Table 4. *A comparison of bond lengths* $d(\mathrm{Hg}-X)$, (X = Cl, Br, I) *and* $d(\mathrm{Hg}-L)$ (L = *pyridine, THT, THSe) with the bond angles* X–Hg–X *and* L–Hg–L *in pseudotetrahedral* $\mathrm{Hg}X_2L_2$ *complexes*

Mean values are given for the distances in the solids.

	$d(\mathrm{Hg}-X)$ (Å)	$d(\mathrm{Hg}-L)$ (Å)	$\angle(X-\mathrm{Hg}-X)$ (°)	$\angle(L-\mathrm{Hg}-L)$ (°)
$HgCl_2$ in pyridine[a]	2·375 (10)	2·47 (2)	150	
$HgCl_2(THT)_2$[b]	2·459	2·57	115·4	109·1
$HgBr_2$ in pyridine[a]	2·497 (2)	2·45 (2)	147 (2)	
$[HgBr_2(py)_2]$[c]	2·481	2·39	141·2 (1)	90·7 (7)
$HgBr_2$ in THT[d]	2·535 (6)	2·62	132 (2)	
$[HgBr_2(THT)_2]$[b]	2·553	2·60	117·6 (1)	107·7
$[HgBr_2(THSe)_2]$[e]	2·604 (1)	2·648 (1)	110·06 (4)	114·79 (4)
HgI_2 in pyridine[a]	2·665 (2)	2·43 (2)	141 (2)	
$[HgI_2(py)_2]$[a]	2·666	2·424 (9)	142·7 (1)	93·8 (4)
HgI_2 in THT[d]	2·670 (4)	2·72	143 (2)	
$[HgI_2(THSe)_2]$[e]	2·742	2·703	120·79 (3)	109·62 (4)

References: (*a*) Persson, Sandström, Goggin & Mosset (1985); (*b*) Sandström & Persson (In preparation); (*c*) Canty, Raston, Skelton & White (1982); (*d*) Sandström, Persson & Goggin (1986); (*e*) Present work.

The present compounds consist of discrete molecular complexes of approximate C_{2v} point symmetry with the Hg atoms coordinating two halogens and two THSe Se atoms. In $HgBr_2.2THSe$, the angles Br–Hg–Br and Se–Hg–Se are 110·06 (4) and 114·79 (4)° and the Hg–Se distance is 2·648 (1) Å. Corresponding angles in the iodide are 10·7° wider and 5·2° smaller and the average Hg–Se distance is shortened by 0·05 Å. Distances and angles in similar pseudotetrahedral complexes $\mathrm{Hg}X_2L_2$, with L = THT, THSe and pyridine (py), are listed in Table 4, which also includes complexes found in THT and pyridine solutions. In the solid compounds HgBr_2L_2 a considerable decrease in the Br–Hg–Br angle (141·2 to 110·1°) is, as expected, associated with an increasing Hg–Br bond length (2·481 to 2·604 Å) in the sequence L = py, THT and THSe. The $[HgCl_2(py)_2]$ structure (Canty, Raston, Skelton & White, 1982) is of a different type, with Hg octahedrally coordinated. Crystals of $[HgCl_2THSe]$ and not $[HgCl_2(THSe)_2]$ are obtained from a solution of $HgCl_2$ in excess THSe. In $[HgCl_2THSe)]$ (Stålhandske & Zintl, 1986), the coordination around Hg is a distorted trigonal bipyramid.

Some of the distances and angles in one of the THSe ligands in the $[HgI_2(C_4H_8Se_2)_2]$ molecule deviate from the expected values (Nahlovska, Nahlovsky & Seip, 1970), which might indicate conformational disorder.

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Structure of Dichlorobis(pentane-2,4-dionato)bis(tetrahydrofuran)uranium(IV)

By P. Charpin, M. Nierlich, D. Vigner, M. Lance and C. Baudin

CEA–CEN Saclay, IRDI/DESICP/DPC/SCM, CNRS–UA 331, 91191 *Gif sur Yvette CEDEX, France*

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Abstract. $[U(C_5H_7O_2)_2Cl_2(C_4H_8O)_2]$, $M_r = 655{\cdot}4$, monoclinic, $C2/c$, $a = 14{\cdot}873$ (4), $b = 8{\cdot}728$ (1), $c = 17{\cdot}518$ (3) Å, $\beta = 97{\cdot}62$ (2)°, $V = 2254$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}919$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 7{\cdot}095$ mm^{-1}, $F(000) = 1264$, $T = 295$ K, final $R_F = 0{\cdot}039$ for 1429 unique reflections. The structure is of molecular type: the U atom is eight coordinated by two Cl [U–Cl 2·684 (3) Å] and six O atoms from two bidentate diketonato ligands [U–O 2·265 (8), 2·366 (9) Å] and from two tetrahydrofuran ligands [U–O 2·618 (8) Å]. The stereochemistry of the U atom corresponds to a dodecahedral environment.

