Acta Cryst. (1974). B**30**, 1481

Neutron and X-ray Powder Diffraction Studies of the Structure of Uranium Hexachloride

BY J. C. TAYLOR AND P. W. WILSON

A.A.E.C. Research Establishment, P.M.B., Sutherland, N.S.W., Australia 2232

(*Received* 11 *January* 1974; *accepted* 19 *February* 1974)

The structure of uranium hexachloride, UCl_6, was refined with neutron and X-ray powder diffraction data. UCl_6 is hexagonal, with $a=10{\cdot}95$ (1), $c=6{\cdot}016$ (6) Å, space group $P\bar{3}m1$ (D^3_{3d}), and $Z=3$. The neutron data were refined by the least-squares profile-fitting technique to a value of $[\sum_i w(I_o-I_c)^2]^{1/2}/(\sum_i wI_o^2)^{1/2}$, where I is the intensity corrected for background at a point i along the scan, of 0·16. The single uranium variable positional parameter was more reliably obtained by a least-squares refinement of the integrated intensities on a Debye–Scherrer photograph, the final value of $\sum_i(\sum_j JF_o^2-\sum_j JF_c^2)/\sum_i\sum_j JF_o^2$ for the X-ray powder data being 0·22, where i is a line in the X-ray pattern and j an hkl component with multiplicity J. The structure proposed by Zachariasen [*Acta Cryst.* (1948). **1**, 285–287] was confirmed. The octahedron around the uranium atom at (000) is nearly regular, and around the uranium atom at ($\frac{1}{3},\frac{2}{3}$,0·518) slightly distorted. The U–Cl distances lie between 2·41 (4) Å and 2·51 (4) Å.

Introduction

Uranium hexachloride is important in the nuclear industry since it is a volatile uranium hexahalide, similar, in some respects, to uranium hexafluoride. 25 years have elapsed since the classic X-ray powder study by Zachariasen (1948), and no further structural investigations appear to have been carried out on UCl_6 since that time. Historically, UCl_6 is difficult to prepare in pure form and in large quantities. Zachariasen worked with a few micrograms of sublimed material in a capillary tube, which also contained zones of UCl_4 and UCl_5. From packing considerations and the X-ray powder diffraction intensities, Zachariasen (1948) deduced an idealized structure for UCl_6 in the space group $P\bar{3}m1$ (D^3_{3d}), with U atoms in positions 1(*a*): (0,0,0) and 2(*d*): $\pm(\frac{1}{3},\frac{2}{3},z)$ and three independent Cl atoms, each in positions of type 6(*i*): $\pm(x,\bar{x},z;\ x,2x,z;\ 2\bar{x},\bar{x},z)$. The chlorine atoms were in hexagonal close packing and the uranium atoms in octahedral holes. The chlorine atoms were contracted around occupied holes and expanded around vacant holes. All U–Cl distances were estimated to be 2·42(1) Å. The crystal data for UCl_6 are given in Table 1.

It was considered worthwhile to confirm the above idealized structure and measure the parameters by least-squares refinements with X-ray and neutron diffraction data for UCl_6. As uranium is a strong X-ray scatterer it was thought that the sole uranium positional parameter, z U(2), Table 2, would be best determined from the X-ray powder pattern. Chlorine is a weak X-ray scatterer compared to uranium, but has a larger coherent neutron scattering amplitude than uranium. Thus it was thought the chlorine atoms would be more effectively located by neutron diffraction. A combination of the two techniques was therefore expected to give reliable structural parameters for UCl_6.

Experimental

Preparation

UCl_6 was prepared using the exchange reaction between UF_6 and BCl_3 (O'Donnell, Stewart & Wilson, 1966; O'Donnell & Wilson, 1973). This method gives very pure UCl_6 and yields 1–2 g of UCl_6 for each preparation. Since approximately 10 g of UCl_6 were required, the preparation was repeated until sufficient UCl_6 was prepared. This meant portions of UCl_6 had to be transferred several times into various containers and, although this was done in a dry box, contamination by hydrolysis occurred since UCl_6 is extremely hygroscopic. The whole sample of UCl_6 was therefore purified by sublimation (100°C, 1 mPa). This in turn introduced a small amount of UCl_4 contamination due to decomposition of the thermally unstable UCl_6, but this was insufficient to interfere with the structural study.

