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The Crystal Structure of $ThCl_4$ and UCl_4

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The crystal structure of $ThCl_4$ and of UCl_4 has been determined from X-ray powder diffraction photographs.

The structures are isomorphous. The lattice is body-centered tetragonal; the space group symmetry is D_{4h}^{19}–$I4/amd$. There are four molecules in the unit cell. The cell dimensions are as follows:

$ThCl_4$	UCl_4
$a_1 = 8{\cdot}473 \pm 0{\cdot}003$ A.	$a_1 = 8{\cdot}296 \pm 0{\cdot}009$ A.
$a_3 = 7{\cdot}468 \pm 0{\cdot}003$ A.	$a_3 = 7{\cdot}487 \pm 0{\cdot}009$ A.
$\rho_{\text{calc.}} = 4{\cdot}60$ g.cm.$^{-3}$	$\rho_{\text{calc.}} = 4{\cdot}866$ g.cm.$^{-3}$

Positions have been found for the atoms such that the calculated intensities are in good agreement with observations. Each metal atom is co-ordinated to eight chlorines. Four chlorines are at significantly smaller distances than the remaining four, indicating that the bonds tend towards covalency.

Introduction

This investigation of the structure of thorium tetrachloride and of uranium tetrachloride was based on diffraction patterns obtained from powder samples, since no single crystals were available. The author is indebted for these compounds to Dr C. A. Krauss of Brown University, who supplied the uranium salt, and to Drs Sherman Fried and Norman Davidson of the Chemistry Division, Metallurgical Laboratory, who prepared the thorium compound, and sealed small samples in thin-walled glass capillaries suitable for X-ray exposure. The capillaries were loaded in a dry box to prevent hydration of the salts.

The X-ray powder diffraction photographs were taken with nickel-filtered copper radiation in a 9 cm. diameter Bradley-type camera. Measurements were made with a steel scale and vernier, and the intensities were visually estimated. Though a number of patterns of both the uranium and thorium compounds were examined and intercompared, the structure determination is based on an exceptionally sharp and completely measurable pattern of thorium tetrachloride. This pattern was obtained from a very thin sample prepared by sublimation directly into the X-ray capillary.

Crystal cell dimensions and symmetry

As would be expected, the tetrachlorides of thorium and of uranium are isomorphous, and are closely similar in cell dimensions. The tetragonal unit contains four molecules. The measured values are as follows:

$ThCl_4$	UCl_4
$a_1 = 8{\cdot}473 \pm 0{\cdot}003$ A.	$a_1 = 8{\cdot}296 \pm 0{\cdot}009$ A.
$a_3 = 7{\cdot}468 \pm 0{\cdot}003$ A.	$a_3 = 7{\cdot}487 \pm 0{\cdot}009$ A.
$\rho = 4{\cdot}60$ g.cm.$^{-3}$ (calc.)	$\rho = 4{\cdot}866$ g.cm.$^{-3}$ (calc.)

The handbook values for directly determined densities are 4·59 g.cm.$^{-3}$ for thorium tetrachloride, and 4·86 g.cm.$^{-3}$ for uranium tetrachloride, in good agreement with the X-ray values.

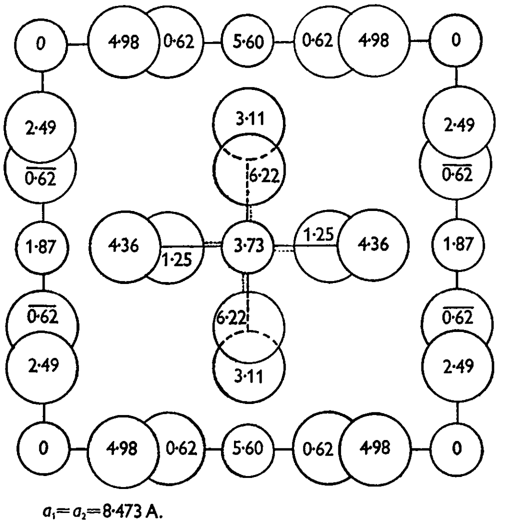

Fig. 1. Projection of the structure of thorium tetrachloride on the 001 face. The small circles represent thorium positions, the large circles chlorine positions. Distances in the *c* direction are given in Ångström units. The co-ordination is indicated by connecting lines for one thorium.

The following regularities were observed in the reflections:

hkl	present if	$h+k+l=2n$,
$hk0$	present if	$h=2n$ and $k=2n$,
$0kl$	present if	$k+l=2n$,
hhl	present if	$l=2n$ and $2h+l=4n$.

The cells are therefore body-centered, and the atomic arrangement has the symmetry of D_{4h}^{19}–$I4/amd$.

