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Structure of Tetrakis(acetonitrile)tetrachlorouranium(IV)

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Abstract. $[UCl_4(CH_3CN)_4]$, $M_r = 544{\cdot}05$, monoclinic, $C2/c$, $a = 14{\cdot}677$ (4), $b = 8{\cdot}452$ (2), $c = 13{\cdot}959$ (3) Å, $\beta = 91{\cdot}77$ (2)°, $V = 1731$ (2) Å^3, $Z = 4$, $D_x = 2{\cdot}087$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 9{\cdot}5054$ mm^{-1}, $F(000) = 992$, $T = 295$(1) K, $R = 0{\cdot}052$ for 1224 observed reflections. Molecular symmetry C_2. The U atom is eight-coordinated with dodecahedral geometry. The Cl atoms occupy the dodecahedral *B* sites, U—Cl 2·614 (2) and 2·624 (2) Å, and the acetonitrile N atoms the *A* sites, U—N 2·567 (6) and 2·599 (6) Å. A statistical comparison with an earlier structure determination [Cotton, Marler & Schwotzer (1984). *Acta Cryst.* C**40**, 1186–1188] has been carried out.

Introduction. Since the original analysis of eight-coordinate geometry by Hoard & Silverton (1963), many structures of eight-coordinate complexes have been published. Few examples of complexes containing two distinctly different ligands, of the type M(unidentate ligand X)$_4$(unidentate ligand Y)$_4$, have, however, been investigated. For those complexes in which eight unidentate ligands are bound to a central atom, two stereochemistries are expected: the square antiprism and the triangular dodecahedron. Calculations (Kepert, 1978) suggest that the energy equivalence between the square antiprism and the dodecahedron may be upset, in this case, in favour of the dodecahedron where the ligands may be sorted into the two different coordination sites. Complexes of the actinide metals provide examples in which effects such as π bonding, which may also enhance dodecahedral stability (Orgel, 1960), should be small and hence provide a good test of theoretical predictions. Accordingly we have investigated the structure of the title compound to provide further structural information on this type of complex. After completion of our study, we heard that an earlier X-ray investigation on the same material had been performed at lower temperature (Cotton, Marler & Schwotzer, 1984). The two sets of experimental results have been analysed and the results are discussed below.

Experimental. Complex prepared by the method of Bagnall, Brown & Jones (1966). Single crystal (0·2 × 0·3 × 0·2 mm), suitable for X-ray analysis, obtained at room temperature from acetonitrile solution and sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group established from systematic absences and successful refinement. 2595 reflections collected (θ–2θ scan mode) in range $4 \leq 2\theta \leq 50°$, 2304 considered observed [$I > 1\sigma(I)$, index range h −18/18, k 0/11, l 0/16], averaged to 1515 unique reflections ($R_{\rm int} = 0{\cdot}01$). Three reflections monitored periodically showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors range from 42·78 to 99·56%). Structure solved by direct methods and Fourier techniques; full-matrix least-squares refinement; minimizing $\sum w(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/\mathrm{Lp}$ where A (the ignorance factor) = 0·04 on 1224 independent reflections with $F^2 \geq 3\sigma(F^2)$. Anisotropic thermal parameters for non-H atoms; H atoms in calculated positions, included in final structure-factor

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calculation with $B_{\rm iso} = 4{\cdot}0$ Å^2, $R = 0{\cdot}052$, $wR = 0{\cdot}031$, $S = 1{\cdot}14$, $(\Delta/\sigma)_{\rm max} = 0{\cdot}02$, $\Delta\rho$ in final difference Fourier map within $+1{\cdot}483$ and $-0{\cdot}815$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. The molecular structure, with the numbering system used, is represented in Fig. 1. Table 1* contains final atomic positional parameters for the non-H atoms. Bond distances and angles are listed in Table 2.

The U atom is eight-coordinated. Since it is located on a twofold axis, the coordination polyhedron has C_2 symmetry. Differences in the ligands of necessity result in distortion of the polyhedron. It is thus important to establish certain criteria for identifying exactly the polyhedron and the extent of its distortion from an ideal geometry.

Application of the δ and φ criteria (Porai-Koshits & Aslanov, 1972) shows that the polyhedron shape is dodecahedral with the acetonitrile N atoms in the *A* sites and the Cl atoms in the *B* sites (Table 3). The site preferences in the dodecahedron are very likely determined by a combination of electronic (σ, π) and steric effects; on those grounds the larger and more electronegative Cl atoms are expected, and are observed at the *B* sites (Burdett, Hoffmann & Fay, 1978). In addition Table 3 gives the basic parameter ω of the Lippard & Russ (1968) criterion. The shape parameters are also very close to those predicted for the 'most favourable' dodecahedral polyhedron (Hoard & Silverton, 1963): $\theta_A = 34{\cdot}1$ (1), 33·9 (1)°, predicted 35·2°; $\theta_B = 73{\cdot}18$ (5), 73·51 (5)°, predicted 73·5°.

