cdot}026$ {with $w = 1/[\sigma(F)]^2$}; $S = 5{\cdot}4$; applying extinction correction [$g = 2{\cdot}6(2)\times10^{-5}$], $R = 0{\cdot}056$ and $wR = 0{\cdot}0215$ with max. shift/e.s.d. = 0 in last cycle of refinement (six parameters refined); $0{\cdot}22 \geq \Delta F \geq -0{\cdot}47$ e Å^{-3} from final ΔF synthesis. Max. electron density found in position 32(f) (space group $Fm\bar{3}m$) with $x = 0{\cdot}322$ at 1·25 Å from the N atom. The N—H distance in NH_4^+ should be about 1·05 Å, so this peak is not significantly correlated with an H-atom position. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Program used was *STRUCSY* from the diffractometer software package.*

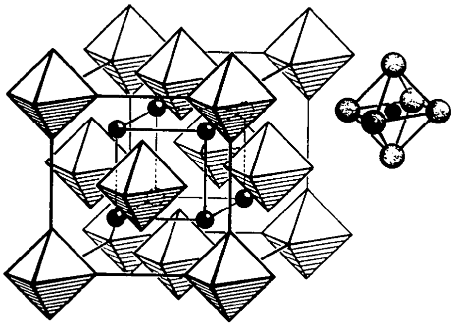

Fig. 1. K_2PtCl_6 structure (from D'Ans Lax, 1970); small spheres K (N), octahedra $PtCl_6$ ($SeCl_6$).

Table 1. *Final structural parameters for* $(NH_4)_2SeCl_6$ *at* 293 K

$$U = \exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2)].$$

Space group $Fm\bar{3}m$ (No. 225)

Se in 4(a) (0,0,0)	$U_{11} = 0{\cdot}0229$ (2) Å²
Cl in 24(e) (x,0,0)	$x = 0{\cdot}24111$ (6), $U_{11} = 0{\cdot}0204$ (3), $U_{22} = U_{33} = 0{\cdot}0427$ (2) Å²
N in 8(c) ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$)	$U_{11} = 0{\cdot}0402$ (10) Å²

Table 2. *Interatomic distances* (Å)

Se—Cl (6×)	2·402 (1)	Cl—Cl (4×)	3·647 (1)†
Cl—Cl (4×)	3·397 (1)*	N—Cl (12×)	3·523 (1)

* Within anion.
† Between anions.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42997 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The K_2PtCl_6-type structure (Fig. 1) was confirmed with the final structural parameters given in Table 1; a positional disorder of the NH_4^+ ion should be assumed. For the first time a high-quality atomic distance Se—Cl for the hexacoordinated complex ion is available (interatomic distances are in Table 2). A subsequent correction of the positional parameter of the Cl atom was applied because of the shortening of the Se—Cl bond due to thermal motion (Schomaker & Trueblood, 1968) on the assumption that the rigid $SeCl_6^{2-}$ ion is librating about the central Se atom. The new corrected atomic distance Se—Cl is now 2·411 (1) 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* by Roberts & Sheldrick (1975): $R_G = 0{\cdot}026$]. The angular displacement of the libration is 3·44° off the center position.

Although the rigid-body model fits rather well, the broad T_{1u} deformation vibration band of the $SeCl_6^{2-}$ ion (Stufkens, 1970) indicates slightly distorted octahedra averaged by the X-ray diffraction experiments. As already pointed out for the TeX_6^{2-} salts (Abriel, 1986), the high-symmetry crystal field yielding at least a center of symmetry for the Se position stabilizes this dynamic structure.

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Hexasodium Hexatungstotellurate(VI) 22-Hydrate

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Abstract. $Na_6[TeW_6O_{24}].22H_2O$, $M_r = 2149{\cdot}0$, triclinic, space group $P\bar{1}$, $a = 10{\cdot}269$ (3), $b = 10{\cdot}575$ (2), $c = 11{\cdot}104$ (5) Å, $\alpha = 90{\cdot}95$ (3), $\beta = 115{\cdot}13$ (4), $\gamma = 104{\cdot}96$ (2)°, $U = 1044$ (2) Å^3, $Z = 1$, $D_x = 3{\cdot}42$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 17{\cdot}7$ mm^{-1}, $F(000) = 974$, $T = 298$ K, $R_1 = 0{\cdot}0638$ ($wR = 0{\cdot}0698$) for 3774 reflections with $I > 3\sigma(I)$. The lattice contains sodium ions and a centrosymmetric Anderson type II anion $TeW_6O_{24}^{6-}$ surrounded by 22 water molecules. The hexatungstotellurate(VI) anion has approximate D_3 symmetry and is isostructural with the known molybdenum analogue. The central tellurium atom is in a slightly flattened octahedral environment with an average Te—O distance of 1·924 (11) Å.

Introduction. Heteropolynuclear oxometallates of Mo and W have been known in solution for some time and several crystal structures have been determined (Evans, 1971; Nomiya & Miwa, 1984). With recent advances in the field of multinuclear magnetic resonance spectroscopy and the general accessibility of nearly all NMR-active nuclides to observation by the technique, suitable reference compounds are not always readily available. Although the probiem generally does not arise for spin-$\frac{1}{2}$ nuclides, difficulties may arise when the nuclide chosen for study possesses a spin greater than $\frac{1}{2}$.

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