Structure and Stereochemistry in *f*-Block Complexes of High Co-ordination Number. Part 1. The [M(unidentate ligand X)-(unidentate ligand Y)$_7$] System: Crystal Structure* of Bis[chloroheptakis(dimethylformamide)uranium(IV)] Tris[tetrachlorodioxouranate(VI)]

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A reaction product of uranium tetrachloride and dimethylformamide (dmf) from acetone solution has been studied crystallographically and shown to have the stoicheiometry $[U^{IV}Cl(dmf)_7]_2[U^{VI}O_2Cl_4]_3$; for the 4 295 ' observed ' *X*-ray diffraction data at 295 K the final residual was 0.046. Crystals are *monoclinic*, space group $P2_1/n$, with a = 14.132(4), b = 26.160(6), c = 12.092(2) Å, β = 97.83(2)°, and Z = 2. The asymmetric unit comprises one cation, one full anion, and one half-anion, the uranium of which lies on a crystallographic inversion centre. Within the anions, the stereochemistry about the uranium atoms is pseudo-octahedral, U=O ranging from 1.73(1) to 1.77(1) Å while U–Cl lie between 2.650(7) and 2.672(5) Å. The uranium of the cation is eight-co-ordinated by the chloride [U–Cl 2.665(5) Å] and seven dimethylformamide ligands [U–O 2.30(1)—2.40(1) Å]. The stereochemistry is dodecahedral with the chloride in one of the ' B ' sites, as expected from repulsion-energy calculations.

For transition-metal and other complexes a considerable array of experimentally determined geometrical data has been accumulated which generally lends itself to ready interpretation by simple stereochemical models based on electron-pair repulsion theory.[1] Much less data are available for the large lanthanoid and actinoid ions where high co-ordination numbers and hitherto uncharacterised stereochemistries may be expected.

In the present paper we describe the single-crystal structure determination of the dimethyl formamide complex $[U^{IV}Cl(dmf)_7]_2[U^{VI}O_2Cl_4]_3$, isolated by recrystallising uranium tetrachloride from dimethylformamide–acetone solution.

Experimental

Previous reports of reactions of uranium tetrachloride with dimethylformamide have been recorded,[2] yielding complexes with stoicheiometry indicative of the presence of possibly unusual co-ordination, such as $UCl_4 \cdot 2.5dmf$.

In the preparation of the present material, dimethylformamide (1 cm^3, 13 mmol) was added dropwise with stirring to a solution of uranium tetrachloride (0.3 g, 0.8 mmol) in acetone (30 cm^3). A pale green solid precipitated immediately; but after allowing the mixture to stand for 2 d dark green crystals appeared, and after 2 weeks the whole of the solid product comprised dark green crystals which were filtered off. All operations were carried out under nitrogen, the specimen for the *X*-ray analysis being mounted in a capillary. Crystals may also be obtained using a much more dilute solution of uranium tetrachloride (*ca.* 0.1 g, 50 cm^3) and a stoicheiometric amount of dimethylformamide. No initial powder is formed, and crystals appear hours or days later with lower yield.

Crystallography.—We give first a general summary of the general procedure adopted for the crystallographic work in this and the following papers.

Each of the samples was examined photographically to ascertain approximate cell dimensions, probable space groups, and probable extent of data prior to mounting on the diffractometer; for data collection, Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers equipped with graphite single-crystal monochromatised molybdenum radiation sources were used for data acquisition and cell determination, T being 295(1) K and λ being presumed to be 0.7106$_9$ Å. Unique data sets were measured within a preset maximum 2θ limit using a conventional 2θ—θ scan mode. N Independent intensities were measured, N_o of these with $I > 3\sigma(I)$ being considered ' observed ' and used in the refinement after solution of the structure by the heavy-atom method. Where possible, an analytical absorption correction was applied to the data.

