acetylacetonato ligands (U—O 2·265–2·366 Å) and from two tetrahydrofuran ligands (U—O 2·618 Å). The U—Cl distance is similar to that in $[UCl_3(dmf)_5]^+$ (dmf = dimethylformamide; Charpin, Lance, Nierlich, Vigner & Marquet-Ellis, 1988) with the same coordination number of eight for the U^{IV} oxidation state. The mean U—O(acac) distance of 2·32 (4) Å is usual for eight-coordinate derivatives of U^{IV}, while the U—O(thf) distance of 2·618 (8) Å is longer than that found in $UO_2Cl_2(thf)_2$, 2·48 (5) Å (Charpin, Lance, Nierlich, Vigner & Baudin, 1987). The stereochemistry of the U corresponds to a dodecahedral environment: the defining trapezoids are O(1)—O(2)—O(1^{i})—O(2^{i}), O atoms of the β diketones [deviations from a least-squares plane 0·050 (8), −0·068 (8) Å] and O(3)—Cl—O(3^{i})—Cl^{i} [deviations −0·081 (8), 0·045 (3) Å], the dihedral angle between these two planes being 91·8 (7)°. The diketones are bidentate on two *mm* edges of the dodecahedron (Hoard & Silverton, 1963).

The β diketones have the usual planar geometry [the atoms are within 0·02 (1) Å of the best least-squares plane] and the folding angle along the line O(1)—O(2) is 7 (1)°.

One of the two thf rings, *B*, is planar while ring *A* deviates slightly from a plane [deviations from least-squares plane: *A*: O(3) −0·244 (8), C(11*A*) 0·19 (2), C(12*A*) −0·08 (2), C(13) −0·05 (2), C(14) 0·18 (2); *B*: O(3) −0·030 (8), C(11*B*) 0·04 (4), C(12*B*) −0·03 (4), C(13) 0·01 (2), C(14) 0·01 (2) Å]. The dihedral angle between these two thf conformations is 21 (2)°: they can be considered as the two extreme conformations with maximum and minimum deviations from planarity for *A* and *B*, respectively, and may result from intra- and intermolecular steric requirements, but motion of these molecules cannot be excluded.

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N,N-Dimethylformamide–Uranium Tetrachloride Complex: Structure of Trichloropentakis(*N,N*-dimethylformamide)uranium(IV) Hexachlorouranate(IV)

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Abstract. $[U(C_3H_7NO)_5Cl_3]_2[UCl_6]$, M_r = 1870·48, monoclinic, $P2_1/n$, a = 9·313 (6), b = 24·815 (5), c = 13·681 (3) Å, β = 95·65 (4)°, V = 3146 (2) Å^3, Z = 2, D_x = 1·974 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 78·66 cm^{-1}, F(000) = 3520, T = 295 K, R_F = 0·047 for 1181 independent observed reflections. The structure determination establishes the complex stoichiometry to be $2[U^{IV}Cl_3(dmf)_5]^+.[U^{IV}Cl_6]^{2-}$. In the cationic species the U atom is eight coordinated by three Cl atoms [U—Cl 2·67 (1) Å] and five O atoms [U—O 2·37 (6) Å], while in the classical anion the U atom has an octahedral coordination of Cl atoms [U—Cl 2·62 (2) Å].

Introduction. Complexes resulting from the reaction of UCl_4 with *N,N*-dialkylamides of moderate size generally possess the formula UCl_4.2·5*L* [where $L = C_2H_5CON(C_2H_5)_2$ (depa), $C_2H_5CON(CH_3)_2$ (dmpa) (Al-Daher & Bagnall, 1984; Bagnall, Beddoes, Mills & Li, 1982) or $CH_3CON(CH_3)_2$ (dmaa) (Bagnall, Deane, Markin, Robinson & Stewart, 1961)]. However, with smaller amides such as $HCONMe_2$ (dmf), several formulas have been proposed, UCl_4.2·5dmf (Gans & Smith, 1964) or UCl_4.2dmf (du Preez & Koorts, 1973), in the absence of monocrystalline material to determine the crystal structure.