Introduction. Recent interest in studies of the high coordination numbers of U^{IV} has turned our attention to the synthesis of compounds such as $[UCl_2(acac)_2L_n]$ (acac ≡ $CH_3COCHCOCH_3$) in the hope of understanding the influence of the nature of the ligand L on

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the ligand-exchange process. The first study concerns the complex $[UCl_2(acac)_2(thf)_2]$ ($thf \equiv OC_4H_8$) which had been prepared (Bagnall, Edwards, Richard & Tempest, 1979), but whose structure was not available.

Experimental. Crystals were obtained from tetrahydrofuran/pentane solution; crystal dimensions $0{\cdot}55 \times 0{\cdot}45 \times 0{\cdot}12$ mm; cell parameters from setting angles of 25 reflections with $8 < \theta < 12°$; Enraf–Nonius CAD-4 diffractometer, graphite monochromator; $\omega/2\theta$ scan mode; sphere up to $\theta = 25°$; $0 \leq h \leq 17$, $-10 \leq k \leq 0$, $20 \leq l \leq 20$; three standard reflections after every hour, decay of 29% in 30 hours, linearly corrected; 3180 reflections measured, 2216 independent, 1429 observed with $I > 3\sigma(I)$; empirical absorption correction using *DIFABS* (Walker & Stuart, 1983), max. and min. transmissions, 1·530–0·723; structure solved by Patterson function and difference Fourier syntheses, refined by full-matrix least squares on F; anisotropic thermal parameters for U, Cl; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974); H atoms introduced at calculated positions for the acac molecules only (C—H = 0·95 Å, $B = 5$ Å^2), not refined but constrained to ride on their C atoms. In the final difference Fourier map, two residual peaks were observed near two C of the thf molecule. These peaks at 0·83 Å from C(11) and 0·68 Å from C(12) cannot be accounted for by anisotropy: thus, alternative positions were introduced in the least-squares refinements with occupation factors fixed from their relative intensities, respectively 0·7 for the main ring (A) and 0·3 for the other ring (B). The two other C atoms of the ring, C(13) and C(14), only have larger thermal parameters [C(13) 5·59, C(14), 6·56 Å^2]; $R = 0{\cdot}039$, $wR = 0{\cdot}047$ ($w = 1$); $(\Delta/\sigma)_{max} = 0{\cdot}01$, $S = 5{\cdot}7$, $\Delta\rho_{max} = 1$ e Å^{-3} in the vicinity of the U atom; calculations carried out on a PDP 11/23 Plus using the *SDP-Plus* suite of programs (Frenz, 1983).

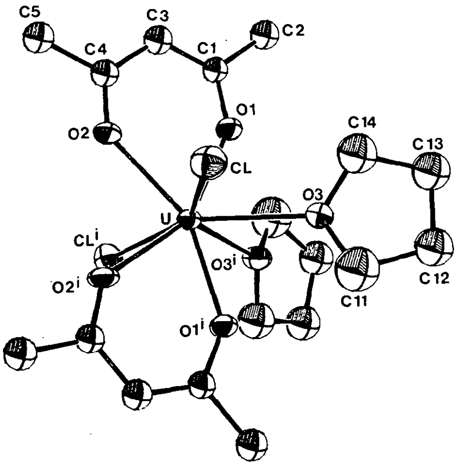

Fig. 1. Drawing of the molecule showing the atomic numbering. Marked atoms (i) are related to the unmarked atoms by the diad axis. For clarity, thf ring B is omitted.

