Cyclopentadienyl Complexes of Uranium(IV) Chlorides. Crystal Structures of Trichloro(η^5-cyclopentadienyl)bis(triphenylphosphine oxide)uranium(IV) Tetrahydrofuran Solvate and of Trichloro(η^5-cyclopentadienyl)bis(hexamethylphosphoramide)uranium(IV)†

Kenneth W. Bagnall
Chemistry Department, The University of Manchester, Manchester M13 9PL
Franco Benetollo *
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., 35100 Padova, Italy
Gabriella Bombieri
Dipartimento di Chimica Inorganica e Struttura Molecolare, Università di Messina, 98100 Messina, Italy
Giovanni De Paoli
Istituto di Chimica Generale, Università di Padova, 35100 Padova, Italy

The crystal and molecular structures of $[U(cp)Cl_3(PPh_3O)_2]\cdot thf$ (thf = tetrahydrofuran) (1) and $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ (cp = η^5-cyclopentadienyl) (2) have been determined from three-dimensional *X*-ray diffraction data. The compounds crystallize in space groups $P2_1/c$ (1) and $P2_1/n$ (2), with a = 21.725(5), b = 11.699(2), c = 17.269(4) Å, β = 97.9(2)°, and Z = 4 for (1), and a = 9.942(6), b = 32.005(15), c = 9.576(6) Å, β = 106.3(1)°, and Z = 4 for (2). The structures were solved by Patterson and Fourier methods and refined by least squares to final R values of 0.054 for 3 888 independent reflections for (1) and 0.032 for 3 777 independent reflections for (2). In both compounds the uranium atom is octahedrally co-ordinated with the two neutral ligands [PPh_3O and $P(NMe_2)_3O$] in *cis* positions; the chlorine atoms are in the *mer* arrangement and the cyclopentadienyl group is *trans* to one neutral ligand. The appearance of *cis* octahedral geometry in complexes of the type $[U(cp)Cl_3L_2]$ is discussed in terms of the operation of a possible *trans* effect.

Complexes of composition $[U(cp)Cl_3L_x]$ [cp = η^5-cyclopentadienyl; x = 2, L = PPh_3O or $P(NMe_2)_3O$] have been recently reported. The structures of the analogous compounds $[UCl_4L_2]$ have demonstrated a *cis* disposition of the PPh_3O ligands in $[UCl_4(PPh_3O)_2]$ [1] while a *trans* arrangement of hexamethylphosphoramide ligands is reported for $[UCl_4\{P(NMe_2)_3O\}_2]$.[2]

The structure analyses of the title compounds have been undertaken with the aim to clarify the conformational changes induced by the substitution of the chlorine atom with the bulkier cp ligand in the precursors $[UCl_4L_2]$. A preliminary account has been reported elsewhere [3,4] and the full results are described in this paper together with a discussion of the unexpected *cis* geometry of the complexes.

Experimental

$[U(cp)Cl_3(PPh_3O)_2]\cdot thf$ (1) [3] and $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ (2) [4] were prepared by published methods.

X-Ray Measurements and Structure Determination.—The crystal and refinement data are summarized in Table 1. The *X*-ray intensity data were collected on a Philips pw 1100 four-circle automated diffractometer with graphite-monochromated Mo-K_α radiation. The unit cells were determined on the basis of 25 strong reflections found mounting the crystal at random, varying the orientation angles φ and χ over a range of 120° each with the detector position varying between $\theta = 6$ and $\theta = 10°$. For the determination of precise lattice parameters 20 strong reflections with $9 \leqslant \theta \leqslant 14°$ were considered.

The intensities of three standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects, and for absorption following the method of North *et al.*[5] The structures were solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least squares. The structure of complex (1) was refined with anisotropic thermal parameters assigned to all the atoms with the exception of the phenyl rings and the thf molecule. The phenyl rings were refined as rigid groups and restricted to their normal geometry (D_{6h} symmetry, C–C 1.395 Å) using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen-atom contributions (for the phenyl and cyclopentadienyl groups) were used as fixed atoms in calculated positions (d_{C-H} = 0.95 Å and $B_{iso.}$ = 6 Å^2). The structure of complex (2) was refined with anisotropic thermal parameters assigned to all non-hydrogen atoms, hydrogens were introduced as fixed atoms in calculated positions (d_{C-H} = 0.95 Å and $B_{iso.}$ = 5 Å^2). In all the refinements $w = 1$ was used as it showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to $|F_o|$ and to $\sin\theta/\lambda$.

The anomalous dispersion terms [6] for U and P were taken into account in the refinement. Atomic scattering factors for U and P were from ref. 7, for the other non-hydrogen atoms from ref. 8, and for hydrogen atoms from ref. 9. Data processing and computation were carried out using the SHELX 76 program package.[10] Final positional parameters for (1) and (2) are presented in Tables 2 and 3.

