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The Structure of Uranium(III) Trichloride by Neutron-Diffraction Profile Analysis

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A precise neutron-diffraction powder study of UCl_3 was carried out which confirmed the structure proposed in an early X-ray powder study of Zachariasen. UCl_3 is hexagonal with space group $P6_3/m$ (C_{6h}^2) and $a=7{\cdot}443$, $c=4{\cdot}321$ Å, and $Z=2$. A least-squares analysis with the profile-fitting technique gave $R=\sum_i(|I_{oi}-I_{ci}|)/\sum I_{oi}=0{\cdot}077$, where I_i is a background-corrected intensity at a point i on the pattern. The uranium atoms are in positions 2(d), $\pm(\frac{2}{3},\frac{1}{3},\frac{1}{4})$ and the six chlorine atoms in 6(h), $\pm(x,y,\frac{1}{4};\ \bar{y},x-y,\frac{1}{4};\ y-x,\bar{x},\frac{1}{4})$. Measured parameters were $x_{Cl}=0{\cdot}3009$ (4) and $y_{Cl}=0{\cdot}3858$ (4). The uranium coordination polyhedron is a tricapped trigonal prism with U–Cl (6×) = 2·931 (2) Å and U–Cl (3×) = 2·938 (3) Å.

Introduction

The structures of UCl_3 and 17 other isostructural compounds have been briefly described by Zachariasen (1948). The structure proposed was hexagonal, with space group $P6_3/m$ (C_{6h}^2), and unit-cell dimensions $a=7{\cdot}443$ and $c=4{\cdot}321$ Å. The atoms were placed as follows: 2U in 2(d), $\pm(\frac{2}{3},\frac{1}{3},\frac{1}{4})$ and 6Cl in 6(h), $\pm(x,y,\frac{1}{4};\ \bar{y},x-y,\frac{1}{4};\ y-x,\bar{x},\frac{1}{4})$ with $x=0{\cdot}292$ and $y=0{\cdot}375$. This arrangement, shown in Fig. 1, gave nine chlorine atoms around each uranium atom, the U–Cl distances being 2·96 Å. The final results only were given with no description of the X-ray analysis. Since that time, no further structural work appears to have been done on UCl_3. In X-ray diffraction, the uranium scattering greatly predominates, making precise location of the lighter atoms difficult. However, using neutron diffraction, chlorine atoms can be located as accurately as uranium atoms. It was therefore considered worth while to re-examine the structure of this important compound by neutron diffraction.

Preparation and experimental

Several methods for the preparation of UCl_3 were tried but the most successful method was the reduction of UCl_4 by Zn as described by Brown & Edwards (1972). Approximately 20 g of UCl_4 were used in the preparation. The reduction was carried out at 870 K for 24 h. Since UCl_3 is hygroscopic it was only handled in a dry-box. The UCl_3 sample was placed in a 1 cm diameter vanadium can and a neutron-diffraction powder pattern was collected on the AAEC research reactor HIFAR, with the elastic diffraction technique (Caglioti, 1970) to $\sin\theta/\lambda=0{\cdot}366$, with $\lambda=1{\cdot}083$ Å. The lines were all accounted for on the basis of the Zachariasen cell and there was no evidence for any large amount of impurity in the pattern, which is shown in Fig. 2. The unit-cell dimensions, as determined by a least-squares analysis of the 2θ positions on the neutron pattern, were $a=7{\cdot}469$ (4) and $c=4{\cdot}334$ (2) Å, slightly higher than the Zachariasen (1948) values which are given, along with the other crystal data, in Table 1. A small amount of UO_2 was present; seven points between 32° and 33° (220 reflexion of UO_2) were omitted from the profile refinement below.

Table 1. *Some crystal data for uranium trichloride**

Hexagonal, space group $P6_3/m$ (C_{6h}^2), $a=7{\cdot}443$, $c=4{\cdot}321$ Å, $V=207{\cdot}3$ Å^3, $Z=2$, $D_x=5{\cdot}52$ g cm^{-3}, M.W. 344·39, volume per Cl atom 34·5 cm^3

* Zachariasen (1948).

