Crystal and Molecular Structure of Potassium Tetrachlorothallate(III)

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The crystal structure of $KTlCl_4$ has been determined from single-crystal X-ray diffraction data collected at room temperature on a Syntex $P2_1$ four-circle diffractometer using graphite monochromatized $MoK\alpha$-radiation.

The compound crystallizes in the tetragonal space group $I4_1/a$ (No. 88) with parameters:

$a = 6.892(2)$ Å, $c = 15.327(2)$ Å and $Z = 4$.
$D_x = 3.51$ g cm^{-3}; $3.4 < D_m < 3.5$ g cm^{-3} (by flotation); $\mu = 242.2$ cm^{-1}.

The Tl atom is surrounded by four Cl atoms forming a distorted tetrahedron with a Tl$-$Cl distance of 2.433(3) Å (corrected for thermal motion) and Cl$-$Tl$-$Cl angles of 106.9(1) and 114.8(1)°.

The K atom is surrounded by eight chlorine atoms with an average distance of 3.252(3) Å.

The structure is of the $CaWO_4$ type and isomorphous with Tl(I)Tl(III)Cl$_4$.

The structure was refined to a conventional R-value of 3.5 % for 278 independent reflections. $R_w = 4.6$ %.

This work is part of a series of structure determinations of crystalline Tl(III) compounds, which was undertaken in order to investigate structure relationships between different complexes of the type TlX$_n^{(3-n)}$, where X = Cl$^-$, Br$^-$.

Experimental. The transparent crystals were prepared by mixing concentrated aqueous solutions of TlCl$_3$ and KCl in a mol ratio 1:1 and evaporating at room temperature. They were analyzed for Tl (bromatometric titration), Cl$^-$ (Volhard titration) and K$^+$ (flame atomic absorption). The analysis gave Tl 51.3; Cl 36.6; K 10.2 (calc. for KTlCl$_4$: Tl 53.04; Cl 36.81; K 10.15).

The data collection and the data reduction to scaled F_o values were performed as described previously, using computer programs and scattering factors from the same sources.[1]

The space group was uniquely determined from the systematic extinctions.

Structure determination and refinement. The positions of all the atoms were determined from a three-dimensional Patterson map. A least squares refinement with anisotropic temperature factors led to $R = 4.4$ % ($R_w = 5.4$ %, $S = 1.6$). When 10 reflexions, obviously suffering from a secondary extinction effect, were removed, the R-value decreased to 3.5 % ($R_w = 4.6$ %, $S = 1.3$).

The highest remaining peaks (all less than 1.5 e Å^{-3}) in the final difference Fourier map were positioned close to the Tl atom, thus indicating errors in the absorption correction and in the model of the thermal movement. The refinements were based on minimization of $\sum w\{|F_o| - |F_c|\}^2$, including reflexions with $|F_o| > 3.92\ \sigma(F_o)$. The weighting function used was $w = 1/\{\sigma^2(F_o) + (0.03F_o)^2\}$.

Discussion. The structure (Fig. 1) is of the $CaWO_4$ (scheelite) type and the crystals are isomorphous with those of Tl(I)Tl(III)Cl$_4$.[2]

The ratios of the unit cell edges, $\frac{c}{a}$, are 2.224 for KTlCl$_4$ and 2.230 for TlTlCl$_4$.

The Tl$-$Cl distance obtained in the present work (2.423(3) Å) is not significantly different from the value of Ref. 2 (2.418(6) Å) and is in agreement with the average Tl$-$Cl distance in [Co(en)$_2$Cl$_2$]-TlCl$_2$ (2.418(2) Å).[3] However, the Cl$-$Tl$-$Cl angles in the TlCl$_4^-$ tetrahedron show a slightly larger deviation from the value expected for a regular

Table 1. Final fractional atomic positional parameters and isotropic mean square amplitudes of vibration in Å^2. Estimated standard deviations are given in parentheses.

