

Refinement of the Crystal Structure of ThCl₄*

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The crystal structure of ThCl₄ was determined by Mooney [*Acta Cryst.* (1949) **2**, 189] from X-ray diffraction powder data. Each Th atom was found to be dodecahedrally coordinated, the Th-Cl bond distances falling into two sets, 2.46 (4×) and 3.11 Å (4×). We have refined this crystal structure using diffractometrically recorded intensities from a single crystal. The crystals are tetragonal, $a=8.48_6$, $c=7.46_5$ Å; the space group is $I4_1/amd$. The calculated density for four molecules of ThCl₄ per unit cell is 4.62 g.cm⁻³. Full-matrix, least-squares refinement resulted in an R index of 3.8% (anisotropic temperature parameters) and in significant shifts in the positional parameters. The two sets of Th-Cl bond distances now become much more nearly equal: 2.718 ± 0.008 (4×) and 2.903 ± 0.007 Å (4×). The angles which these bond directions make with the \bar{z} axis of the dodecahedron are 78.0° and 33.1°, respectively. No evidence was found to support the claim of Takeuchi & Obata [*Nuclear Sci. Abstr.* (1967) **21**, 856] that this tetragonal phase is actually a hydrated form.

Introduction

The crystal structure of ThCl₄, as well as that of the isostructural compound UCl₄, was determined by Mooney (1949) from X-ray diffraction powder data. Several other tetrahalide compounds of actinide metals are listed by Wyckoff (1964) as also being isostructural with ThCl₄, e.g. ThBr₄, PaCl₄, NpCl₄. In the structure found by Mooney (1949), each Th (or U) is surrounded by a dodecahedron of eight Cl atoms. A remarkable feature is the occurrence of decidedly dissimilar metal-Cl bond distances, e.g. in ThCl₄, Th-Cl=2.46 (4×) and 3.11 Å (4×). In view of the current interest in the geometry of eightfold coordination, it seemed of interest to redetermine the atomic positions of ThCl₄ by the use of diffractometer data from a single crystal.

Experimental

A commercial sample of ThCl₄ was so visibly contaminated with hydrolysis products that rechlorination was deemed necessary. The material was placed in a quartz container, and all material volatile at 650°C was removed by pumping until the pressure was 10⁻⁶ mmHg. The residue was then chlorinated by treatment with CCl₄ vapors at 650°C. After chlorination, all material volatile between 750–800°C was collected; the more

volatile portion was then removed by pumping at 400°C to a pressure of 10⁻⁶ mmHg. The tube was sealed off, and crystals were grown at 600–620°C by vapor deposition. After cooling, the tube was opened in an argon atmosphere drybox where a half-dozen or so crystals were inserted into thin-walled glass capillaries for X-ray examination.

Oscillation and Weissenberg photographs showed $4/mmm$ diffraction symmetry. The systematic extinctions (hkl for $h+k+l$ odd; $hk0$ for h and k odd; hhl for $2h+l=4n+2$) are those uniquely characterizing the space group $I4_1/amd$ (*International Tables for X-ray Crystallography*, 1952). Lattice constants obtained from measurements with a single-crystal orienter are: $a=8.48_6$, $c=7.46_5$ Å (based on λ Mo $K\alpha=0.7107$ Å; probable errors in the lattice constants are estimated to be about 0.2%). By way of comparison, Elson, Fried, Sellers & Zachariasen (1950) reported lattice constants for ThCl₄ of $a=8.490 \pm 0.001$, $c=7.483 \pm 0.001$ Å. The density calculated for four molecules of ThCl₄ per unit cell is 4.62 g.cm⁻³ (present lattice constants); the observed value listed by *Handbook of Chemistry and Physics* (1964) is 4.59 g.cm⁻³.

Intensities were measured diffractometrically using the stationary-crystal stationary-counter technique (Furnas, 1957), Zr-filtered Mo $K\alpha$ radiation and pulse-height discrimination. The crystal specimen was a rectangular bipyramid measuring 0.18 × 0.25 mm along the base and 0.18 mm in height; the axis of the pyramid was c . A total of 104 independent reflections were recorded

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Table 1. *Final parameters for ThCl₄*

Space group is $I4_1/amd$ with origin at $2/m$. E.s.d.'s of least significant digits are given in parentheses. Temperature factor is expressed as $\exp[-\frac{1}{4}(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2klb^*c^*B_{23})]$.