Analysis of the data

The neutron powder pattern of UCl_3 was analysed by the profile-fitting method of Rietveld (1967). The neutron scattering lengths used were $b_U=8{\cdot}5$ fm and $b_{Cl}=9{\cdot}6$ fm (Neutron Diffraction Commission, 1972). The starting parameters were those of Zachariasen (1948), and an overall isotropic Debye–Waller factor was assumed. The refinement converged to a value of $R=\sum_i(|I_{oi}-I_{ci}|)/I_{oi}$ of 0·077 where I_i is a background-corrected intensity at a point i on the pattern, and a value of $\chi=\{\sum w(I_o-I_c)^2/(\mathrm{NO}-\mathrm{NV})\}^{1/2}$ of 1·34. The overall B factor was 1·00 (6) Å^2. The observed and calculated neutron powder pattern profiles in Fig. 2 show

Table 2. *Final neutron diffraction parameters in* UCl_3, *compared with the estimated parameters of Zachariasen* (1948) (×10^4)

	x	y	z
U	6667	3333	2500
Cl	3009 (4)	3858 (4)	2500*
	2920	3750	2500†

* Present neutron study.
† Zachariasen (1948).

excellent agreement between theory and experiment The final parameters are given in Table 2.

Discussion

The present neutron-diffraction analysis of UCl_3 has confirmed the structure proposed by Zachariasen (1948) and also given precise parameters. The precision in the x and y coordinates of the chlorine atom in Table 2 is $\pm 0{\cdot}003$ Å, and the bond lengths and angles in Table 3 have computed errors of $\pm 0{\cdot}1\%$. The x and y parameters of Cl are 0·07 and 0·08 Å distant from those estimated by Zachariasen (1948).

UCl_3 is the standard example of the nine-coordinate symmetrically tricapped trigonal prism configuration. This polyhedron is shown in Fig. 3. The three capping atoms lie outward from uranium through the centres of the three rectangular prism faces The U–Cl distance to the three central capping atoms, 2·938 (3) Å, is nearly identical with the U–Cl distance to the six atoms at the vertices of the trigonal prism, 2·931 (2) Å. These U–Cl distances are close to the original estimate of Zachariasen (1948) U–Cl(9×)=2·96 Å. Around the edges of the polyhedron, the Cl–Cl approaches are 3·431 (3) Å about the prism end-faces, 4·321 (3) Å along the prism axial length and the capping atoms are 5·088 (5) Å apart. The 3·431 (3) Å contact is less than the ionic diameter of the chloride ion, 3·64 Å.

The crystal structure is illustrated in Fig. 1. The atoms lie at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. Chains of polyhedra joined

Table 3. *Interatomic distances and angles in* UCl_3 *by neutron diffraction, in* Å *and degrees, calculated with the Zachariasen* (1948) *cell dimensions* (*see also Figs.* 3 *and* 4)

In UCl_9 polyhedron		
U–Cl (3×)	2·938 (3)	
U–Cl (6×)	2·931 (2)	
Cl–U–Cl	70·59 (7)	
Cl–U–Cl	71·63 (6)	
Cl–U–Cl	120°	
Cl–Cl	3·431 (4)	(trigonal prism face edge)
Cl–Cl	5·088 (5)	(between capping atoms)
Cl–Cl	3·391 (3)	(face atom–cap atom)
$Cl[U_3Cl_{10}]$ polyhedron		
Cl–Cl (4×) chlorine to square base atom	3·391 (3)	
Cl–Cl (2×) along c axis	4·321 (3)	
Cl–U	2·938 (3)	
Cl–U (2×)	2·931 (2)	
Cl–Cl (2×)	3·362 (4)	
Cl–Cl (2×)	3·431 (4)	
U–U distances	4·811 (2)	related by centre of symmetry
	4·321 (3)	c-repeat