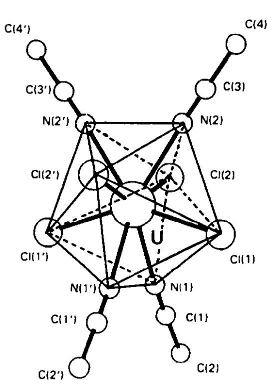

Fig. 1. The molecule $[UCl_4(CH_3CN)_4]$ showing the coordination polyhedron (H atoms are omitted for clarity).

The U—Cl distances (Table 2) average 2·619 (2) Å. In UCl_4 (Taylor & Wilson, 1973) where all Cl atoms are bridging, the structure is again dodecahedral. The two independent U—Cl distances are 2·869 (3) (*A* sites) and 2·638 (4) Å (*B* sites); this latter distance is similar to the distance observed here. The U—N distances (Table 2) can be compared with values of 2·61 (2) and 2·58 (2) Å in $[U(C_5H_5)_3(NCMe)_2]_2[UO_2Cl_4].2C_4H_6$ (Bombieri, Benetollo, Klähne & Fischer, 1983) and 2·41 (2) and 2·68 (2) Å in $U(C_5H_5)_3Cl(NCMe)$ (Fischer, Klähne & Kopf, 1978). As shown in Table 2, ligation to the metal does not seem to affect the

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$B_{\rm eq} = \frac{1}{3}\,{\rm trace}\,\tilde{\mathbf{B}}$.

	x	y	z	$B_{\rm eq}$
U	0·5	0·31789 (5)	0·25	2·981 (6)
Cl(1)	0·5779 (1)	0·2284 (3)	0·0931 (1)	4·61 (4)
Cl(2)	0·3479 (1)	0·4060 (3)	0·1618 (1)	4·85 (4)
N(1)	0·4127 (4)	0·0631 (8)	0·1977 (4)	4·4 (1)
N(2)	0·5475 (4)	0·5699 (8)	0·1619 (4)	4·5 (1)
C(1)	0·3697 (5)	−0·0379 (9)	0·1714 (5)	3·9 (1)
C(2)	0·3117 (6)	−0·166 (1)	0·1347 (7)	6·4 (2)
C(3)	0·5767 (5)	0·6746 (9)	0·1225 (5)	4·0 (1)
C(4)	0·6164 (6)	0·810 (1)	0·0714 (6)	5·4 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

U–Cl(1)	2·614 (2)	N(1)–C(1)	1·117 (8)
U–Cl(2)	2·624 (2)	C(1)–C(2)	1·46 (1)
U–N(1)	2·599 (6)	N(2)–C(3)	1·133 (8)
U–N(2)	2·567 (6)	C(3)–C(4)	1·47 (1)
Cl(1)–U–Cl(1')	146·35 (9)	Cl(1)–U–N(2)	72·9 (1)
Cl(1)–U–Cl(2)	94·39 (6)	Cl(1)–U–N(2')	140·7 (1)
Cl(1)–U–Cl(2')	95·04 (6)	Cl(2)–U–N(1)	72·4 (1)
Cl(2)–U–Cl(2')	147·02 (9)	Cl(2)–U–N(1')	140·6 (1)
N(1)–U–N(1')	68·1 (3)	Cl(2)–U–N(2)	77·3 (1)
N(1)–U–N(2)	133·8 (2)	Cl(2)–U–N(2')	75·5 (1)
N(1)–U–N(2')	133·1 (2)	U–N(1)–C(1)	173·9 (6)
N(2)–U–N(2')	67·9 (3)	N(1)–C(1)–C(2)	178·0 (8)
Cl(1)–U–N(1)	75·5 (1)	U–N(2)–C(3)	173·3 (6)
Cl(1)–U–N(1')	76·8 (1)	N(2)–C(3)–C(4)	179·0 (8)

The primes designate atoms related to the original atoms by the twofold axis at $x = \frac{1}{2}$, $z = \frac{1}{4}$.

