Seven-co-ordination in Chlorohexakis(trimethylphosphine oxide)-uranium(IV) Trichloride: Crystal and Molecular Structure

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The structure of the title compound has been determined by single-crystal *X*-ray diffraction methods from diffractometer data and refined to a final *R* of 0.023. The compound crystallises in space group $R\bar{3}c$ with a_{hex} = 18.447(3), c_{hex} = 19.348(3) Å, *Z* = 6. The uranium atom is co-ordinated to one chlorine (U–Cl 2.813 Å) and six oxygen atoms (mean U–O 2.26 Å); the co-ordination polyhedron can be described as a distorted monocapped trigonal antiprism or as a distorted monocapped octahedron. The anionic chlorines are more than 6.22 Å from the uranium atoms. The results are discussed in relation to spectral data for this and related uranium(IV) complexes.

ALTHOUGH a large number of actinide tetrachloride complexes with oxygen and nitrogen donor ligands have been reported [1-3] with compositions ranging from $MCl_4\cdot 2L$ to $MCl_4\cdot 7L$ (M = Th to Pu inclusive; L = oxygen or nitrogen donor ligand) structural data are available only for the octahedral complexes $UCl_4\cdot 2$tppo (tppo = triphenylphosphine oxide),[4] $UCl_4\cdot 2$hmpa (hmpa = hexamethylphosphoramide),[5] and for $ThCl_4\cdot 5$dmso (ref. 6) and $UCl_4\cdot 3$dmso (ref. 7) (dmso = dimethyl sulphoxide), which were recently shown to crystallise as $[Th(dmso)_5Cl_3]^+Cl^-$ and $[UCl_2(dmso)_6]^{2+}[UCl_6]^{2-}$, respectively. Solid-state spectral data are known [8] to be of little value for identifying the stereochemistry of uranium(IV) compounds apart from those which are octahedral, and the structural results for $UCl_4\cdot 3$dmso suggest that conductivity measurements [9] give little indication of the species present in non-aqueous media. As part of an investigation of the structures and spectral properties of a selected range of actinide-(IV) and -(V) complexes we now report the structure of $UCl_4\cdot 6$tmpo (tmpo = trimethylphosphine oxide) and, on the basis of solid-state and solution spectra, discuss the species present in non-aqueous media.

EXPERIMENTAL

$UCl_4\cdot 6$tmpo was prepared as described previously [10] and recrystallised from anhydrous methyl cyanide. It decomposes rapidly in air and crystals were therefore mounted in thin-walled Lindemann glass capillaries for data collection. Solid-state spectra were recorded as described previously.[11]

Crystal Data.—$C_{18}H_{54}Cl_4O_6P_6U$, *M* = 932.3, green rectangular prisms, Trigonal, a_{hex} = 18.447(3), c_{hex} = 19.348(3) Å, *U* = 5 701.9 Å^3, D_c = 1.63, *Z* = 6, D_m = 1.6 g cm^{-3} (flotation), *F*(000) = 2 760. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 59 cm^{-1}. Space group $R\bar{3}c$.

Structure Determination.—Lattice parameters and *X*-ray intensities were obtained by use of an automatic computer-controlled four-circle diffractometer (Philips PW 1100) and graphite-monochromated Mo-K_α radiation. 1 204 Independent reflections with $h > 0$, $k \geqslant 0$, $l \geqslant 0$ were collected between θ 3 and 25° by the θ—2θ scan method (scan width 1.2°, scan speed 1.2° min^{-1}, two 30 s background counts). Three check reflections, which were measured periodically, showed no detectable deterioration of the crystal during data collection.

The intensities were corrected for Lorentz and polarisation effects but not for absorption (crystal dimensions, *ca.* 0.04 × 0.04 × 0.08 mm). The longest edge of the crystal was parallel to the crystallographic *c* axis. 877 Reflections having net intensities $>3\sigma(I)$ were considered observed [$\sigma(I)$ based on counting statistics] and the refinement was based on these reflections with the addition of 143 unobserved reflections having calculated structure factors greater than the threshold value.