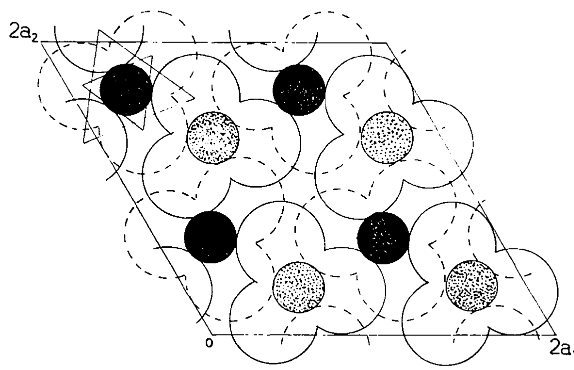

Fig. 1. The crystal structure of uranium trichloride as seen along [001]. The radii of the circles correspond to ionic radii. The dark circles are uranium atoms at $z=0{\cdot}75$ and the circles filled with dots uranium atoms at $z=0{\cdot}25$. The dashed circles are chlorine atoms at $z=0{\cdot}25$ and full-line circles chlorine atoms at $z=0{\cdot}75$. One uranium coordination polyhedron is outlined.

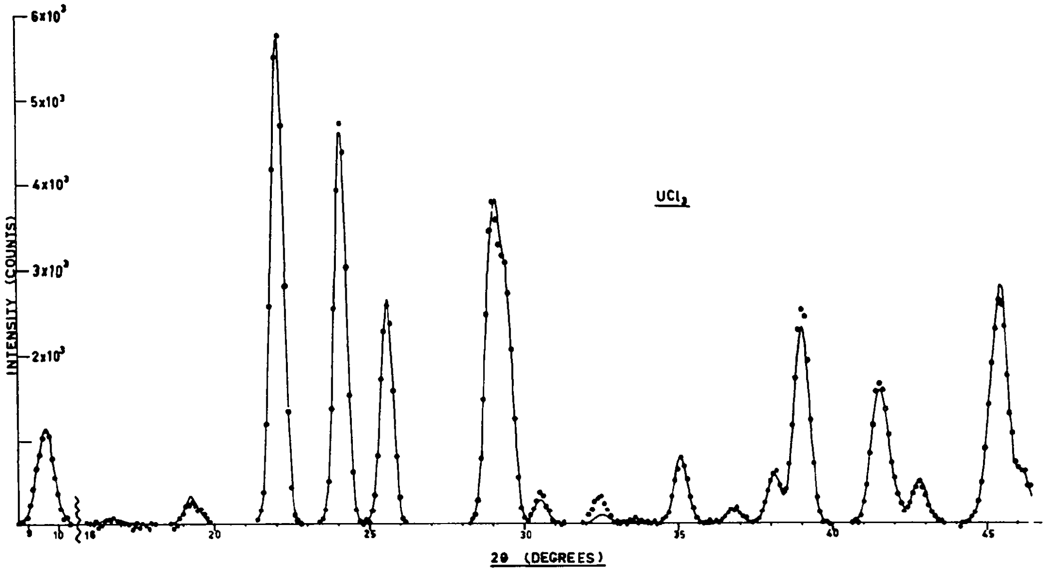

Fig. 2. Observed and calculated neutron-diffraction pattern profiles for uranium trichloride.