X-ray diffraction data

Some UCl_6 was sealed inside a quartz capillary of 0·6

Table 1. *Crystal data for uranium hexachloride*

Molecular weight 450·75

Reference	a (Å)	c (Å)	U (Å^3)	D_x (g cm^{-3})	Z	Space group
Zachariasen (1948)	10·97 (2)	6·04 (1)	629·5	3·567	3	$P\bar{3}m1$ (D^3_{3d})
Present work, X-rays	10·95 (1)	6·016 (6)	624·7	3·594		
Present work, neutrons	10·97 (1)	6·025 (8)	627·9	3·576		

mm diameter, and an X-ray diffraction pattern was taken with a Philips 114·6 mm diameter powder camera with Cu $K\alpha$ radiation. The intensities of 29 powder lines were estimated visually by comparison with a standard line. 22 additional *hkl* were unobservably small, but were still useful in the least-squares refinement, being given intensities $\frac{1}{2}I_{\text{min}}$, where I_{min} was the estimated minimum observable intensity. After correction for film shrinkage, a least-squares refinement with 27 2θ values to $2\theta = 85°$, with a $\cos^2\theta$ drift term (Mueller, Heaton & Miller, 1960), gave $a = 10·95(1)$ Å and $c = 6·016(6)$ Å.

Neutron diffraction data

Approximately 12 g of UCl_6 powder were mixed with aluminum powder to dilute the sample so as to fill a 1 cm diameter vanadium can. A neutron powder pattern of the sample was taken with the elastic diffraction technique (Caglioti, 1970) to $2\theta = 41·4°$ with $\lambda = 1·082$ Å. Lattice constants found by least-squares refinement of the neutron line positions were $a = 10·97$ (1) Å and $c = 6·025(8)$ Å.

The various crystal data for UCl_6 are collected in Table 1.

Calculations

Refinement with X-ray data

Each X-ray line consisted of *j* Bragg reflexions *hkl* with multiplicities *J*. The observed intensities I_o were converted to $\sum_j JF_o^2$ values with the expression

$$\sum_j JF_o^2 \propto I_o \sin^2\theta \cos\theta (1+\cos^2 2\theta)^{-1} A^*$$

where A^* is an absorption correction factor. The linear absorption coefficient, μ, for UCl_6 was 840 cm^{-1} for Cu $K\alpha$. The estimated value of μR, where R is the capillary radius, was 18, allowing a 70% packing density. The absorption corrections were obtained from tables of A^* *vs.* 2θ (*International Tables for X-ray Crystallography* 1959).

The Zachariasen coordinates were used as the starting point for a least-squares refinement with the X-ray powder data. The function minimized was $\sum_i [w_i(\sum_j JF_o^2 - \sum_j JF_c^2)^2]$, where i denotes a line in the pattern. The X-ray scattering curves for neutral Cl and U were used (*International Tables for X-ray Crystallography*, 1962) uncorrected for anomalous dispersion. An overall isotropic Debye–Waller temperature factor was assumed. The computer program was a modification of *ORFLS* (Busing, Martin & Levy, 1962).

It was found that the chlorine parameters, as well as the U(2) z parameter, could be refined with the X-ray data. At convergence, the value of the residual $\sum_i(\sum_j JF_o^2 - \sum_j JF_c^2)/\sum_i\sum_j JF_o^2$ was 0·22. The X-ray positional parameters are given in Table 2 and the observed and calculated $\sum JF_o^2$ values in Table 3.

Table 2. *Positional parameters in uranium hexachloride from the X-ray and neutron powder refinements, compared with those of Zachariasen* (1948)

Atom	Position	$10^3\,x$	$10^3\,y$	$10^3\,z$	Reference
U(1)	1(*a*)	0	0	0	
U(2)	2(*d*)	333	667	500	*
		333	667	518 (5)	†
		333	667	518 (not refined)	‡
Cl(1)	6(*i*)	100	−100	250	*
		105 (8)	−105 (8)	228 (16)	†
		109 (2)	−109 (2)	222 (8)	‡
Cl(2)	6(*i*)	430	−430	250	*
		442 (7)	−442 (7)	203 (15)	†
		431 (2)	−431 (2)	237 (8)	‡
Cl(3)	6(*i*)	770	−770	250	*
		761 (7)	−761 (7)	243 (14)	†
		777 (2)	−777 (2)	286 (8)	‡

* Zachariasen (1948).
† This work, X-ray refinement.
‡ This work, neutron refinement.