	Wyckoff notation	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}
Th	$4a$	0	$\frac{3}{4}$	$\frac{1}{8}$	1.2 (1)	B_{11}	1.2 (1)	0
Cl	$16h$	0	0.5633 (8)	0.7992 (8)	3.9 (4)	1.6 (3)	1.2 (3)	-0.2 (2)

up to a 2θ -cutoff of 45° . The $h00$ reflections occurring at $\chi=90^\circ$ showed a significant variation of intensity with φ , maximum and minimum readings being in the ratio of 3.1 to 1. These measurements, made at four different 2θ values, were used to obtain φ -dependent absorption corrections which were applied to all reflections. Corrected intensities were reduced to $|F|^2$'s through the application of Lorentz and polarization factors.

The starting model for refinement was that of Mooney (1949), namely Th in the positions $4a$ (0,0,0; $0, \frac{1}{2}, \frac{1}{4}$ + body-centering) of space group $I4_1/amd$ (origin at $42m$) and Cl in positions $16h$ (0, y , z etc.) with $y=0.280$ and $z=0.917$. Refinement of the variable parameters was by means of the full-matrix, least-squares program of Gantzel, Sparks & Trueblood (ACA Program No. 319, unpublished). The quantity minimized was $\sum w[|F_o| - (1/K)|F_c|]^2$ where K is the scale factor relating F_o and F_c ; in the present case, unit weights were used (see below). Atomic scattering factors with corrections for anomalous dispersion were those listed in *International Tables for X-ray Crystallography* (1962) for neutral Th and singly ionized Cl. Extinction corrections of the form F_o (corrected) = $KF_o(1 + \beta I_o)$, where β is the extinction parameter and I_o is the raw intensity, were employed. A value of 1.3×10^{-5} for β gave the lowest $R = [\sum(K|F_o| - |F_c|) / \sum K|F_o|]$ and was not refined further. Five cycles of least-squares refinement reduced R to 4.8% (all reflections); without the extinction corrections, R was 5.6%. A difference synthesis indicated anisotropic thermal motion for the Cl atoms. A refinement series with anisotropic temperature parameters for both Th and Cl

gave an R index of 3.8% (all reflections). Changes in parameter values in the last cycle were less than 0.1% of the standard deviations. The largest peak in a final difference synthesis was $0.7 \text{ e.}\text{\AA}^{-3}$.

Additional refinement using a weighting scheme designed to take counting statistics and time-wise drift of the X-ray equipment into account, failed to reduce the R index below the value obtained with unit weights. We suspect that uncertainties in the absorption corrections may constitute an important source of errors in the $|F_o|$'s. We are doubtful as how to weight the reflections under these circumstances; the unit weights used do not seem inappropriate. In any event, the two refinement schemes gave positional parameters which agreed to within 0.2σ of each other in all cases. (A refinement series with $|F_o|$'s having no absorption corrections gave an R index of 14.3%, and the ΔF 's exhibited a φ -dependency.)

Final parameters are given in Table 1. Table 2 lists observed and calculated structure factors.