In refining the structures, block-diagonal least-squares methods were used, with parameters of discrete moieties (*e.g.* phenyl rings) refined in single blocks. In nearly all structures the non-hydrogen atoms were refined with anisotropic thermal parameters according to the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$; where the precision did not justify this, or where the particular atom was ill defined because of partial occupancy or disorder, the corresponding isotropic form was used. In the more precise structures, hydrogen-atom parameters (x,y,z,U) were included at calculated positions as invariants at idealised trigonal or tetrahedral locations. Estimates of U_H were 1.50 $\langle U_{ii}$ (parent C)$\rangle$ for terminal methyl hydrogen atoms and 1.25 $\langle U_{ii}$(parent C, N, O)$\rangle$ for the others. The function minimised in the least squares was $\sigma w(\Delta|F|)^2$, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. At convergence in all cases parameter shifts were $<0.2\sigma$; in the more precise structures, considerably better (0.01σ). Residuals quoted are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = \Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2$. Neutral-atom scattering factors were used throughout, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[3] Computation was carried out using the *X*-RAY 76 program system,[4] implemented by S. R. Hall on a Perkin-Elmer 3 240 computer.

Non-hydrogen-atom numbering systems for each ligand (or sub-section thereof) are given in each paper; where distinction between more than one ligand or section is required, the ligand number precedes the atom number. Hydrogen-atom numbers follow those of the parent atom, suffixed A,B,C, as needful for distinguishing purposes. Sample densities were determined where possible by neutral buoyancy. Any abnormal features associated with each individual structure, *e.g.* disorder, decomposition, use of capillary, refinement abnormalities, ex-

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* *Supplementary data available* (No. SUP 23431, 25 pp.): thermal parameters, ligand geometries, least-squares planes, structure factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