Overall $B = 4·0$ (4) Å^2 (X-rays).
$= 4·5$ (2) Å^2 (neutrons).

Refinement with neutron data

The Zachariasen parameters were used as the starting point of a least-squares refinement based on the neutron powder diffraction data, by the profile-fitting technique of Rietveld (1967). In this method, considered to be the best powder-refinement procedure available, the powder pattern was assumed to be the superposition of all the *hkl* Gaussians, while the data points are the counts along the scan, corrected for background. The computer program used was a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The neutron scattering lengths were $b_U = 0·85 \times 10^{-12}$ cm, and $b_{Cl} = 0·96 \times 10^{-12}$ cm (Neutron Diffraction Commission, 1972). Initial refinements gave a value for the z parameter of U(2) of 0·63, which was considered to be too high. The high value was thought to be due to the combined effects of (i) some UCl_4 impurity, the effect of which was corrected for later in the refinement (see below) (ii) the much lower proportion of U scattering in the neutron data and (iii) the small range of l indices due to the short c axis. The z parameter of U(2) was therefore fixed at the X-ray value 0·518(5) and not refined. In the later stages of the neutron refinement, some $(|I_o - I_c|)/\sigma(I_o)$ values, where $\sigma(I_o)$ is the standard deviation in I_o, were greater than 3. These occurred at diffraction angles where UCl_4 Bragg intensities were expected. The effect of the probable UCl_4 impurity on the refinement was reduced by increasing the $\sigma(I_o)$ values for the above points so that these $(|I_o - I_c|)/\sigma(I_o)$ values were less than 1. In all, 24 of the 313 data points were considered to be affected by UCl_4 impurity. Excess of observed over calculated intensity at these points can be seen in the final observed and calculated profile, Fig. 1, but, as corrections for the effect were made, as described above, it was considered that the chlorine parameters from the neutron refinement were reliable.

The least-squares weights were $w=\sigma(I_o)^{-2}$, directly based on the counting statistics. Convergence was obtained at a weighted residual $R=[\sum w(I_o-I_c)^2]^{1/2}/(\sum wI_o^2)^{1/2}$ of 0·16. The unweighted residual over the 313 scan points in Fig. 1 $\sum(|I_o-I_c|)/\sum I_o$ was 0·28 (higher owing to the UCl_4).

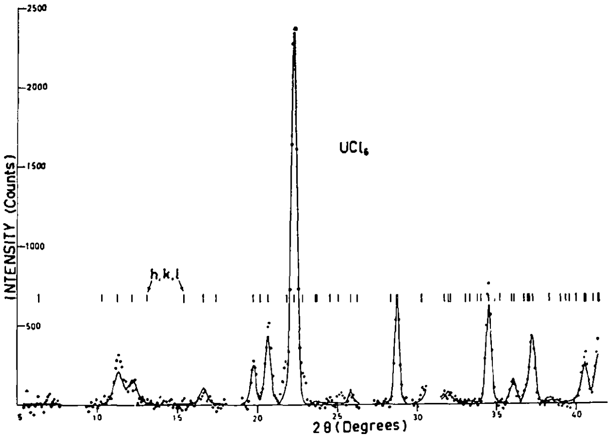

Fig. 1. Observed and calculated neutron diffraction powder pattern profiles for uranium hexachloride.

The neutron and X-ray positional parameters are compared in Table 2. It is seen that, for chlorine, the neutron e.s.d.'s are lower than the X-ray e.s.d.'s by a factor of two for the z coordinates and up to 4 for the x,y coordinates. The final parameters taken were the X-ray value for the z coordinate of U(2) (the only uranium variable parameter) and the neutron parameters for the chlorine atoms. Bond lengths and angles calculated with these parameters are given in Table 4.