The synthesis followed by a modified crystallization process has allowed us to obtain, from a single crystal, a structure which points to a different stoichiometry.

Experimental. Synthesis identical to that of Gans & Smith (1964): previously distilled dmf added to UCl_4,

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Table 1. *Positional, isotropic (or equivalent isotropic) thermal parameters and their e.s.d.'s*

	x	y	z	B(Å²)
U(2)	0·000	0·000	0·000	3·65 (5)*
Cl(21)	0·190 (1)	0·0251 (5)	0·1444 (8)	6·6 (3)*
Cl(22)	0·082 (1)	0·0815 (5)	−0·1022 (8)	6·0 (3)*
Cl(23)	−0·188 (1)	0·0639 (5)	0·0735 (9)	6·6 (3)*
U(1)	0·3352 (2)	0·14940 (6)	0·5263 (1)	3·13 (3)*
Cl(11)	0·546 (1)	0·0887 (4)	0·4645 (8)	5·6 (3)*
Cl(12)	0·463 (1)	0·2406 (4)	0·4820 (7)	5·1 (3)*
Cl(13)	0·072 (1)	0·1929 (6)	0·493 (1)	7·8 (4)*
O(1)	0·292 (2)	0·201 (1)	0·668 (2)	4·9 (6)
O(2)	0·542 (2)	0·155 (1)	0·652 (2)	5·4 (6)
O(3)	0·196 (3)	0·076 (1)	0·463 (2)	7·2 (8)
O(4)	0·304 (3)	0·090 (1)	0·650 (2)	5·8 (7)
O(5)	0·296 (3)	0·158 (1)	0·354 (2)	6·8 (7)
N(1)	0·272 (3)	0·272 (1)	0·776 (2)	5·4 (8)
N(2)	0·757 (3)	0·174 (1)	0·730 (2)	3·3 (7)
N(3)	0·101 (3)	0·002 (1)	0·392 (2)	5·5 (8)
N(4)	0·411 (3)	0·049 (1)	0·787 (2)	4·1 (7)
N(5)	0·291 (3)	0·158 (2)	0·192 (2)	6·3 (9)
C(11)	0·283 (3)	0·250 (2)	0·682 (3)	4·2 (9)
C(12)	0·277 (4)	0·235 (2)	0·853 (3)	7 (1)
C(13)	0·279 (4)	0·328 (1)	0·789 (3)	5 (1)
C(21)	0·671 (3)	0·171 (1)	0·652 (3)	3·8 (9)
C(22)	0·905 (4)	0·192 (2)	0·730 (3)	7 (1)
C(23)	0·712 (4)	0·164 (2)	0·828 (3)	5 (1)
C(31)	0·212 (4)	0·031 (2)	0·439 (3)	6 (1)
C(32)	−0·028 (4)	0·031 (2)	0·354 (3)	6 (1)
C(33)	0·110 (4)	−0·051 (2)	0·365 (3)	6 (1)
C(41)	0·346 (4)	0·089 (2)	0·736 (3)	5 (1)
C(42)	0·441 (4)	0·001 (2)	0·728 (3)	8 (1)
C(43)	0·454 (4)	0·050 (2)	0·883 (3)	5 (1)
C(51)	0·348 (5)	0·150 (2)	0·282 (3)	8 (1)
C(52)	0·369 (6)	0·156 (3)	0·111 (4)	15 (2)
C(53)	0·152 (6)	0·172 (2)	0·177 (5)	13 (2)

$* B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

Table 2. *Bond distances* (Å) *and bond angles* (°) (*e.s.d.'s in parentheses*) *in uranium environments*