Structure determination

The space-group symmetry provides 32-fold general positions. Since the unit cell of thorium tetrachloride contains four thoriums and sixteen chlorines, all atoms must occupy special positions. These positions, as given in the *International Tables*, and summarized here for easy reference, are:

4-fold sets (a) and (b), point symmetry $\bar{4}2m$, parameters $0, 0, 0$ or $0, 0, \frac{1}{2}$;
8-fold sets (c) and (d), point symmetry $2/m$, parameters $0, \frac{1}{4}, \frac{1}{8}$ or $0, \frac{1}{4}, \frac{5}{8}$;
8-fold set (e), point symmetry mm, parameters $0, 0, z$;
16-fold sets (f) and (g), point symmetry 2, parameters $x, \frac{1}{4}, \frac{1}{8}$ or $x, x, 0$;
16-fold set (h), point symmetry m, parameters $0, x, z$.

The thorium atoms are necessarily in one of the fourfold sets, with all parameters defined by symmetry. If set (a) is chosen, the positions are

$$(a)\quad 0, 0, 0;\quad 0, \tfrac{1}{2}, \tfrac{1}{4};\quad \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2};\quad \tfrac{1}{2}, 0, \tfrac{3}{4}.$$

A number of possibilities for the chlorine distribution exist, namely, arrangements based on one of the sixteenfold sets, or on pairs of eightfold sets. If no preliminary assumptions are made concerning interatomic distances or probable configurations, all the possible distributions must be explored. Now, the thorium scattering power is roughly five to seven times that of chlorine over the range of useful glancing angles. It is often quite impossible to locate light atoms in the presence of heavy ones without preliminary structural assumptions, particularly when only powder data are available. However, thorium tetrachloride is a peculiarly favorable case; convincing evidence of the chlorine distribution can be obtained directly from intensity data, as will be shown.

The simplified structure-amplitude expressions, as given in Lonsdale's tables for the general positions, take the following forms, if

$$C_1 = \cos 2\pi hx \cos 2\pi ky, \quad C_2 = \cos 2\pi kx \cos 2\pi hy,$$

and C and S are, respectively, $\cos 2\pi lz$ and $\sin 2\pi lz$:

(1) For planes where

$$2h+l=4n, \quad A=16C(C_1+C_2); \quad B=0.$$

(2) For planes where

$$2h+l=4n\pm 1, \quad A=8C(C_1+C_2)\mp S(C_1-C_2); \quad B=\mp A.$$

(3) For planes where

$$2h+l=4n+2, \quad A=0, \quad B=16S(C_1-C_2).$$

It follows that thorium, with parameters 0, 0, 0, will make no contribution to the structure amplitude of planes of the third type, while contributions to planes of the first and second type are, respectively, $A=4f_{\mathrm{Th}}$, $B=0$ and $A=2f_{\mathrm{Th}}$, $B=-2f_{\mathrm{Th}}$. Planes of the third type, whose intensities must be due solely to chlorine, might be expected to prove useful in fixing the parameters of the light atoms. Only one plane of this type, namely 202, is measurable, though several others, for instance 402, 422, 314, are definitely absent; i.e. they are not masked by superposition. These observations are significant, first, in eliminating from consideration the sixteenfold set (g), for which planes satisfying the relation $2h+l=4n+2$ never reflect; and secondly, for limiting possible parameters to values which will give a high chlorine contribution for 202 and a low one for 402.

If the chlorine contributions were negligible with respect to thorium, planes of the first and second type, when multiplicities are accounted for, should show only natural decline in intensities with increasing glancing angle. This is not so; even cursory inspection shows that intensities are substantially modified by chlorine contributions. For instance, planes 220, 620 and 440 are either very weak or absent; that is, the chlorine contributions to these planes must be nearly maximum and out of phase with thorium. This observation eliminates the possibility of chlorines being in a pair of eightfold sets (e), for then chlorines would always be in phase with thorium for planes $hk0$; and also eliminates a combination of set (e) with (c) or (d).

Detailed consideration of the eightfold sets, (c) and (d), as possible chlorine positions proves conclusively that the z parameter cannot be 45° or 225°, and thus eliminates the sixteenfold set (f) as well. However, rough agreement found for the $hk0$ planes indicates that the x and y parameters cannot be far from 0° and 90° respectively.

The sole remaining possibility for the chlorine distribution is the sixteenfold set (h), which requires the determination of two parameters. These parameters are easily arrived at by systematically investigating the chlorine structure amplitudes over ranges of values indicated by the previous calculations. The final result, based on intensity considerations alone, is that the chlorines are lying in

(h) $0, x, z;\ 0, \bar{x}, z;\ x, 0, \bar{z};\ \bar{x}, 0, \bar{z};\ 0, \frac{1}{2}+x, \frac{1}{4}-z;$
$0, \frac{1}{2}-x, \frac{1}{4}-z;\ \ x, \frac{1}{2}, \frac{1}{4}+z;\ \ \bar{x}, \frac{1}{2}, \frac{1}{4}+z;$
and each of these plus $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;

and that the most satisfactory values for the parameters, given here in angular measure, are

$$x=101°, \quad z=330°.$$

Table 1 gives a shortened list of the data for thorium tetrachloride. The indexing accounts excellently well for the measured line positions, and the calculated intensities are in good agreement with those observed. The intensities were calculated from the expression:

$$I \propto \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\,\rho F^2,$$

where ρ is the multiplicity and F is the structure amplitude. The numerical values were reduced by a convenient factor, that is $\frac{1}{4} \times 10^{-4}$. Table 2 gives the measurements for the first part of the uranium tetrachloride pattern. The slightly higher scattering power of uranium introduces no significant differences in the intensities. The compounds are isostructural, and have identical parameters within the limits of the available data.