Discussion

The present results have confirmed the structure proposed 25 years ago by Zachariasen (1948) for uranium hexachloride, and has provided the first refined positional parameters. While the x and y parameters of chlorine, Table 2, are close to the values estimated by Zachariasen (1948), the z coordinates differ slightly from the ideal values of $\frac{1}{4}$, and the U(2) atom from the value $z=\frac{1}{2}$. The original solution of the UCl_6 structure by Zachariasen with a sublimed microgram-range sample containing UCl_4 and UCl_5 must be regarded as a remarkable achievement. The structure is shown in Fig. 2. The octahedron around U(1) at (0,0,0) is nearly regular, all U(1)–Cl(1) distances being 2·47(4) Å and the Cl(1)–U(1)–Cl(1) angles being 86·6(15)° and

Table 3. *Observed and calculated intensities in Debye–Scherrer X-ray pattern of* UCl_6

Where a reflexion of type *hkil* is given, the presence of the reflexion $hk\bar{i}l$, which occurs at the same angle but has a different F_c in $P\bar{3}m1$, is implied. The same holds for reflexions $h0\bar{h}l$. J is the multiplicity of the reflexion, and the $\sum$ sign indicates a summation over all reflexions in a line.

hkl	$10^{-4}\sum JF_o^2$	$10^{-4}\sum JF_c^2$	*hkl*	$10^{-4}\sum JF_o^2$	$10^{-4}\sum JF_c^2$	*hkl*	$10^{-4}\sum JF_o^2$	$10^{-4}\sum JF_c^2$
*100	2	0	103	12	26	104	20	24
*001	1	0	411			512		
110	84	47	*500	1	0	323		
101	27	33	*113	1	3	521		
*200	1	0	*402	2	0	114	21	24
*111	2	7	203	80	69	610		
201	33	34	330			413		
*210	4	0	501			204		
300	17	8	*420	2	0	602	40	47
211	38	48	322	30	34	611		
*002	1	0	213			214		
*102	2	2	331			432		
301	48	43	412	91	91	503	24	22
220	29	19	421			440		
112	38	41	303			304	33	34
310			510			522		
*202	2	1	511	31	24	530		
*221	1	6	*223	2	2	700		
311	47	45	*502	3	1	333		
400			313	20	22	*441	2	1
212	6	1	600			*423	4	13
*401	2	16	*332	1	2	*224	2	1
302	85	80	*430	1	0	531	33	31
320			422	23	23	701		
410	56	63	601			620		
321			403			*612	7	0
222	54	47	520	62	53	*314	7	2
003			004			513	16	19
*312	2	2	431			621		
						*404	7	2
						710	16	8

* Denotes an unobservably small intensity, estimated as described in the text.

Table 4. *Interatomic distances and angles in uranium hexachloride*

U–Cl distances (Å)

U(1)–Cl(1) (6×)	2·47 (4)	U(2)–Cl(3) (3×)	2·41 (4)
U(2)–Cl(2) (3×)	2·51 (4)		

Intralayer Cl–Cl distances (Å)

Cl(1)–Cl(1)	3·59 (6)*	Cl(1)–Cl(2)	3·70 (3)
Cl(2)–Cl(2)	3·22 (5)*	Cl(1)–Cl(3)	3·69 (4)
Cl(3)–Cl(3)	3·63 (8)*	Cl(2)–Cl(3)	3·89 (3)

Interlayer Cl–Cl distances (Å)

Cl(1)–Cl(1)	3·38 (9),* 3·94 (9)	Cl(1)–Cl(3)	3·67 (8), 3·75 (9)
Cl(2)–Cl(2)	3·88 (8), 4·11 (9)	Cl(2)–Cl(3)	3·49 (8),* 3·73 (9)

Cl–U–Cl angles (°)

Cl(1)–U(1)–Cl(1)	86·6 (15), 93·4 (15)
Cl(2)–U(2)–Cl(2)	79·7 (28)
Cl(2)–U(2)–Cl(3)	90·4 (15)
Cl(3)–U(2)–Cl(3)	98·0 (28)

U–U distances (Å)

U(1)–U(2)	6·97 (4), 7·06 (4)	U(2)–U(2)	6·34 (1)

* in octahedron.