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

	x	y	z	B(Å^2)
U	0·000	0·03872 (8)	0·250	2·41 (1)*
Cl	−0·1512 (2)	−0·0437 (5)	0·1582 (2)	4·47 (7)*
O(1)	0·0645 (5)	0·1332 (9)	0·1498 (4)	3·2 (1)
O(2)	0·0535 (6)	−0·166 (1)	0·1800 (5)	3·7 (2)
O(3)	−0·0877 (5)	0·2891 (9)	0·2038 (4)	3·5 (2)
C(1)	0·0966 (7)	0·087 (1)	0·0879 (6)	3·0 (2)
C(2)	0·1271 (9)	0·214 (2)	0·0395 (7)	4·0 (3)
C(3)	0·1037 (8)	−0·065 (1)	0·0695 (7)	3·5 (2)
C(4)	0·0842 (8)	−0·183 (1)	0·1161 (7)	3·2 (2)
C(5)	0·1054 (9)	−0·348 (2)	0·0951 (8)	4·2 (3)
C(11*A*)	−0·166 (1)	0·355 (2)	0·238 (1)	4·3 (4)
C(11*B*)	−0·117 (3)	0·399 (5)	0·252 (2)	3·0 (7)
C(12*A*)	−0·184 (1)	0·510 (2)	0·200 (1)	4·1 (4)
C(12*B*)	−0·147 (3)	0·535 (6)	0·200 (2)	4·4 (8)
C(13)	−0·144 (1)	0·495 (2)	0·1201 (9)	5·6 (3)
C(14)	−0·104 (1)	0·332 (2)	0·122 (1)	6·6 (4)

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

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Environment of the U atom			
U—Cl	2·684 (3)	Cl—U—Cl^i	148·9 (1)
U—O(1)	2·265 (8)	O(1)—U—O(1)^i	137·3 (3)
U—O(2)	2·366 (9)	O(2)—U—O(2)^i	81·7 (3)
U—O(3)	2·618 (8)	O(3)—U—O(3)^i	66·8 (2)
β Diketone			
O(1)—C(1)	1·304 (14)	O(2)—C(4)	1·272 (15)
C(1)—C(2)	1·51 (2)	C(4)—C(5)	1·52 (2)
C(1)—C(3)	1·37 (2)	C(4)—C(3)	1·38 (2)
O(1)—C(1)—C(2)	114 (1)	O(2)—C(4)—C(5)	116 (1)
O(1)—C(1)—C(3)	123 (1)	O(2)—C(4)—C(3)	124 (1)
C(2)—C(1)—C(3)	123 (1)	C(3)—C(4)—C(5)	120 (1)
C(1)—C(3)—C(4)	124 (1)		
Tetrahydrofuran			
O(3)—C(14)	1·46 (2)	C(13)—C(14)—O(3)	106 (1)
C(14)—C(13)	1·54 (2)		
O(3)—C(11*A*)	1·49 (2)	O(3)—C(11*B*)	1·38 (4)
C(11*A*)—C(12*A*)	1·52 (3)	C(11*B*)—C(12*B*)	1·53 (6)
C(12*A*)—C(13)	1·60 (3)	C(12*B*)—C(13)	1·44 (5)
C(14)—O(3)—C(11*A*)	105 (1)	C(14)—O(3)—C(11*B*)	113 (2)
O(3)—C(11*A*)—C(12*A*)	105 (2)	O(3)—C(11*B*)—C(12*B*)	105 (3)
C(11*A*)—C(12*A*)—C(13)	104 (2)	C(11*B*)—C(12*B*)—C(13)	101 (3)
C(12*A*)—C(13)—C(14)	104 (1)	C(12*B*)—C(13)—C(14)	105 (2)

Discussion. An *ORTEP* drawing (Johnson, 1976) of the molecule is shown in Fig. 1. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.*

The U atom is eight coordinated by two Cl atoms (U—Cl 2·684 Å) and six O atoms from two bidentate

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* Lists of structure factors and anisotropic thermal parameters and a full list of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44445 (14 pp.). Copies may be obtained through The Executive Secretary International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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)

By P. Charpin, M. Lance, M. Nierlich, D. Vigner and H. Marquet-Ellis

CEA-CEN/Saclay IRDI/DESICP/DPC/SCM, UA-CNRS 331, 91191 *Gif sur Yvette CEDEX, France*

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Abstract. $[U(C_3H_7NO)_5Cl_3]_2[UCl_6]$, $M_r = 1870{\cdot}48$, monoclinic, $P2_1/n$, $a = 9{\cdot}313\ (6)$, $b = 24{\cdot}815\ (5)$, $c = 13{\cdot}681\ (3)$ Å, $\beta = 95{\cdot}65\ (4)°$, $V = 3146\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}974$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 78{\cdot}66$ cm^{-1}, $F(000) = 3520$, $T = 295$ K, $R_F = 0{\cdot}047$ 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 $UCl_4.2{\cdot}5L$ [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, $UCl_4.2{\cdot}5$dmf (Gans & Smith, 1964) or $UCl_4.2$dmf (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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