Table 2. Absolute values of observed and calculated structure factors

h,k,l 0, 0	L FOB FCA 2 57 53	3 193 206	L FOB FCA 1 92 89	h,k,l 7, 5
L FOB FCA 4 201 188	4 244 242	6 11 10	0 275 280	3 132 134
8 74 72			2 9 1	L FOB FCA 2 127 127
h,k,l 1, 0	h,k,l 3, 0	h,k,l 4, 1	h,k,l 5, 1	h,k,l 6, 6
L FOB FCA 1 272 304	L FOB FCA 2 167 166	L FOB FCA 4 130 139	L FOB FCA 6 13 2	L FOB FCA 0 193 184
1 214 218	3 180 180	1 150 147	4 37 29	L FOB FCA 0 138 135
3 283 278	5 84 81	3 170 166	6 179 190	2 56 53
5 88 87	7 49 49	5 125 125	1 142 133	
7 85 81		7 99 103	h,k,l 5, 2	
			L FOB FCA 3 166 160	
			L FOB FCA 5 69 74	
			1 88 88	
			h,k,l 4, 2	
			L FOB FCA 3 141 137	
			0 188 191	
			5 137 136	
			0 293 199	
			2 59 51	
			L FOB FCA 4 150 153	
			2 179 188	
			h,k,l 6, 2	
			L FOB FCA 1 88 84	
			h,k,l 7, 1	
			3 75 72	
			2 168 167	
			L FOB FCA 0 96 92	
			h,k,l 8, 2	
			L FOB FCA 4 28 24	
			h,k,l 7, 2	
			L FOB FCA 1 130 125	
			3 82 84	
			L FOB FCA 1 109 108	
			h,k,l 8, 3	
			L FOB FCA 1 111 109	
			3 123 120	
			5 70 70	
			1 91 92	
			h,k,l 6, 4	
			3 137 141	
			5 100 101	
			L FOB FCA 0 204 198	
			2 30 25	
			L FOB FCA 4 131 133	
			2 126 125	
			h,k,l 6, 5	
			L FOB FCA 3 87 90	
			h,k,l 8, 4	
			L FOB FCA 2 168 177	
			4 14 10	
			0 105 101	
			h,k,l 7, 4	
			L FOB FCA 1 119 117	
			L FOB FCA 1 122 112	
			h,k,l 9, 0	
			L FOB FCA 1 119 117	
			L FOB FCA 1 122 112	

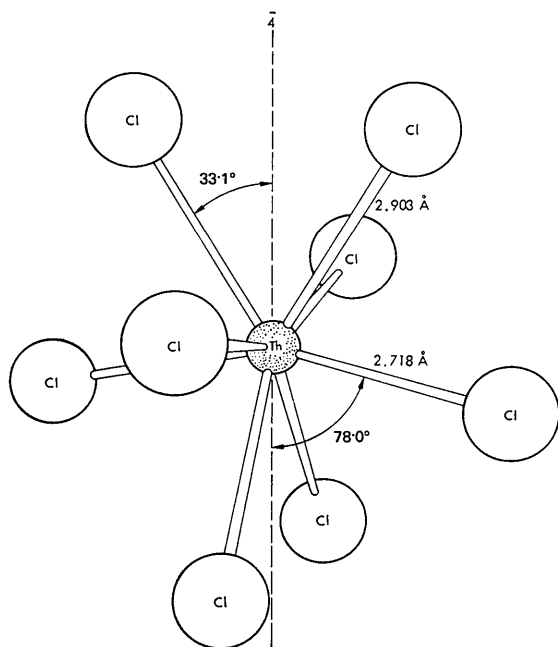


Fig. 1. Coordination about Th in ThCl_4 . The polyhedron is a dodecahedron having $42m$ symmetry.

Discussion

The overall crystal structure remains the same as found by Mooney (1949), *i.e.* each Th atom is situated at a point of $42m$ symmetry and is surrounded by a dodecahedron of eight Cl atoms (Fig. 1); each Cl atom is shared between two Th atoms. The bond data, however, are appreciably altered. The two sets of fourfold Th-Cl bond distances now become 2.903 and 2.718 Å (Table 3), rather than 3.11 and 2.46 as reported by Mooney (1949).