(i) $[UCl_3(dmf)_5]^+$			
U(1)–Cl(11)	2·68 (1)	U(1)–O(2)	2·45 (2)
U(1)–Cl(12)	2·66 (2)	U(1)–O(3)	2·35 (3)
U(1)–Cl(13)	2·68 (1)	U(1)–O(4)	2·29 (3)
U(1)–O(1)	2·40 (3)	U(1)–O(5)	2·36 (3)
Cl(11)–U(1)–Cl(12)	92·8 (3)	Cl(12)–U(1)–Cl(13)	92·4 (4)
Cl(11)–U(1)–Cl(13)	149·5 (4)	Cl(11)–U(1)–O(3)	80·9 (7)
U(1)–O(1)–C(11)	132 (2)	U(1)–O(4)–C(41)	132 (3)
U(1)–O(2)–C(21)	135 (2)	U(1)–O(5)–C(51)	144 (3)
U(1)–O(3)–C(31)	139 (3)		
(ii) $[UCl_6]^{2-}$			
U(2)–Cl(21)	2·59 (2)	Cl(22)–U(2)–Cl(23)	91·2 (4)
U(2)–Cl(22)	2·62 (1)	Cl(22)–U(2)–Cl(21)	90·5 (4)
U(2)–Cl(23)	2·64 (1)	Cl(21)–U(2)–Cl(23)	89·5 (4)

crystal obtained on leaving mixture for several days at 263 K, after the addition of either C_6H_6 or solid UCl_4 to reduce the excess dmf; pale-green crystals manipulated in the absence of air and selected under Nujol; crystal 0·50 × 0·15 × 0·10 mm; Enraf–Nonius CAD-4 diffractometer; unit-cell parameters refined from 25 reflections in range $16 < 2\theta < 24°$; three standard reflections monitored at 100-reflection intervals, loss of 7·1% in 26 h, linearly corrected; scans by $\omega/2\theta$ method; $4 < 2\theta < 50°$; 2450 reflections collected, 2363 unique, 1185 with $I > 3\sigma(I)$; $-8 \leq h \leq 8, 0 \leq k \leq 21, 0 \leq l \leq 11$; Lorentz and polarization corrections; empirical absorption correction based on ψ scans (North, Phillips & Mathews, 1968), minimum transmission coefficient 0·938; structure solved by Patterson method for U, remaining atoms located by difference Fourier technique; full-matrix least-squares refinement on F; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); anisotropic thermal parameters for U and Cl; H atoms introduced at calculated positions (C—H = 0·95 Å, $B = 1·3\,B_C$), not refined but constrained to ride on their C atoms; $R = 0·047$, $wR = 0·057$ ($w = 1$); max (shift/e.s.d.) = 0·04, $S = 5·0$; highest peak in final difference map = 0·9 e Å^{-3} [near U(1)]; program: Enraf–Nonius *Structure Determination Package, SDP-Plus* (Frenz, 1983), PDP 11/23 Plus; figures plotted using *ORTEP*II (Johnson, 1976).

Discussion. Positional parameters and isotropic (or equivalent isotropic) temperature factors are listed in Table 1,* characteristic bond lengths and angles in Table 2.

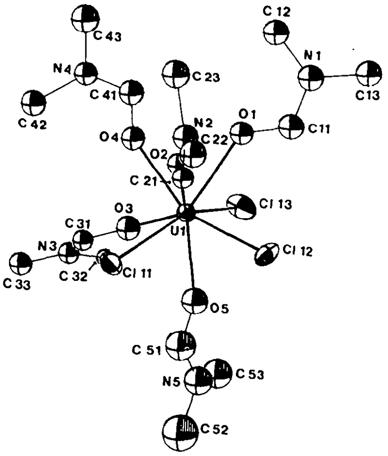

Fig. 1. Drawing of the cation $[UCl_3(dmf)_5]^+$ showing the atom numbering.