The structure was resolved by the standard heavy-atom method and refined by a full-matrix least-squares procedure using unit weight factors and minimising $\Sigma|(|F_o| - |F_c|)|^2$. Anisotropic thermal parameters were employed for all non-hydrogen atoms. The *z* co-ordinate of the uranium atom was held constant to define the origin along the *z* axis. The atomic scattering factors of ref. 12 were used, and the anomalous dispersion correction [13] applied to the uranium atom ($\Delta f'$, $\Delta f''$). Programmes used were those of the '*X*-Ray '70' package.[14]

Refinement of non-hydrogen atoms was terminated with a final conventional *R* value of 0.023 for the observed reflections when all parameter shifts were $<0.1\sigma$. Attempts to locate hydrogen atoms were unsuccessful, only a random distribution of positive and negative residuals (all <0.6 Å^{-3}) being observed on the final difference-Fourier map.

Final atomic co-ordinates and thermal parameters are listed in Table 1 with their standard deviations. Observed and calculated structure factors are contained in Supplementary Publication No. SUP 21635 (3 pp., 1 microfiche).†

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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TABLE 1

Fractional co-ordinates and anisotropic * temperature factors (× 10^4), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	0	0	1 000	257(2)	257(2)	203(2)	128	0	0
Cl(1)	0	0	2 454(2)	585(20)	585(20)	310(25)	292	0	0
Cl(2)	311(2)	3 362(3)	37(2)	701(27)	686(24)	605(24)	116(23)	93(22)	68(20)
P(1)	−1 672(2)	−260(2)	−168(2)	416(19)	462(19)	415(17)	227(16)	−156(16)	−50(16)
P(2)	2 023(2)	594(2)	1 787(2)	363(18)	478(20)	388(17)	192(16)	−121(15)	−84(15)
O(1)	−1 067(6)	−412(6)	249(5)	542(54)	488(56)	598(57)	285(46)	−324(49)	−130(48)
O(2)	1 373(5)	599(6)	1 295(4)	336(42)	661(63)	358(43)	179(44)	−84(37)	13(44)
C(1)	−1 897(12)	−824(13)	−958(8)	1 060(145)	1 223(168)	379(79)	774(135)	−320(92)	−279(96)
C(2)	−2 640(11)	−620(14)	306(10)	564(106)	1 190(171)	922(133)	492(113)	69(102)	9(123)
C(3)	−1 254(11)	817(10)	−359(10)	758(116)	513(93)	939(123)	272(90)	−259(98)	142(87)
C(4)	2 996(10)	993(12)	1 366(10)	421(85)	1 090(146)	750(106)	344(94)	−42(82)	−92(103)
C(5)	2 171(10)	1 227(11)	2 540(8)	607(94)	842(124)	600(91)	366(90)	−347(85)	−242(90)
C(6)	1 689(12)	−468(10)	2 065(8)	969(133)	528(94)	764(110)	433(97)	−295(101)	21(84)

* In the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

RESULTS AND DISCUSSION

Description of the Structure.—Selected bond lengths and angles are listed in Table 2. The codes for symmetry related atoms are: I $-y, x-y, z$; II $y-x, -x, z$; III $-y, -x, \frac{1}{2}+z$; IV $x, x-y, \frac{1}{2}+z$; V $y-x, y, \frac{1}{2}+z$; VI $\frac{1}{3}+y-x, \frac{2}{3}-x, -\frac{1}{3}+z$; VII $\frac{1}{3}+x, \frac{2}{3}+x-y, \frac{1}{6}+z$; VIII $-\frac{1}{3}+y-x, \frac{1}{3}+y, -\frac{1}{6}+z$.

The structure consists of $[UCl(tmpo)_6]^{3+}$ units having crystallographic three-fold symmetry with the uranium and chlorine atoms lying on the axis, and three ionic chlorine atoms. The asymmetric unit is composed of one third of the cation and one anionic chlorine.

TABLE 2

Bond distances (Å) and bond angles (°) with their estimated standard deviations in parentheses