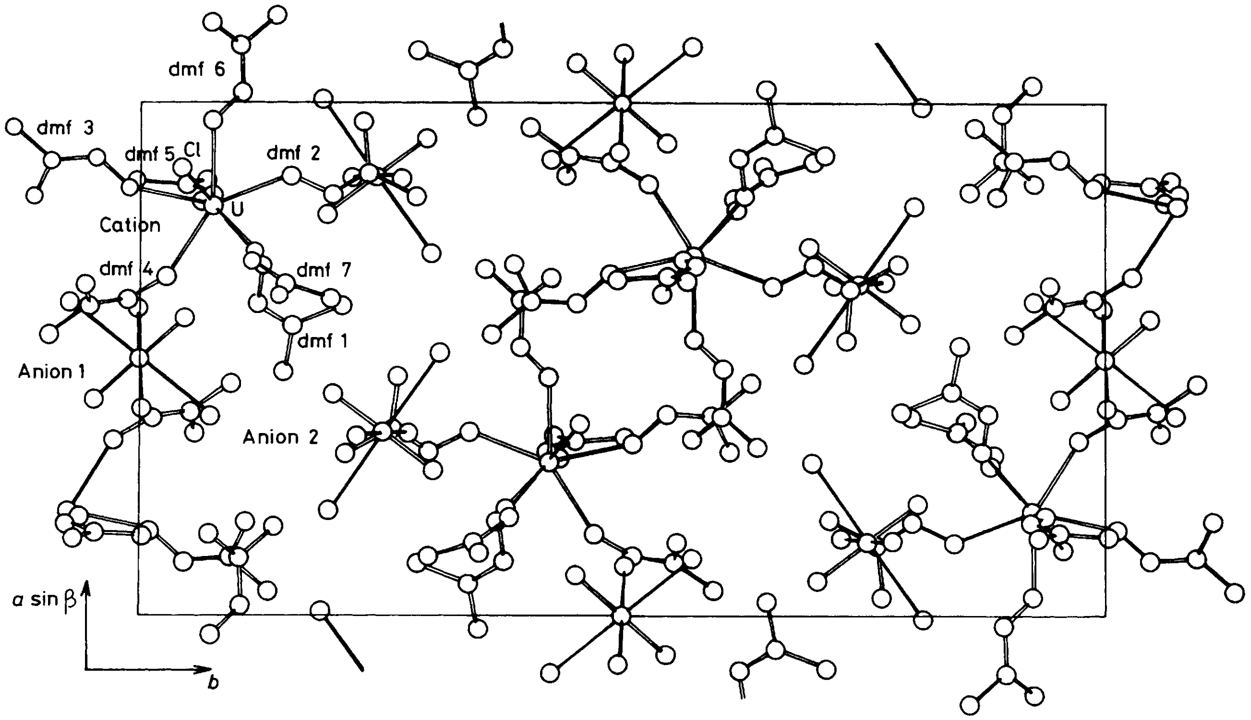

Figure 1. Unit-cell contents of the complex projected down *c*, showing non-hydrogen atoms, and ligand labelling

tinction, or final-difference-map irregularities, are noted where appropriate. Thermal ellipsoids, where shown in the diagrams, are given at the 20% probability level; associated hydrogen atoms where shown have an arbitrary radius of 0.1 Å. Any least-squares planes are given in the form $pX + qY + rZ = s$ where the right-handed orthogonal Å frame (X,Y,Z) has X parallel to a and Z in the ac plane.

Specific crystal data. $C_{42}H_{98}Cl_8N_{14}O_{20}U_5$, $M = 2\,805.8$, Monoclinic, space group $P2_1/n$ (variant of $P2_1/c$, C^5_{2h}, no. 14), $a = 14.132(4)$, $b = 26.160(6)$, $c = 12.092(2)$ Å, $\beta = 97.83(2)°$, $U = 4\,430(2)$ Å^3, $Z = 2$, $D_c = 2.10$ g cm^{-3}, $F(000) = 2\,612$, $\mu_{Mo} = 92$ cm^{-1}, wedge dimensions 0.30 × 0.30 × 0.38 mm, $2\theta_{max.} = 50°$, $N = 7\,873$, $N_o = 4\,295$, $R = 0.046$, $R' = 0.051$.

Abnormal features. The crystal was mounted in a capillary. Hydrogen atoms could not be located in difference maps and were ignored in the refinement.

Discussion

The structure determination establishes the stoicheiometry of the complex to be $[U^{IV}Cl(dmf)_7]_2[U^{VI}O_2Cl_4]_3$ (see Figures 1 and 2, and Tables 1 and 2). The valence states of the uranium atoms in the cation and anion are assigned respectively as IV and VI on the grounds of chemical reasonableness, and on the basis of the observed geometries.

The unit cell contains two of the above formula units, so that the asymmetric unit is one-half of the formula unit; it comprises one cation with no crystallographically imposed symmetry, one anion with no crystallographically imposed symmetry but, nevertheless, approximating closely to D_{4h} internal point symmetry, and one half-anion, of the same stoicheiometry and atomic disposition, which lies with the uranium located on a crystallographic inversion centre.

Both of the independent anions are *trans*-tetrachlorodioxouranate(VI), $[U^{VI}O_2Cl_4]^{2-}$. Deviations of the angular geometry from orthogonality in the six-co-ordinate environment of the uranium are negligible. The independent uranium–oxygen distances are 1.77(1), 1.77(1), and 1.73(1) Å, in good agreement with the many previously established values for the uranyl species. The difference between the values appears to be a consequence of experimental error as there appear to be no