Table 3. *Dihedral δ and φ angles* (°)

Points through which the planes were calculated*	Type of angle	Ideal dodecahedron	U coordination polyhedron (this work)
[N(2),Cl(2),Cl(1)] and [N(1),Cl(2),Cl(1)]	$\delta_1 = \delta_2$	29·5	35·8
[N(2),Cl(2'),Cl(1)] and [N(1'),Cl(2'),Cl(1)]	$\delta_3 = \delta_4$	29·5	34·8
[N(2),N(2'),[Cl(1)+Cl(1')]/2] and [Cl(1),Cl(1'),[N(2)+N(2')]/2]	φ_1	0	1·9
[N(1),N(1'),[Cl(2)+Cl(2')]/2] and [Cl(2),Cl(2'),[N(1)+N(1')]/2]	φ_2	0	0·8
[Cl(1),N(2),N(2'),Cl(1')] and [Cl(2),N(1),N(1'),Cl(2')]	ω	90	90·1

* An expression of the type [Cl(1)+Cl(1')]/2 designates the point halfway between atoms Cl(1) and Cl(1').

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* Lists of structure amplitudes, anisotropic thermal parameters, intermolecular short contacts and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43119 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

geometry of the acetonitrile molecule (Barrow, 1981; Karakida, Fukuyama & Kuchitsu, 1974).

The difference between the mean U—Cl and U—N bond lengths is 0·20 Å lower than the difference between the appropriate bond radii of Cl and N (Pauling, 1960), again providing evidence that in the dodecahedron *M—A* type bonds tend to be the weaker.

The stacking in the crystal is through van der Waals contacts with possible C—H···Cl hydrogen bonds (details deposited).

The main differences between the two crystal structure determinations [*A* = Cotton *et al.* (1984), *B* = this work] are in the diffractometer measurements. In the cell-parameter determination 15 reflections in the range $15 \le 2\theta \le 28°$ are used in *A* and 25 reflections in the range $13 \le 2\theta \le 35°$ in *B*. This fact, the different sample size, the centring of the crystal and the specimen temperature (278 and 295 K respectively) lead to cell parameters $a = 14·709$ (4), $b = 8·459$ (3), $c = 13·938$ (4) Å, $\beta = 91·79$ (2)° for *A* and $a = 14·677$ (4), $b = 8·452$ (2), $c = 13·959$ (3) Å, $\beta = 91·77$ (2)° for *B*, showing the typical underestimation of standard deviations in cell parameters. The ranges of intensity data collected are the same, $4 \le 2\theta \le 50°$, but *h*0/17, *k*0/11, *l*−17/17 for *A* and *h*−18/18, *k*0/11, *l* 0/16 for *B*, and the number of independent reflections used in the refinements are 1051 and 1224 respectively. The ratios of number of reflections/number of parameters are 12·98 and 15·11. The final *R* and *wR* values are 0·040, 0·049 for *A* and 0·052, 0·031 for *B*. A half-normal probability-plot comparison (Abrahams & Keve, 1971) of non-hydrogen parameters shows that only one, the *y* coordinate of the U atom, deviates by $>2·5\ (\sigma_1^2 + \sigma_2^2)^{1/2}$, σ_i being the e.s.d. in the coordinates for each structure; slope 1·8 (1) and intercept −0·1 (1) (the large slope, however, indicating that the standard deviations are significantly underestimated). A χ^2 test shows that the two structure determinations are in good agreement if the *y* coordinate of the U atom is neglected; indeed $\chi^2 = \sum(\Delta/\sigma)^2 = 44·27$ and $\chi^2(25)_{0.995} = 46·93$ (Coppens *et al.* 1984; Hamilton, 1964). A half-normal probability plot of the differences in 72 non-hydrogen interatomic lengths gives a straight line with a slope of 1·22 (1) [intercept 0·09 (1)] (De Camp, 1973). Only the distance Cl(1)···Cl(2′) 3·878 (6) Å [*A*], 3·858 (2) Å [*B*] deviates by greater than $3 \times (\sigma_1^2 + \sigma_2^2)^{1/2}$.

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Bis[1,2-bis(dimethylamino)ethane]tetrachlorouranium(IV)

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Abstract. $[UCl_4\{(CH_3)_2NCH_2CH_2N(CH_3)_2\}_2]$, $M_r = 612·26$, orthorhombic, $P2_12_12_1$, $a = 13·094$ (4), $b = 13·265$ (4), $c = 12·633$ (4) Å, $V = 2194$ Å^3, $Z = 4$, $D_x = 1·853$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $\mu = 74·9$ cm^{-1}, $F(000) = 1168$, $T = 296$ K, $R = 0·041$ for 2617 unique reflections with $F^2 > 2\sigma(F^2)$. The uranium

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