In their analysis of discrete eight-coordination, Hoard & Silverton (1963) pointed out that the geometry of the $42m$ dodecahedron is characterized by (a) two sets of bond distances, d_A and d_B , and (b) the angles, θ_A and θ_B , which these bond directions make with the 4 axis. In the hard-sphere idealization, $d_A = d_B$, $\theta_A = 36.9^\circ$ and $\theta_B = 69.5^\circ$. Hoard & Silverton further showed that minimization of the repulsive energy ($k \sum R_{ij}^{-n}$) between ligands leads to a lower energy and a 'most favorable' configuration having, for $n=7$, $\theta_A =$

35.2° and $\theta_B = 73.5^\circ$. Structural data for the Zr(C₂O₄)₄ ion placed the ratio d_A/d_B at 1.03; on the basis of additional data for Zr^{IV} complexes, this value was later revised to 1.05 (Hoard, Silvertown & Silvertown, 1968). The dodecahedra in ThCl₄ and isostructural compounds are not discrete, whereas the above analysis is, strictly speaking, only applicable to discrete complexes. Nevertheless, the present configurational parameters ($d_A/d_B = 2.903/2.718 = 1.068$, $\theta_A = 33.1^\circ$ and $\theta_B = 78.0^\circ$) approach those of the 'most favorable' polyhedron. Similarly, a recent refinement of PaBr₄ (Brown, Petcher & Smith, 1968) gives $d_A/d_B = 3.01/2.83 = 1.064$.

It may be remarked that considerable information about the atomic configuration can be obtained solely from the lattice constants. For example, simple geometric arguments show that, given the c/a ratios (0.88–0.90) observed for these MX₄ compounds, no y and z positional parameters can be found such that $d_A = d_B$ and θ_A , θ_B take on values required by the hard-sphere model. Conversely, ideal c/a ratios can be derived in terms of d_A/d_B , θ_A and θ_B for both the hard-sphere and 'most favorable' configurations. Numerically, $c/a = 0.585$ for the former and 0.734 for the latter (d_A/d_B

taken as 1.05). Thus, the c/a ratio serves by itself as a sensitive test to indicate, for example, that observed distortions from the geometry of the 'most favorable' polyhedron are indeed real.

Each Cl atom has two Th atoms and ten other Cl atoms as nearest neighbors. The rather unusual coordination polyhedron is shown in Fig. 2; nearest neighbor Cl···Cl distances are given in Table 3. Even though the Cl atoms are not in a closest-packed arrangement, the V_{Cl} figure (= volume of unit cell/number of Cl atoms within the unit cell) of 33 Å³ is very similar to values found in several anion closest-packed structures of metal pentachlorides (Mucker, Smith & Johnson, 1968).

In some recent studies of ThCl₄, Takeuchi & Obata (1966*a, b*) reported that (a) the body-centered tetragonal phase shows a 6–10% weight loss upon heating to 400°C, (b) a distinctly different phase is obtained under highly dry conditions and that this phase does not show a corresponding weight loss. It was concluded that the former is actually a hydrated phase and that the latter is the truly anhydrous phase. We, however, find no evidence to support these claims. On the con-

Table 3. *Interatomic distances and selected angles in ThCl₄*

The e.s.d.'s include contributions from standard deviations of 0.01 Å in the lattice constants.

Th-Cl	2.718 ± 0.008 Å	Cl···Cl	3.168 ± 0.014 Å
Th-Cl	2.903 ± 0.007	Cl	3.185 ± 0.013
<Cl-Th-Cl	66.2 ± 0.3° (=2θ _A)	2Cl	3.432 ± 0.009
<Cl-Th-Cl	156.0 ± 0.3° (=2θ _B)	4Cl	3.614 ± 0.004
		2Cl	3.927 ± 0.011