(*a*) Distances			
U–Cl(1)	2.813(4)	P(1)–C(2)	1.81(2)
U–O(1)	2.25(1)	P(1)–C(3)	1.77(2)
U–O(2)	2.27(1)	P(2)–C(4)	1.76(2)
O(1)–P(1)	1.51(1)	P(2)–C(5)	1.80(2)
O(2)–P(2)	1.54(1)	P(2)–C(6)	1.82(2)
P(1)–C(1)	1.78(2)		
(*b*) Angles			
Cl(1)–U–O(1)	130.2(2)	O(1)–P(1)–C(3)	111.8(7)
Cl(1)–U–O(2)	75.4(2)	C(1)–P(1)–C(2)	108.8(9)
O(1)–U–O(2)	154.2(3)	C(1)–P(1)–C(3)	108.7(9)
O(1)–U–O(1^{I})	82.8(4)	C(2)–P(1)–C(3)	108.2(11)
O(2)–U–O(2^{I})	113.9(3)	O(2)–P(2)–C(4)	110.3(8)
O(1)–U–O(2^{I})	75.9(4)	O(2)–P(2)–C(5)	111.3(8)
O(1)–U–O(2^{II})	80.2(3)	O(2)–P(2)–C(6)	110.2(7)
U–O(1)–P(1)	152.1(7)	C(4)–P(2)–C(5)	108.1(8)
U–O(2)–P(2)	146.8(5)	C(4)–P(2)–C(6)	108.2(11)
O(1)–P(1)–C(1)	109.2(10)	C(5)–P(2)–C(6)	108.6(8)
O(1)–P(1)–C(2)	110.2(8)		

Figure 1 shows the projection of two $[UCl(tmpo)_6]^{3+}$ units along [010] together with the labelling of the atoms. This is the first example of mononuclear seven-co-ordination for tetravalent uranium. The only other known example of this co-ordination number is found in UBr_4 which contains [15] bromine bridges with pentagonal bipyramidal stereochemistry. The co-ordination polyhedron in $[UCl(tmpo)_6]^{3+}$ can be described as a distorted monocapped antiprism or as a distorted monocapped octahedron. The angle between the planes U–Cl(1)–O(2) and U–Cl(1)–O(1^{I}) is 63.3°. If we consider ideal trigonal antiprismatic geometry for a $U(tmpo)_6$ group, and introduce into the uranium co-ordination sphere in the direction of the *c* axis one chlorine atom, we observe an increase of *ca.* 31° in the O(2)–U–O(2^{I}) angle with respect to the angle O(1)–U–O(1^{I}) (Table 2), as a consequence of steric hindrance between chlorine and oxygen atoms.

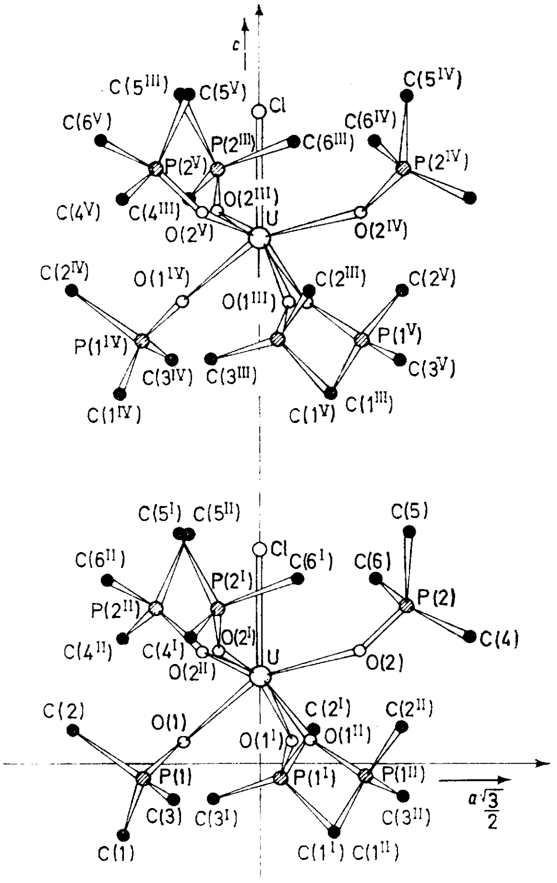

FIGURE 1 Projection of two $[UCl(tmpo)_6]^{3+}$ units along [010]

The U–Cl(1) bond length [2.813 (4) Å] is significantly greater than those reported for the octahedral species $UCl_4 \cdot 2tppo$ [2.609(4) and 2.626(3) Å],[4] and $UCl_4 \cdot 2hmpa$ [2.58(1) and 2.60(1) Å],[5] and for the dodecahedral group [7] $[UCl_2(dmso)_6]^{2+}$ in $[UCl_2(dmso)_6]^{2+}[UCl_6]^{2-}$[2.70(2) Å

