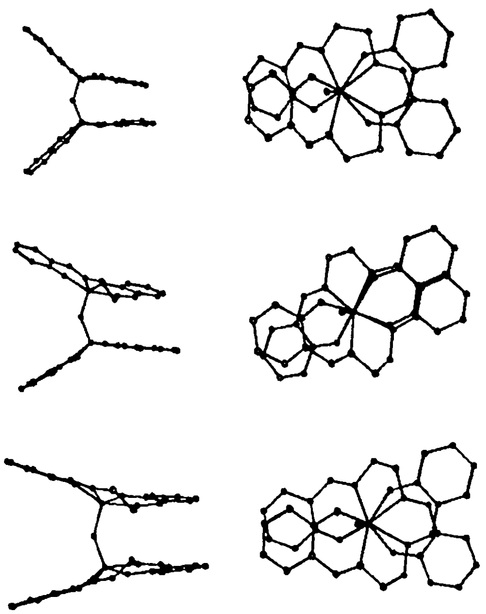

Fig. 6. (*a*) [Fe(salen)]$_2$O.2py (Gerloch, McKenzie & Towl, 1969), (*b*) [Fe(salen)]$_2$O.CH$_2$Cl$_2$ (Coggon, McPhail, Mabbs & McLachlan, 1971), and (*c*) unsolvated [Fe(salen)]$_2$O (this work). In each case, the diagram on the left is drawn with the Fe–O–Fe plane parallel to the plane of the paper and that on the right is drawn looking down the Fe–Fe direction.

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A Neutron-Diffraction Study of Anhydrous Uranium Tetrachloride

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A neutron diffraction powder study of UCl$_4$ was carried out, and confirmed the structure derived in an earlier X-ray diffraction powder study. The space group is $I4_1/amd$ (D_{4h}^{19}, No. 141). The X-ray positional parameters for Cl were found to need revision and are now: $y_{\text{Cl}} = 0{\cdot}3125$ (5) and $z_{\text{Cl}} = 0{\cdot}9261$ (5). The two sets of U–Cl distances in the coordination dodecahedron were found to be more nearly equal: U–Cl = 2·869 (3) (4 ×) and U–Cl = 2·638 (4) Å (4 ×). The angles these bonds make with the $\bar{4}$ axis are 32·7 (1) and 77·9 (1)°.

Introduction

UCl$_4$, ThCl$_4$, PaCl$_4$ and NpCl$_4$ are said to be isostructural (Brown & Jones, 1967; Elson, Fried, Sellers & Zachariasen, 1950; Fried & Davidson, 1948; Mooney, 1949). The latter author found UCl$_4$ to be body-centred tetragonal with the space group $I4_1/amd$ (D_{4h}^{19} No. 141) and the unit-cell dimensions $a = 8{\cdot}296$ (9) and

$c = 7{\cdot}487$ (9) Å. From powder patterns taken with Cu $K\alpha$ radiation, Mooney deduced that the uranium atoms were in position $4(a)$: $(0,0,0;\ 0,\frac{1}{2},\frac{1}{4})+(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and that the chlorine atoms were in position $16(h)$: $(0,x,z;\ 0,\bar{x},z;\ x,0,\bar{z};\ \bar{x},0,\bar{z};\ 0,\frac{1}{2}+x,\frac{1}{4}-z;\ 0,\frac{1}{2}-x,\frac{1}{4}-z;\ x,\frac{1}{2},\frac{1}{4}+z;\ \bar{x},\frac{1}{2},\frac{1}{4}+z)+(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, with $x = 0{\cdot}281$ and $z = 0{\cdot}917$. The uranium atom was surrounded by eight chlorine atoms, four being 2·41 Å distant from the uranium atom and four 3·09 Å from the uranium atom, and the coordination polyhedron was a dodecahedron of $\bar{4}2m$ symmetry. The X-ray chlorine positions were not accurate because of the heavy X-ray scattering by the uranium atom.

It seemed to us that the difference of 0·68 Å between the two sets of U–Cl bond distance was too large. Differences between nominally similar bond lengths can occur in coordination polyhedra, as a result of mutual repulsion of ligands (Hoard & Silverton, 1963) or cation–cation repulsions (Taylor, Wilson & Kelly, 1973), but these are usually not larger than 0·2–0·3 Å. A neutron diffraction powder study of UCl_4 was undertaken to obtain reliable positional parameters in the UCl_4 structure. The chlorine parameters from neutron diffraction were expected to be of high accuracy as chlorine has a relatively large coherent scattering amplitude for thermal neutrons. In addition, the absorption and extinction factors were negligible with the neutron powder technique.

