Crystal structure of lithium ammonium hexachlorotellurate(IV), $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$

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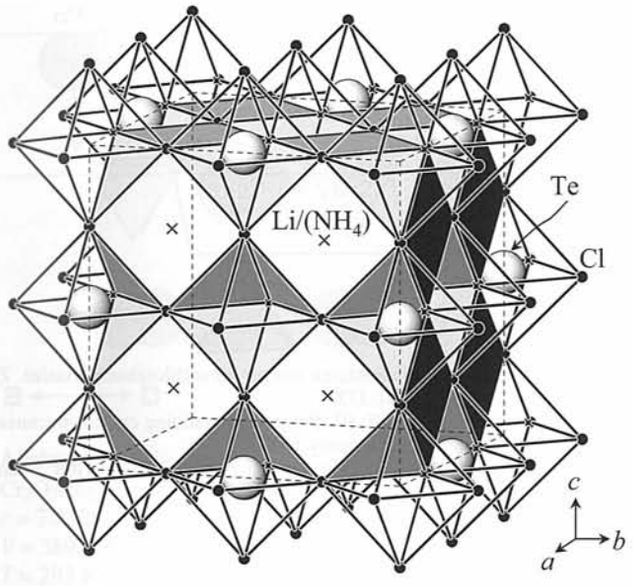

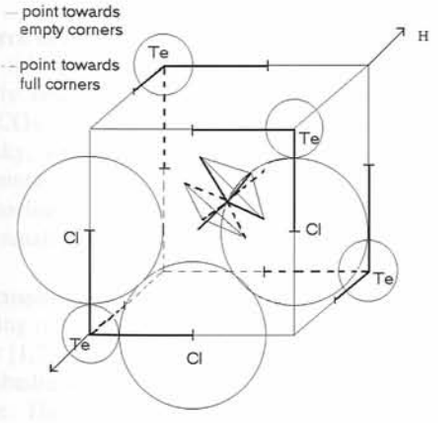

Abstract

$Cl_6H_{6.4}Li_{0.4}N_{1.6}Te$, cubic, $Fm\bar{3}m$ (No. 225), $a = 10.357(2)$ Å, $V = 1111.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.060$, $wR_{ref}(F^2) = 0.149$, $T = 299$ K.

Source of material

From the mixed solutions of LiCl, NH_4Cl and TeO_2 in concentrated HCl with the molar ratio 1:1:1, bright yellow crystals grew within several days using a desiccator filled with concentrated H_2SO_4 as water absorber. As for other hexachlorotellurates(IV), the crystals are very sensitive to moisture. Therefore, they were protected by paraffin oil.

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Experimental details

The H atoms (by implication) would be at a 36(*f*) (*x*, *x*, *x*) sites. Diffraction experiments on the isomorphous $(NH_4)_2SiF_6$ [1,2] have provided information on the orientation and the thermal motion of the ammonium group, and similar models have been tested in the structural refinement of $[Li_{0.2}(NH_4)_{0.8}]_2TeCl_6$. The ammonium tetrahedron may be placed in two similar positions with its axis along [111]. But, it was hard to confirm the 36(*f*) (*x*, *x*, *x*) position for the H atoms. A model was tested with $x(H) = 0.19$ converging to $R_{gt}(F) = 0.061$. However, with the help of three-dimensional Fourier synthesis, it was found that the H atoms lie at a 96(*k*) site leading to a three-fold disordering.

Discussion

As expected, the salt crystallizes in the $K_2[PtCl_6]$-type cubic face-centered antifluorite lattice (figure, top). Each Te atom is surrounded by six Cl atoms forming a regular octahedron with distances of 2.585(3) Å. The $TeCl_6$ octahedra are found to be regular despite the coexistence of two different types of chlorine bonding, with x(Cl) value of 0.2504(3) which can also be calculated from the following equation [3] : $x_{calc} = (0.5 - r_{Cl}/a_0)$; where x_{calc} is the calculated chlorine site fraction. This correlation between Te—Cl distance and the unit cell parameter is derived from the fact that the Cl^- ions of each octahedron are in contact (figure, bottom) and this may determine a_0. The calculated value of $x_{calc} = 0.2493$ is in close proximity to that measured indicating that the density of the hexachloride lattice is not influenced by the Cl^-/NH_4^+ repulsion. The presence of both Li^+ and NH_4^+ cations induce the coexistence of two types of bonds:

– Ionic bonding between cationic entities Li^+ and $[TeCl_6]^{2-}$ anionic complexes.

– H bonding contacts N–H···Cl providing a linkage between cationic entities NH_4^+ and $[TeCl_6]^{2-}$ anionic complexes.

Li/N atoms are twelve-fold coordinated by Cl neighbors. The average distance d(Li—Cl) is 3.662(1) Å. Comparison with $(NH_4)_2TeCl_6$ [4] leads us to assume that the title compound crystallizes in the same structure with more extension in the cavity around Li/N atoms. This increase is deduced by the coexistence of two types of bonds. The values of Te—Cl distances are close to those observed in $(NH_4)_2TeCl_6$.

Table 1. Data collection and handling.

Crystal:	yellow cube, size 0.24 × 0.24 × 0.24 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	40.55 cm^{-1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur CCD, ω
$2\theta_{max}$:	59.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2243, 113
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 110
$N(param)_{refined}$:	9
Programs:	SHELXL-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	96*k*	0.267	0.240(4)	0.189(4)	y	0.082

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te(1)	4*a*		1/2	0	0	0.0328(7)	U_{11}	U_{11}	0	0	0
Cl(2)	24*e*		0.2504(3)	0	0	0.020(1)	0.067(1)	U_{22}	0	0	0
N(1)	8*c*	0.8(1)	1/4	1/4	1/4	0.069(8)	U_{11}	U_{11}	0	0	0
Li(1)	8*c*	0.2	1/4	1/4	1/4	0.069(8)	0.069(8)	0.069(8)	0	0	0

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