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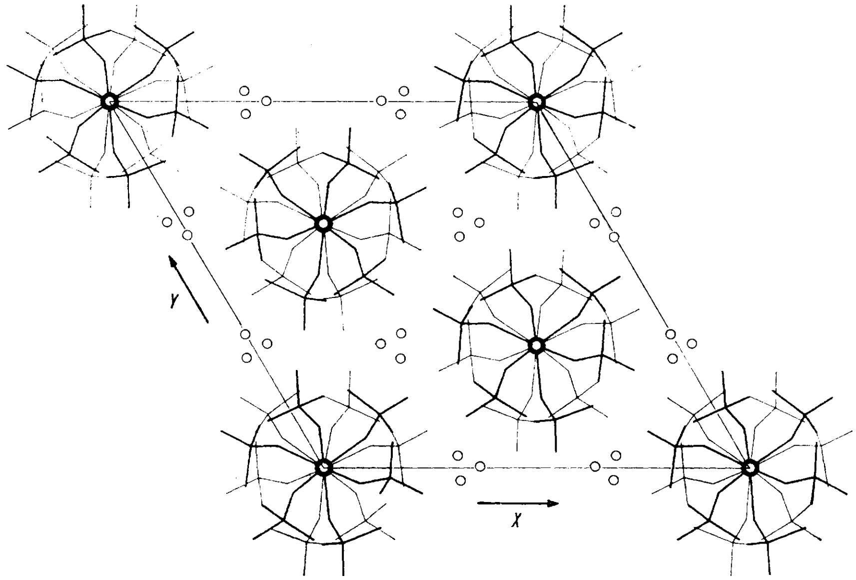

FIGURE 2 Unit-cell packing viewed down the *c* axis Thick lines represent the upper molecules, thin lines the lower ones

and the octahedral $[UCl_6]^{2-}$ group in the same complex [mean 2.60(2) Å]. This lengthening can probably be ascribed to steric factors, as indicated by the close contacts of chlorine (Table 3) with the adjacent oxygen, carbon, and phosphorus atoms and the increase in the angle $O(2)-U-O(2^I)$ already mentioned.

TABLE 3

Some relevants contacts (Å) in the structure

(*a*) Intramolecular			
Cl(1) · · · C(5)	3.48	O(2) · · · $O(1^I)$	2.91
Cl(1) · · · P(2)	3.56	O(2) · · · $O(1^{II})$	2.78
Cl(1) · · · C(6)	3.70	O(2) · · · $O(2^I)$	3.81
Cl(1) · · · O(2)	3.14	O(1) · · · $O(1^I)$	2.98
(*b*) Intermolecular			
Cl(2) · · · $C(4^I)$	3.56	Cl(2) · · · $C(1^{VII})$	3.80
Cl(2) · · · $C(6^{VI})$	3.61	Cl(2) · · · $C(3^{VII})$	3.80
Cl(2) · · · $C(5^{VI})$	3.69	Cl(2) · · · $C(2^{VIII})$	3.76

The U–O(1) and U–O(2) bond lengths do not appear to be influenced by the presence of the chlorine atom, being comparable [2.27(1) and 2.25(1) Å], to each other. They are similar to the U–O distances observed in UCl_4·2tppo [2.24(1) Å] [4] and UCl_4·2hmpa [2.24(3) Å].[5] The P–O and P–C bond lengths (Table 2) are also close to those reported for these two octahedral uranium(IV) complexes.[4,5]

Figure 2 shows the packing of the unit-cell contents viewed down the *c* axis. The anionic chlorines are located in tunnels along [001] of diameter *ca.* 4.4 Å. The U · · · Cl(2) distance is 6.22 Å and each anionic chlorine has close contacts (Table 3) with carbon atoms of four surrounding molecules.

Spectral Studies.—Although solid-state spectra have been recorded [8] for a variety of uranium(IV) complexes known to possess six- (octahedral) and eight- (cubic, square antiprismatic, dodecahedral) co-ordinate stereochemistries, the only data available for a seven-co-ordinate compound are those for UBr_4 which was only found [15] to possess this co-ordination number after publication of the spectral data. There is little resemblance between the solid-state spectrum (400—2 000 nm) of UCl_4·6tmpo and that of UBr_4, perhaps not surprising in view of the different ligands involved, the fact that UBr_4 exhibits pentagonal bipyramidal stereochemistry,[15] and the spectral results published previously [8] for the various eight-co-ordinate compounds. However, it is interesting to compare solid-state and solution spectra for UCl_4·6tmpo with those for UCl_4·3dmso, which, as mentioned earlier, is an anion–cation system in the solid state: $[UCl_2(dmso)_6]^{2+}[UCl_6]^{2-}$. Earlier spectral data for the latter compound indicated [9] that both six- and eight-co-ordinate species were present in non-aqueous