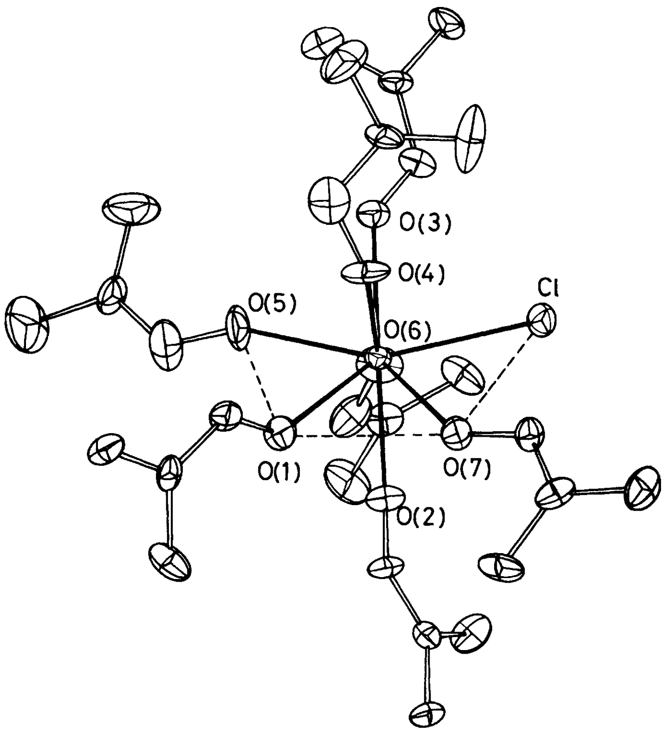

Figure 2. The cation of the complex; 20% thermal ellipsoids are shown for the non-hydrogen atoms

Table 1. Atomic co-ordinates for the complex $[UCl(dmf)_7]_2[UO_2Cl_4]_3$

Atom	*x*	*y*	*z*
Cation			
U	0.798 41(4)	0.074 99(2)	0.141 65(5)
Cl	0.872 2(3)	0.043 1(2)	−0.037 7(4)
Ligand 1			
O	0.682 7(8)	0.127 4(4)	0.209 0(10)
C	0.606 6(13)	0.121 6(6)	0.248 0(15)
N	0.563 3(10)	0.158 8(6)	0.296 3(10)
C(A)	0.603 0(13)	0.211 1(8)	0.303 5(18)
C(B)	0.472 5(14)	0.149 8(7)	0.341 3(18)
Ligand 2			
O	0.858 2(8)	0.156 7(4)	0.142 5(10)
C	0.819 2(13)	0.199 2(6)	0.116 8(15)
N	0.863 2(10)	0.237 0(5)	0.073 7(10)
C(A)	0.814 9(14)	0.285 7(6)	0.042 9(15)
C(B)	0.964 9(13)	0.231 3(8)	0.061 6(17)
Ligand 3			
O	0.833 8(8)	−0.011 7(4)	0.180 5(9)
C	0.892 6(11)	−0.046 6(7)	0.154 8(14)
N	0.886 3(10)	−0.093 9(5)	0.190 2(11)
C(A)	0.816 9(13)	−0.111 9(7)	0.260 3(17)
C(B)	0.952 6(15)	−0.133 7(7)	0.159 1(15)
Ligand 4			
O	0.659 0(8)	0.027 8(4)	0.104 0(12)
C	0.615 4(16)	−0.012 3(11)	0.140 8(19)
N	0.603 6(10)	−0.053 2(5)	0.070 3(14)
C(A)	0.548 4(18)	−0.094 8(10)	0.107 4(20)
C(B)	0.643 6(24)	−0.057 2(15)	−0.025 2(21)
Ligand 5			
O	0.806 4(10)	0.063 2(5)	0.332 5(10)
C	0.818 6(19)	0.076 4(11)	0.431 3(20)
N	0.839 1(11)	0.048 2(7)	0.517 6(12)
C(A)	0.849 2(27)	0.069 2(12)	0.631 4(21)
C(B)	0.845 9(26)	−0.004 3(10)	0.505 1(24)
Ligand 6			
O	0.963 9(9)	0.074 8(5)	0.213 3(11)
C	1.020 6(17)	0.105 5(9)	0.270 2(18)
N	1.112 7(10)	0.103 3(6)	0.266 3(13)
C(A)	1.157 9(21)	0.072 6(9)	0.189 6(22)
C(B)	1.173 4(18)	0.140 5(9)	0.337 1(19)
Ligand 7			
O	0.708 5(8)	0.118 9(4)	−0.011 8(9)
C	0.690 6(12)	0.116 5(7)	−0.116 8(14)
N	0.643 3(10)	0.152 0(6)	−0.178 7(12)
C(A)	0.623 2(15)	0.145 9(8)	−0.304 0(15)
C(B)	0.616 2(15)	0.199 3(7)	−0.128 4(19)
Anion 1			
U	0.500 00(—)	0.000 00(—)	0.500 00(—)
O	0.579 0(8)	0.047 0(5)	0.461 5(9)
Cl(A)	0.402 8(4)	0.002 7(2)	0.294 5(4)
Cl(B)	0.388 3(4)	0.073 1(2)	0.565 7(4)
Anion 2			
U	0.355 71(4)	0.254 27(2)	0.049 87(5)
O(A)	0.430 6(10)	0.201 3(5)	0.088 6(10)
O(B)	0.282 5(10)	0.306 2(4)	0.010 7(10)
Cl(A)	0.350 3(4)	0.227 0(2)	−0.162 2(4)
Cl(B)	0.355 4(3)	0.279 9(2)	0.262 8(4)
Cl(C)	0.508 7(5)	0.311 7(3)	0.036 8(5)
Cl(D)	0.203 2(4)	0.196 8(3)	0.062 5(6)