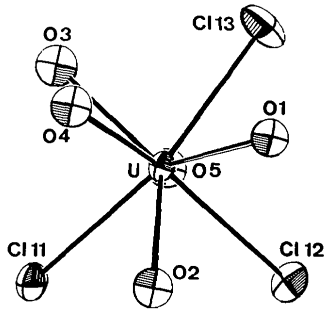

Fig. 2. Coordination geometry of the cation $[UCl_3(dmf)_5]^+$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44488 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The compound $UCl_4.3\cdot3dmf$ is formed by two U^{IV} complex ions $[UCl_3(dmf)_5]^+$ (Fig. 1) and $[UCl_6]^{2-}$. In the cation, the U atom has no imposed crystallographic symmetry while in the anion the U atom lies on an inversion centre. The anion $[UCl_6]^{2-}$ is a nearly regular octahedron, the U—Cl distances ranging from 2·59 (2) to 2·64 (1) Å. The U atom of the cation is eight coordinated by three Cl atoms [U—Cl 2·66 (2)–2·68 (1) Å] and five dmf ligands [U—O 2·29 (3)–2·45 (2) Å]. This eight coordination (Fig. 2) does not fall into the idealized geometries of dodecahedron, bicapped trigonal prism or square antiprism. The three Cl and O(3) atoms are coplanar, plane 1 [deviations of Cl(11), Cl(12), Cl(13) and O(3) from least-squares plane: −0·05 (1), 0·043 (1), −0·05 (1), 0·06 (3) Å respectively] and parallel to the O(1)O(2)O(4) plane (plane 2). The U atom lies at 0·69 (1) Å above plane 1 and 1·78 (2) Å below plane 2; the U—O(5) bond is perpendicular to these planes.

The average U—Cl bond lengths are 2·67 (1) Å in the cation and 2·62 (2) Å in the anion, values which are similar to those reported for $[UCl_3(depa)_4]^+$ [2·65 (3) Å].$[UCl_5(depa)]^-$ [2·58 (3) Å] (Bagnall *et al.*, 1982), $[UCl_3(dcc)]^+$ (dcc = dicyclohexyl-18-crown-6) [2·6512(Å)].UCl_6^{2-} [2·61 (4) Å] (de Villardi, Charpin, Costes, Folcher, Plurien, Rigny & de Rango, 1978): the significantly shorter values in the anion may result from less hindrance around the U atom. The three structures show that $[UCl_3]^+$ is not a rigid cation, its conformation depends on the total U coordination: $[UCl_3]^+$ is planar in $[UCl_3(depa)_4]^+$ with Cl—U—Cl angles 177, 89 and 93° (heptacoordinated U) and in $[UCl_3(dcc)]^+$ with Cl—U—Cl angles 141, 141 and 77° (nonacoordinated U) while in $[UCl_3(dmf)_5]^+$ described here, the U atom is out of the Cl plane with Cl—U—Cl angles of 93, 92 and 149° (octacoordinated U).

The mean U—O distance [2·37 (5) Å] is in good agreement with those found for $2[UCl(dmf)_7]^{3+}$.-$3[UO_2Cl_4]^{2-}$ [2·35 (3) Å: Kepert, Patrick & White (1983)]. However, one dmf ligand seems to be differently attached judging from the U—O—C angle: the value of 144 (3)° for ligand 5, which occupies the apical position in the U coordination sphere, is slightly higher than the mean value of the others, 134 (3)°.

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Structure of Tetrathiafulvalenium Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)aurate(III), (TTF)[Au(DDDT)$_2$]

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Abstract. $[C_6H_4S_4][Au(C_4H_4S_4)_2]$, $M_r = 761\cdot9$, triclinic, $P\bar{1}$, $a = 8\cdot7247$ (8), $b = 9\cdot5089$ (10), $c = 14\cdot7007$ (19) Å, $\alpha = 107\cdot179$ (10), $\beta = 102\cdot372$ (9), $\gamma = 95\cdot934$ (8)°, $V = 1119\cdot8$ (2) Å^3, $Z = 2$, $D_x = 2\cdot26$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71073$ Å) = 7·63 mm^{-1}, $F(000) = 734$, $T = 298$ K, $R(F) = 0\cdot082$ for 2306 observed reflections ($F_o > 2\sigma$). The structure contains two inequivalent, centrosymmetric $[Au(DDDT)_2]^-$ complexes. One of these is located in the same molecular layer as the dimerized TTF^+ cations, whereas the other lies between these layers. The dimerization of the TTF^+ cations and the molecular packing arrangement do not favor high electrical conductivity in the title compound.

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