Experimental

Preparation of uranium tetrachloride

The uranium tetrachloride was prepared in the laboratory by the vapour-phase chlorination of uranium dioxide with carbon tetrachloride (Katz & Rabinowitch, 1951). The uranium dioxide required was prepared by hydrogen reduction of UO_3 at 400 °C. The UO_3 used was a particularly active form prepared by thermal decomposition of $UO_4.2H_2O$ (Dawson, Wait, Alcock & Chilton, 1956). The chlorination apparatus was basically a simple flow reactor (Wilson, 1973). The CCl_4 was introduced into the gas stream by dripping liquid CCl_4 from a dropping funnel into a heated part of the reaction tube. The chlorination was carried out at 400 °C. The UCl_4 so prepared was in the form of black lustrous crystals, about 0·1 mm on a side.

Uranium tetrachloride is hygroscopic, and consequently all handling of the sample was carried out in a dry box.

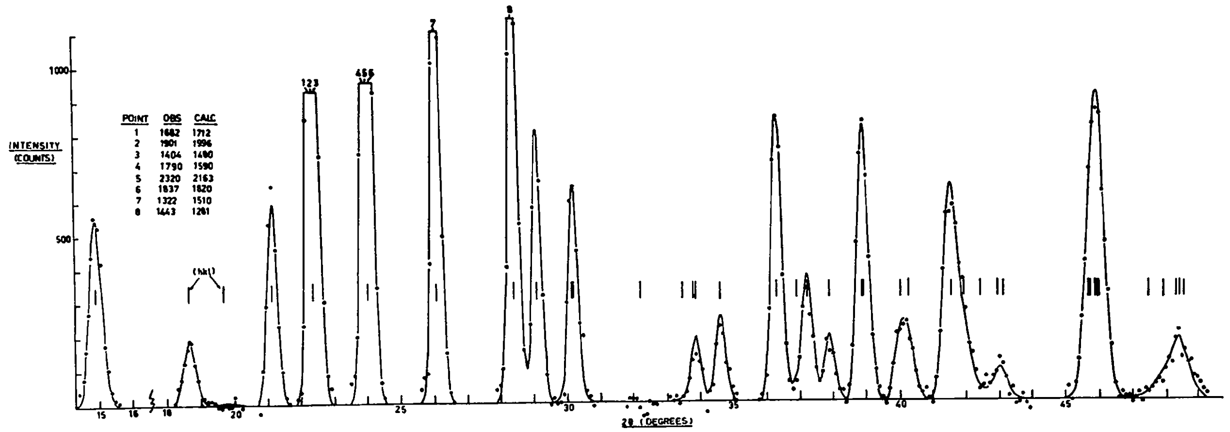
Data collection

A neutron diffraction powder pattern of the UCl_4 sample, which was packed into a Kel–F tube, was collected on the AAEC research reactor HIFAR, using the elastic diffraction technique (Caglioti, 1970), with a neutron wavelength of 1·075 Å. The data were collected to $2\theta = 50°$ ($\sin\theta/\lambda = 0{\cdot}393$). A least-squares analysis of 11 neutron line positions gave the unit-cell dimensions $a = 8{\cdot}263$ (3) and $c = 7{\cdot}457$ (3) Å. These were significantly different from the cell parameters of Mooney (1949) above. An X-ray photograph was taken with a 114·6 mm diameter Philips Debye–Scherrer camera, and least-squares analysis of these X-ray line positions gave $a = 8{\cdot}257$ (4) and $c = 7{\cdot}458$ (4) Å, in agreement with our neutron cell parameters. Our cell dimensions are in better agreement with the parameters $a = 8{\cdot}278$ (2) and $c = 7{\cdot}460$ (9) Å found by Yoshimura, Miyake & Imoto (1971).

The lines present in the neutron pattern were consistent with the space group D_{4h}^{19}.