Table 2. Uranium environments. In each matrix *r* is the uranium–ligand distance (Å). The other entries are the angles (°) subtended at the uranium by the relevant atoms

(*i*) Cation

	r	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
Cl	2.665(5)	145.9(3)	96.4(3)	76.4(3)	95.1(4)	142.9(4)	79.8(4)	75.2(3)
O(1)	2.36(1)		74.3(4)	128.9(4)	76.6(4)	71.1(5)	124.5(4)	70.7(4)
O(2)	2.30(1)			145.7(4)	143.1(4)	98.7(5)	70.0(4)	73.3(4)
O(3)	2.36(1)				71.2(4)	72.1(4)	75.8(4)	133.8(4)
O(4)	2.32(1)					92.8(5)	146.8(4)	75.9(4)
O(5)	2.32(1)						74.0(5)	141.7(5)
O(6)	2.38(1)							132.4(4)
O(7)	2.40(1)							

(*ii*) Anion 1 (independent geometry only)

	r	Cl(1)	Cl(2)
O	1.77(1)	90.0(4)	90.0(4)
Cl(A)	2.672(5)		90.4(2)
Cl(B)	2.669(5)		

(*iii*) Anion 2

	r	O(B)	Cl(A)	Cl(B)	Cl(C)	Cl(D)
O(A)	1.77(1)	179.5(11)	89.0(4)	91.2(4)	89.7(5)	90.2(5)
O(B)	1.73(1)		90.5(4)	89.3(4)	90.0(5)	90.0(5)
Cl(A)	2.652(5)			178.0(3)	90.6(2)	89.2(2)
Cl(B)	2.661(4)				91.3(2)	88.8(2)
Cl(C)	2.654(7)					179.9(2)
Cl(D)	2.650(7)					

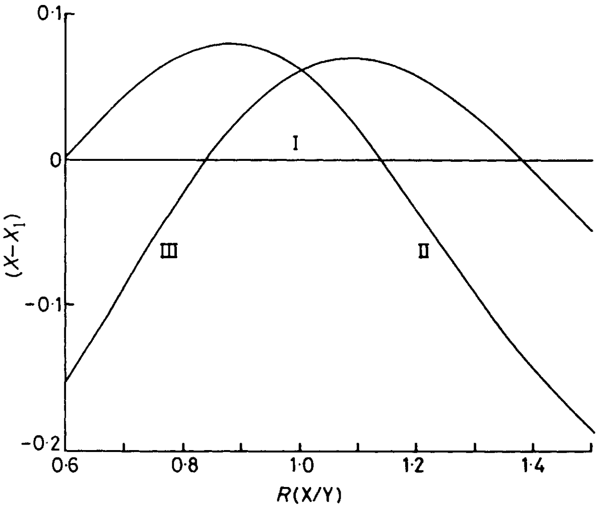

Figure 3. Repulsion-energy coefficients, X, of isomers I—III relative to that of isomer I, for [M(unidentate ligand X)(unidentate ligand Y)$_7$], as a function of bond-length ratio R(X/Y)