Table 1. *Powder diffraction data for thorium tetrachloride*

	$\sin^2 \theta$		I	
$h_1h_2h_3$	calc.	obs.	obs.	calc.
101	0·0190	0·0192	*vs*	121·3
200	0·0333	0·0334	*s*+	77·7
211	0·0523	0·0525	*m*	47·2
112	0·0594	0·0598	*m*+	55·0
220	0·0665	0·0660	*vw*	4·5
202	0·0761	0·0771	*w*	11·6
301	0·0855	0·0860	*s*−	32·7
103	0·1045	0·1050	*s*−	27·1
321	0·1188	0·1191	*s*−	30·6
312	0·1259	0·1266	*s*	49·4
400	0·1330	0·1336	*w*+	23·6
213	0·1378	0·1388	*w*−	11·6
411	0·1520	0·1522	*w*	16·2
420	0·1663	0·1669	*w*	12·8
303 004	0·1710	0·1724	*w*	8·9 1·9
402	0·1758	—	Abs.	0·1
332	0·1924	0·1930	*m*	15·3
204 323	0·2043	0·2051	*w*+	10·2 3·5
422	0·2090	—	Abs.	3·2
431 501	0·2185	0·2187	*m*+	14·3 3·0
224 413	0·2376	0·2380	*m*+	12·9 13·3
521	0·2518	—	Abs.	2·7
314	0·2542	—	Abs.	0·5
512	0·2589	0·2582	*w*+	10·5
440	0·2660	0·2665	*w*−	6·8
105	0·2756	0·2767	*vw*−	1·4
600	0·2993	0·2984	*vw*	3·9
503 433 404	0·3041	0·3038	*m*	6·3 6·2 3·9
215	0·3088	0·3090	*m*−	10·0
611	0·3183	0·3177	*w*−	3·5
532	0·3254	0·3252	*w*	8·9
620	0·3326	—	Abs.	1·9
424 523	0·3373	0·3395	*m*−	9·7 4·3
305 602	0·3421	—	Abs. Abs.	0·8 0·6
541	0·3516	—	Abs.	2·4
622 325	0·3753	0·3750	*w*	0·1 6·3
631 514	0·3848	0·3855	*w*	4·8 0·2

Interatomic distances

In the thorium tetrachloride crystal, each thorium is surrounded by eight chlorines, four at distances of 2·46 A. and four at 3·11 A. The corresponding distances in the uranium compound are 2·41 and 3·09 A. The smallest chlorine–chlorine separation is 3·2 A. That the co-ordination distances are unequal has been conclusively established from the diffraction data. The binding between the metals and chlorine must therefore be regarded as partially covalent in character; and it is to be expected that these compounds behave somewhat as molecular crystals. For instance, both sublime at high temperatures.

Table 2. *Powder diffraction data for uranium tetrachloride*

	$\sin^2 \theta$		I
$h_1h_2h_3$	calc.	obs.	obs.
101	0·0193	0·0193	*s*
200	0·0346	0·0349	*s*
211	0·0538	0·0537	*m*−
112	0·0597	0·0599	*m*
220	0·0691	0·0692	*vw*
202	0·0770	0·0771	*w*−
301	0·0884	0·0882	*m*+
103	0·1041	0·1041	*m*
321	0·1229	0·1225	*m*+
312	0·1288	0·1287	*s*
400	0·1382	0·1380	*m*−
213	0·1386		
411	0·1575	0·1572	*w*+
004	0·1696	—	Abs.
420	0·1728	0·1724	*w*
303	0·1732	—	Abs.
402	0·1806	—	Abs.
332	0·1979	0·1974	*w*+
204	0·2042	0·2041	*w*
323	0·2077	—	Abs.
422	0·2152	—	Abs.
431 501	0·2266	0·2262	*w*+
224	0·2387	0·2384	*w*
413	0·2423	0·2420	*w*−
314	0·2560	—	Abs.
521	0·2612	0·2610	Abs.
512	0·2670	0·2665	*w*−

The four nearest chlorines form a configuration about the thorium (or uranium) which may be described as an extremely flattened tetrahedron, actually approaching a distorted square arrangement. A quite different co-ordination has been found by Zachariasen (1948) in UCl_3, where nine halogen atoms form a regular co-ordination ring around uranium at distances of 2·95 A.

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Reference

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