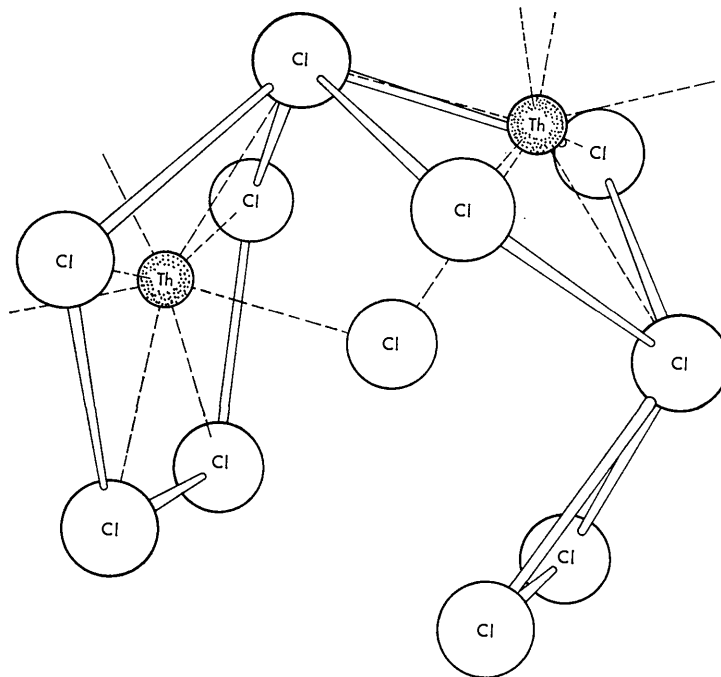


Fig. 2. Coordination polyhedron about Cl. The only required symmetry is a mirror plane lying approximately in the plane of the page. Portions of the dodecahedra about Th atoms are also shown.

trary, the present crystallographic results – acceptably low R index, small residual electron density in the difference synthesis, and in particular a good agreement between observed and calculated densities – rather support an anhydrous character for the body-centered tetragonal phase. (A 10% weight loss, if due to loss of water, would correspond to an original formula of $\text{ThCl}_4 \cdot 2\text{H}_2\text{O}$; the calculated density for such a formulation would, of course, be about 10% higher than observed.) Moreover, an examination of a model of the structure discloses that while there are channels between Cl atoms (extending along the fourfold screw axes), the centers of the largest cavities within these channels are only about 2.3 Å away from Cl atoms. Hence, these channels are too small to house water molecules. (Incidentally, the pronounced anisotropic thermal motion observed for Cl can be interpreted as being due to easy vibrations in and out of these channels; vibrations of the Th atoms, by way of contrast, are isotropic within limits of error.)

As far as the reported second form of ThCl_4 is concerned, we have no evidence of its existence under the present preparative conditions. Furthermore, we have grave doubts about the correctness of the unit cell information. The orthorhombic cell ($a=11.18$, $b=5.93$ and $c=9.09$ Å) proposed by Takeuchi & Obata (1966*a, b*) leads to a calculated density of 4.12 g.cm⁻³, a value which is almost certainly too low. It would seem that either the unit-cell parameters are incorrect or that the material is not ThCl_4 . Evidently, further work is required.

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Remeasurement of the Structure of Piezoelectric $\text{BaS}_4 \cdot \text{H}_2\text{O}$

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The remeasured lattice constants of orthorhombic $\text{BaS}_4 \cdot \text{H}_2\text{O}$ are $a=9.691 \pm 0.001$, $b=8.017 \pm 0.001$ and $c=7.828 \pm 0.001$ Å at 298°K, in space group $P2_12_12$. A total of 7747 structure factors, within a reciprocal lattice hemisphere of radius $(\sin \theta)/\lambda = 1.02 \text{ \AA}^{-1}$ were measured with PEXRAD. The 894 independent F_{meas} above background were used to refine the coordinates determined in 1954 (Abrahams, S. C., *Acta Cryst.* **7**, 423), by the method of least-squares. All atoms vibrate anisotropically. The final agreement index R was 0.0322. The two crystallographically independent tetrasulfide anions are dimensionally equivalent. The four independent S–S bond distances are not significantly different from their mean value of 2.069 ± 0.002 Å. The mean S–S–S bond angle is $104.1 \pm 0.1^\circ$, the mean SSS/SSS dihedral angle in the tetrasulfide anion is $76.4 \pm 0.2^\circ$. The absolute configuration of the atomic arrangement, which may be related to the sense of the piezoelectric polarization induced by compressive stress, has been determined.

Introduction

The crystal structure of piezoelectric $\text{BaS}_4 \cdot \text{H}_2\text{O}$ was first studied fifteen years ago as part of an investigation

of the properties of subgroup VIB of the periodic table (Abrahams, 1956). This work (Abrahams, 1954) showed the S_4^{2-} anion to be nonbranched and nonplanar, with C_2 symmetry and a dihedral SSS/SSS angle of about