close contacts to the uranyl oxygen atoms. The $[\mathrm{U^{VI}O_2Cl_4}]^{2-}$ ion is well studied structurally [5] and values reported for U=O range from 1.65(1) [5c] to 1.79(1) Å [5d] with the bulk of the observed values lying in the range 1.75—1.79 Å. $\mathrm{U^{VI}}$–Cl in the present determination ranges from 2.650(7) to 2.672(5) Å, while other values reported for $[\mathrm{U^{VI}O_2Cl_4}]^{2-}$ species range from 2.646(4) [5a] to 2.706(4) Å.[5d]

In the cation, the uranium atom is eight-co-ordinated by a chlorine atom [U–Cl 2.665(5) Å] and seven oxygen atoms from independent unidentate dimethylformamide ligands [U–O 2.30(1)—2.40(1) Å]; the geometry of the ligands is unremarkable at their low level of precision and will not be further discussed. In the context of the high co-ordination number and the $\mathrm{U^{IV}}$ oxidation state, the U–Cl distance seems unusually short, *cf.* U–Cl 2.813(4) Å in the seven-co-ordinate [6] $[\mathrm{U^{IV}Cl(OPMe_3)_6}]^{3+}$ and 2.70(2) Å in eight-co-ordinate $[\mathrm{U^{IV}Cl_2(OSMe_2)_6}]^{2+}$,[7] although the distance is common enough in six-co-ordinate uranium(IV).[8] The mean U–O distance of 2.35 Å is a familiar one among the eight-co-ordinate derivatives of $\mathrm{U^{IV}}$ with oxygen σ-donor ligands hitherto studied.[9]

The stereochemistry of the cation corresponds to a dodecahedron: the defining trapezoids are O(1,5,7)Cl (deviations from a least-squares plane: 0.02, −0.01, −0.02, and 0.01 Å) and O(2,3,4,6) (deviations: −0.02, −0.03, 0.02, and 0.03 Å). The chlorine lies at a dodecahedral ' B ' site.[1,10]

For the system [M(unidentate ligand)$_8$], repulsion-energy calculations show that the square antiprism is the most stable structure.[1,10] This conclusion is in agreement with the majority of the structurally characterised molecules, although the dodecahedron and intermediate structures have also been observed.[1,10] These calculations are now extended to [M(unidentate ligand X)(unidentate ligand Y)$_7$]. Three isomers were considered, each having an imposed mirror plane. Isomer I is a square antiprism, II a dodecahedron with the unique X atom in an ' A ' site, and III a dodecahedron with the unique atom in a ' B ' site. For each isomer, repulsion-energy coefficients and angular parameters were calculated for effective bond-length ratios R(X/Y) [1,11] in the range 0.6—1.5. The results quoted here were obtained using a value of $n = 6$ in the repulsion law; the results for $n = 1$ and $n = 12$ are very similar.

The relative energies of each isomer are shown in Figure 3. With similar effective bond lengths, $R(\mathrm{X/Y}) \approx 1.0$, the square antiprism, isomer I, is the most stable structure. At low values of R(X/Y) isomer III is stabilised where the unique ligand with the shorter effective bond length occupies one of the sterically less hindered ' B ' sites of the dodecahedron. At high values of R(X/Y) isomer II is the most stable.

The only example of such a system is the cation in $[\mathrm{UCl(dmf)_7}]_2[\mathrm{UO_2Cl_4}]_3$, which is isomer III. The experimental bond angles can be accurately fitted (to $\pm 1°$) against those calculated as a function of R(X/Y) to give $R(\mathrm{Cl^-/dmf}) = 0.7_4$. This is in accord with the values obtained for a large number of transition-metal complexes containing a mixture of both halide and uncharged unidentate ligands.[1,11]

The uranium–oxygen bond lengths to the atoms in the dodecahedron ' A ' sites (2.36, 2.36, 2.38, and 2.40 Å) are longer than those to the ' B ' sites (2.30, 2.32, and 2.32 Å) as expected.[1,10]

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