Calculations

The neutron diffraction data were analysed with the profile-fitting method of Rietveld (1967), using a modified *ORFLS* program. In this method the pattern is treated as the sum of Gaussian (*hkl*) peaks and each count along the scan is treated as an observation. The neutron scattering lengths used were $b_U = 0{\cdot}84 \times 10^{-12}$ cm and $b_{Cl} = 0{\cdot}96 \times 10^{-12}$ cm (Neutron Diffraction Commission, 1969). With the chlorine parameters of Mooney (1949), and an overall isotropic Debye–Waller B factor of 2·0 Å^2, refinement of the scale factor alone



POINT	OBS	CALC
1	1682	1712
2	1901	1996
3	1404	1480
4	1790	1590
5	2320	2163
6	1837	1820
7	1322	1510
8	1443	1281

Fig. 1. Observed and calculated neutron diffraction pattern profiles for anhydrous UCl_4.

gave a large discrepancy index $R=\sum(I_o-I_c)/\sum I_o$ of 0·59 over all the scan points, indicating that the X-ray chlorine parameters needed revision. After several cycles in which y(Cl), z(Cl), B(U) and B(Cl) as well as the scale factor were refined, R finally converged to 0·12, and the value of $\chi=\{\sum[\omega(I_o-I_c)]^2/(\mathrm{NO}-\mathrm{NV})\}^{1/2}$ to 1·17. The fit between the observed and calculated neutron powder pattern profiles (Fig. 1) was excellent, and suggested that the sample was pure, the data were good, and preferred orientation was negligible. The parameters at convergence are given in Table 1.

Table 1. *Structural parameters in anhydrous* UCl_4 *as found by neutron diffraction* (*N*), *compared with the X-ray values* (*XR*) (*Mooney*, 1949)

	x	y	z	B(Å^2)
U	0	0	0	0·79 (22)
Cl(N)	0	0·3125 (5)	0·9261 (5)	1·85 (12)
Cl(XR)	0	0·281	0·917	–

Discussion

The above analysis yielded precise structural parameters for anhydrous UCl_4. The structure found by Mooney (1949) was confirmed, but the neutron diffraction revealed an error of 0·27 Å in the X-ray chlorine location, 50 × the r.m.s. error in the neutron chlorine position (0·0055 Å). With the improved chlorine position there is no longer a large discrepancy in the two sets of U–Cl bond lengths; the difference is now 0·231 ± 0·005 Å and is significant (Table 2).

Table 2. *Interatomic distances and angles in anhydrous* UCl_4 *as found by neutron diffraction*

U–Cl	2·869 (3) Å
U–Cl	2·638 (4)
Cl–U–Cl	69·4 (2)°
Cl–U–Cl	65·3 (2)
Cl–Cl	3·141 (8) Å
Cl–Cl	3·097 (8)
Cl–Cl	3·540 (1)

Recently, Mucker, Smith, Johnson & Elson (1969) carried out a single-crystal X-ray study of $ThCl_4$. The two sets of Th–Cl bonds were found to be $d_A=2{\cdot}903$ (7) Å and $d_B=2{\cdot}718$ (8) Å.

Hoard & Silverton (1963) have pointed out that the $\bar{4}2m$ dodecahedron is characterized by the parameters d_A, d_B and the angles θ_A and θ_B which these bonds make with the $\bar{4}$ axis. For the 'hard sphere' idealized case, $d_A=d_B$ and $\theta_A=36{\cdot}9°$ and $\theta_B=69{\cdot}5°$. For the 'most favourable' configuration, where mutual repulsions between ligands in a discrete dodedahedron are minimized,

$d_A/d_B=1{\cdot}05$ (Hoard, Silverton & Silverton, 1968),
$\theta_A=35{\cdot}2$ and $\theta_B=73{\cdot}5°$.

The parameters d_A/d_B, θ_A and θ_B approach the 'most favourable' values, being 1·068, 33·1° and 78·0° in $ThCl_4$ and 1·088 (2), 32·66 (9)° and 77·94 (7)° in UCl_4.

The above treatment is probably an oversimplification for this structure as the dodecahedra are not discrete and the U arrangement not highly symmetrical.

The smallest Cl–Cl approach in the polyhedron in UCl_4 is 3·097 (8) Å, in agreement with the shortest approach found in UO_2Cl_2, 3·10 (1) Å (Taylor & Wilson, 1973).

The thermal vibration parameters appear to be different with B(U) [0·8 (2) Å^2] being smaller than B(Cl) [1·85 (12) Å^2].

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