93·4(15)°. The octahedron around U(2) may be slightly distorted, with U(2)–Cl(2) and U(2)–Cl(3) distances of 2·51(4) and 2·41(4) Å and Cl(2)–U(2)–Cl(2), Cl(3)–U(2)–Cl(3) and Cl(2)–U(2)–Cl(3) angles of 79·7(28), 98·0(28), and 90·4(15)°.

The Cl–Cl contacts in the octahedra, Table 4, lie between 3·22 and 3·63 Å, and elsewhere between 3·67 Å and 4·11 Å, confirming the contraction around occupied octahedral holes and expansion around vacant holes postulated by Zachariasen. Cl–Cl contacts shorter than 3·22 Å occur in UCl$_4$, UO$_2$Cl$_2$ and ThCl$_4$ (Taylor & Wilson, 1973).

β-WCl$_6$ also has the UCl$_6$ structure-type. Neutron diffraction coordinates for β-WCl$_6$ are in good agreement with the present results for UCl$_6$ (Taylor & Wilson 1974). WCl$_6$ is dimorphic, having rhombohedral (α) and hexagonal (β) forms (Smith, Landingham, Smith & Johnson, 1968) but for UCl$_6$ only the hexagonal form has been observed.

UCl$_6$ can be thought of as a three-dimensional array of UCl$_6$ molecules. Alternatively, it may be described as a hexagonal close-packed chlorine lattice with the small metal atoms in octahedral holes. Zachariasen used the former description to explain its volatility (57·6 mm; 215°C). β-WCl$_6$ has a similar volatility (43 mm., 215°C). Neither compound has a volatility comparable to that of substances with truly molecular lattices and it is felt the second description gives a better representation of the properties of these two compounds.

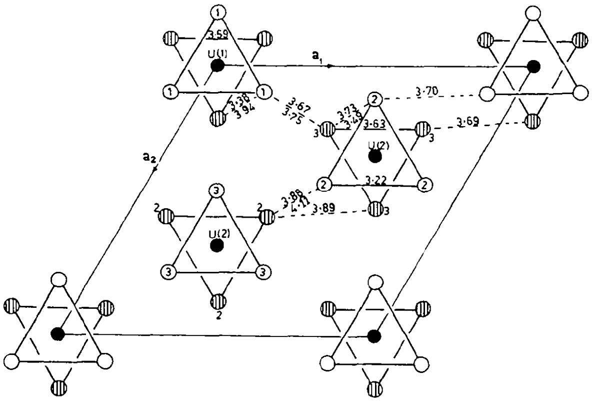

Fig. 2. The structure of uranium hexachloride. The intralayer and interlayer Cl–Cl contacts are shown. Shaded circles are near $z=\frac{1}{4}$, and open circles near $z=\frac{3}{4}$.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Caglioti, G. (1970). In *Thermal Neutron Diffraction*, Chap. 2. Edited by B. T. M. Willis. Oxford Univ. Press.

International Tables for X-ray Crystallography (1959). Vol. II, p. 295. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1962). Vol. III, p. 201. Birmingham: Kynoch Press.

Mueller, M. H., Heaton, L. & Miller, K. T. (1960). *Acta Cryst.* **13**, 828.

Neutron Diffraction Commission (1972). *Acta Cryst.* A**28**, 357–358.

O'Donnell, T. A., Stewart, D. F. & Wilson, P. W. (1966). *Inorg. Chem.* **5**, 1438–1441.

O'Donnell, T. A. & Wilson, P. W. (1973). *Inorg. Synth.* In the press.

Rietveld, H. M. (1967). *Acta Cryst.* **22**, 151–152.

Smith, D. K., Landingham, R. L., Smith, G. S. & Johnson, Q. (1968). *Acta Cryst.* B**24**, 1563.

Taylor, J. C. & Wilson, P. W. (1973). *Acta Cryst.* B**29**, 1942–1944.

Taylor, J. C. & Wilson, P. W. (1974). *Acta Cryst.* B**30**, 1216–1220.

Zachariasen, W. H. (1948). *Acta Cryst.* **1**, 285–287.