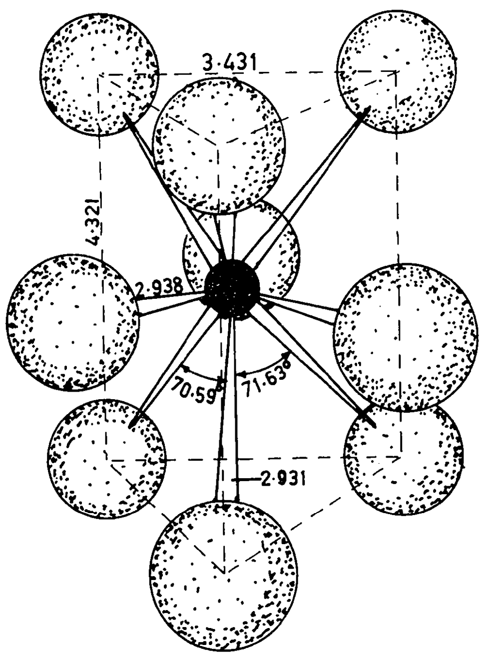

Fig. 3. The nine-coordinate symmetrically tricapped trigonal prism configuration of chlorine atoms around the uranium atom in UCl_3. Atom sizes not to scale.

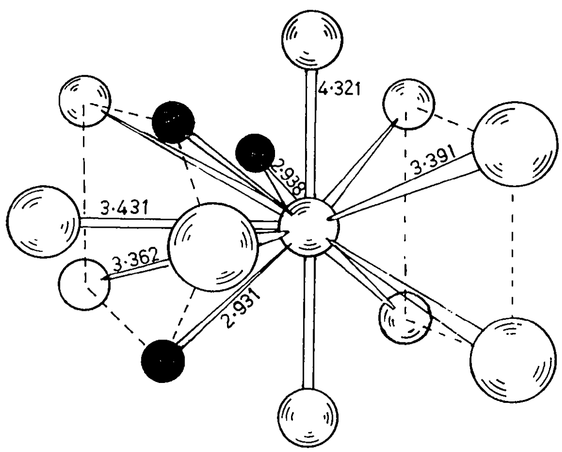

Fig. 4. The chlorine atom environment in uranium trichloride.

on the prism basal faces lie parallel to [001] and along the $\bar{6}$ axes. The chains are not isolated, each being linked symmetrically to three others. The capping atoms of one chain become the basal atoms of an adjacent chain and adjacent chains are displaced by the distance $c/2$. There are large cylindrical voids in the structure about the c axes; these holes have a diameter of 1·6 Å (assuming a Cl^- diameter of 3·64 Å). There are similar channels between chlorine atoms in UCl_4 (Taylor & Wilson, 1973).

The coordination of chlorine in this structure is of interest and is shown in Fig. 4. Each chlorine atom is surrounded by ten chlorine and three uranium atoms. The chlorine coordination polyhedron has a square face of four chlorine atoms 3·391 (3) Å away from the central chlorine atom. In a plane nearly parallel to the square face and through the central atom are two chlorine atoms above and below the central atom and distant 4·321 (3) Å from it, and one uranium atom, 2·938 Å away from the central chlorine. In a plane parallel to the square base, but on the other side of the central chlorine atom lies a pentagon of three chlorine and two uranium atoms, and through the centre of this pentagon lies the final chlorine atom, 3·431 Å away from the central chlorine atom. The chlorine polyhedron is thus very asymmetric, but it is very similar to the square-base chlorine coordination polyhedra described for $ThCl_4$ (Mucker, Smith, Johnson & Elson, 1969), and for the isostructural compound UCl_4 (Taylor & Wilson, 1973). These have ten Cl and two Th (or U) atoms about the central Cl. In UCl_5 (Smith, Johnson & Elson, 1967) the coordination of chlorine is 13 (12 Cl and one U). The 12 chlorine neighbours in UCl_5 lie at the vertices of a cuboctahedron.

The effective ionic radii for uranium (Shannon & Prewitt, 1969) decreases as the valence state increases. Thus, there should be a tendency for the coordination number of uranium to decrease with increasing valence for a given anion. This is observed; the coordination numbers of uranium in UCl_3, UCl_4 (Taylor & Wilson, 1973), UCl_5 (Smith, Johnson & Elson, 1967) and UCl_6 (Taylor & Wilson, 1974) are 9, 8, 6 and 6. The U–Cl bond lengths also decrease on going through the same series.

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