TABLE 4

Bands (nm) in the u.v.–visible spectra of UCl_4·3dmso and UCl_4·6tmpo

UCl_4·3dmso		UCl_4·6tmpo *		
In $MeNO_2$	In $MeNO_2$ + excess dmso	In MeCN	Solid	
451	442	445	406	1 162
		482sh	429sh	1 282
492	497	492	439	1 348
557	559	550	472	1 372sh
590		602	483	1 398
		618	511	1 520br
632sh		628	524	1 589
650	652	645	561sh	1 700
680	677	665	572	1 740
688			596	1 763
770		766	626	1 960
819		811	652	2 022
850		832	680	2 092
909	906br	888	766	2 143
995		997sh	810	2 178
1 035sh		1 027sh	888	
1 083	1 080sh	1 092	921	
1 148	1 168br	1 133	943	
1 267		1 267	992	
1 408br		1 415br	1 027	
1 453br			1 080	
1 562br		1 573br	1 112	

* Spectra are illustrated in Figure 3.

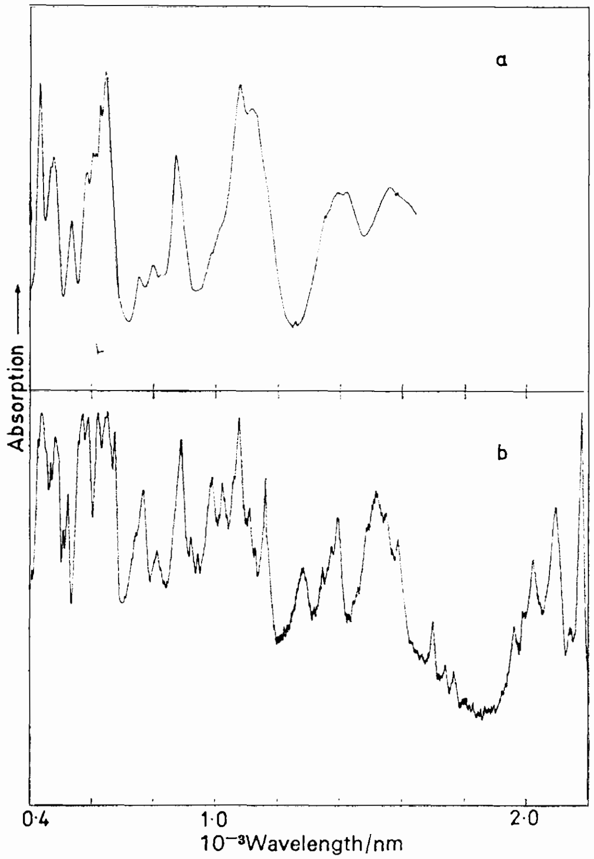

Figure 3 Spectra for (a), saturated solution of UCl_4·6tmpo in MeCN (solvent absorption interferes > *ca.* 1.6 10^3nm), and (b), solid $[UCl(tmpo)_6]Cl_3$ at 85 K

media also, the deductions being based on comparison of solution spectral changes in the region 400—700 nm on the addition of an excess of dmso, which resulted in the disappearance of bands at 401, 592, and 634 nm. These deductions were subsequently confirmed by the structural study and comparison of the solid-state spectrum with the solution spectra.

The spectra of UCl_4·6tmpo in MeCN and $MeNO_2$ are virtually identical with those of UCl_4·3dmso in the same solvents in the range 400—1600 nm indicating that on dissolution in these solvents the seven-co-ordinate structure of solid UCl_4·6tmpo is destroyed and that six- and eight-co-ordinate species are formed. Further studies with UCl_4·3dmso (in $MeNO_2$ and $MeNO_2$–dmso) have resulted in the identification of bands in the former system >700 nm which are associated with six-co-ordinate uranium ions [16] and which, like those below 700 nm, disappear on the addition of an excess of dmso. The results are provided in Table 4, from which the similarities between the solution spectra of UCl_4·6tmpo and UCl_4·3dmso are apparent. Although certain band positions in the solid-state spectrum of UCl_4·6tmpo are similar to those for MeCN solution there are appreciable relative intensity differences as shown in Figure 3, particularly in the 400—700 nm region. Furthermore, there are sufficient similarities in the solid-state spectra of UCl_4·6tmpo and UCl_4·3dmso to preclude positive identification of seven-co-ordination in other uranium(IV) compounds from spectral data alone.

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