Atom	Position	x	y	z
Tl	4(a)	0	1/4	1/8
Cl	16(f)	0.1615(4)	0.4982(4)	0.2102(2)
K	4(b)	0	1/4	5/8

Table 2. Final anisotropic termal parameters (Å^2) with estimated standard deviations in parentheses. The expression used is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

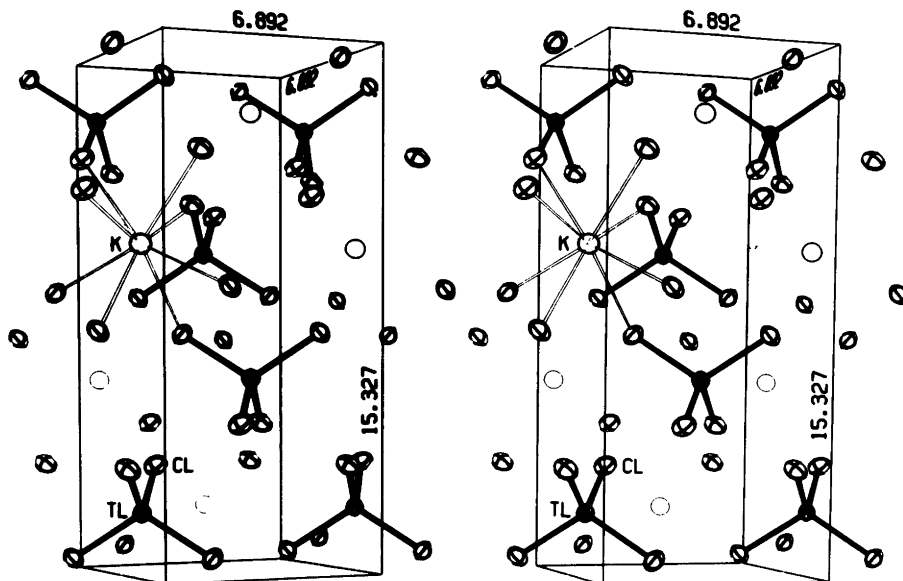| Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tl	0.0273(4)	0.0273	0.0288(6)	0	0	0
Cl	0.043(2)	0.049(2)	0.039(1)	$-0.014(1)$	0.005(1)	$-0.014(1)$
K	0.044(2)	0.044	0.038(3)	0	0	0

Fig. 1. A stereoscopic view of the tetragonal unit cell. The ellipsoids are drawn to enclose 40 % probability.

tetrahedral coordination than in the Tl(I)-compound.

The K–Cl distances are only 0.03 and 0.08 Å shorter than Tl(I)–Cl, whereas the difference in ionic radii is $r_{Tl^+} - r_{K^+} = 0.14$ Å. This is probably caused by a slightly higher degree of covalency in the Tl(I)–Cl bond.

Some bond distances and angles are given in Table 3. The distances have been corrected for thermal movement.[4] Within the $TlCl_4^-$-tetrahedra, the Cl atoms are assumed to ride on the Tl atom. All the other distances were calculated for atoms moving independently.

Table 3. Interatomic distances in Å and angles in degrees. Estimated standard deviations are given in parentheses.

	Corrected for thermal motion[4]	Non-corrected
(a) Within the $TlCl_4^-$-tetrahedron		
4 × Tl – Cl	2.433(3)	2.423(3)
4 × Cl – Cl	3.917(4)	3.893(4)
2 × Cl – Cl	4.105(4)	4.082(4)
4 × Cl – Tl – Cl		106.9(1)
3 × Cl – Tl – Cl		114.8(1)
(b) Other distances		
4 × Tl – Cl	3.856(3)	3.840(3)
4 × K – Cl	3.215(3)	3.187(3)
4 × K – Cl	3.288(3)	3.260(3)
2 × Cl – Cl	3.679(4)	3.655(4)
1 × Cl – Cl	3.848(4)	3.831(4)
1 × Cl – Cl	3.901(4)	3.876(4)
2 × Cl – Cl	3.950(4)	3.928(4)
1 × Cl – Cl	4.141(4)	4.124(4)

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3. Brodersen, K., Rath, J. and Thiele, G. *Z. Anorg. Allg. Chem. 394* (1972) 13.
4. Busing, W. R., Martin, K. O. and Levy, H. A. *Function and Error Program,* Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge 1965.