Results and Discussion

Figure 1 shows the stereochemistry of $[U(cp)Cl_3(PPh_3O)_2]\cdot thf$ and Figure 2 that of the analogous $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ with the atom numbering scheme. The relevant interatomic distances and bond angles are given in Tables 4 and 5 respect-

---

† *Supplementary data available* (No. SUP 23725, 52 pp.): thermal parameters, H-atom positions, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Crystal data

Compound	(1)	(2)
Formula	$C_{45}H_{39}Cl_3O_3P_2U$	$C_{17}H_{41}Cl_3N_6O_2P_2U$
M	1 034.1	767.9
Space group	$P2_1/c$	$P2_1/n$
Crystal system	monoclinic	monoclinic
a/Å	21.725(5)	9.942(6)
b/Å	11.699(2)	32.005(15)
c/Å	17.269(4)	9.576(6)
β/°	97.9(2)	106.3(1)
U/Å^3	4 347	2 925
Z	4	4
D_c/g cm^{-3}	1.58	1.74
F(000)	2 024	1 496
Radiation (λ/Å)	Mo-K_{α} (0.7107)	Mo-K_{α} (0.7107)
Reflections measured	6 028	6 829
Scan method	θ/2θ	θ/2θ
Scan speed/° min^{-1}	3	1.5
Scan width/°	1	1.25
Background counts per s of counting time	20	10
$2\theta_{max.}$/°	46	50
σ limit [$I > n\sigma(I)$]	$n = 3$	$n = 3$
Unique observed reflections	3 888	3 777
Weighting scheme, w	$1.8014[\sigma^2(F_o) + 0.001\ 433(F_o)^2]^{-1}$	1
$R (=\Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\lvert F_o\rvert)$	0.054	0.032
$R' = \left[\frac{\Sigma w \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2}{\Sigma w \lvert F_o\rvert^2}\right]^{\frac{1}{2}}$	0.058	—
μ(Mo-K_{α})/cm^{-1}	38.3	55.6

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for (1)

Atom	x	y	z	Atom	x	y	z
U	2 465(0)	908(0)	2 666(0)	C(19)	1 373(5)	−1 424(10)	4 172(5)
Cl(1)	1 843(2)	2 715(3)	2 049(2)	C(20)	1 477(5)	−2 375(10)	4 660(5)
Cl(2)	3 046(2)	2 174(3)	3 814(3)	C(21)	1 426(5)	−2 277(10)	5 453(5)
Cl(3)	1 664(2)	−610(3)	1 967(2)	C(22)	1 270(5)	−1 229(10)	5 759(5)
P(1)	1 122(2)	802(3)	3 822(2)	C(23)	1 166(5)	−278(10)	5 271(5)
P(2)	3 203(2)	−1 379(3)	4 057(2)	C(24)	2 897(4)	−2 790(7)	3 872(5)
O(1)	1 715(4)	954(7)	3 450(5)	C(25)	2 481(4)	−2 965(7)	3 192(5)
O(2)	2 832(4)	−548(7)	3 511(5)	C(26)	2 231(4)	−4 049(7)	3 020(5)
O(3)	4 787(15)	−1 585(28)	601(19)	C(27)	2 396(4)	−4 957(7)	3 530(5)
C(1)	2 981(10)	154(20)	1 371(14)	C(28)	2 811(4)	−4 783(7)	4 210(5)
C(2)	3 401(11)	−164(20)	2 006(14)	C(29)	3 062(4)	−3 699(7)	4 382(5)
C(3)	3 662(8)	879(23)	2 349(11)	C(30)	3 998(5)	−1 389(7)	3 917(6)
C(4)	3 380(8)	1 756(16)	1 879(11)	C(31)	4 290(5)	−2 337(7)	3 639(6)
C(5)	2 935(9)	1 340(18)	1 302(11)	C(32)	4 918(5)	−2 283(7)	3 548(6)
C(6)	980(4)	2 084(9)	4 321(7)	C(33)	5 253(5)	−1 281(7)	3 736(6)
C(7)	385(4)	2 326(9)	4 492(7)	C(34)	4 961(5)	−333(7)	4 014(6)
C(8)	285(4)	3 283(9)	4 941(7)	C(35)	4 334(5)	−387(7)	4 104(6)
C(9)	781(4)	3 996(9)	5 219(7)	C(36)	3 197(4)	−981(8)	5 051(5)
C(10)	1 377(4)	3 754(9)	5 048(7)	C(37)	2 798(4)	−104(8)	5 209(5)
C(11)	1 476(4)	2 798(9)	4 599(7)	C(38)	2 784(4)	248(8)	5 979(5)
C(12)	452(5)	511(9)	3 113(6)	C(39)	3 168(4)	−278(8)	6 589(5)
C(13)	9(5)	−315(9)	3 225(6)	C(40)	3 567(4)	−1 156(8)	6 431(5)
C(14)	−512(5)	−462(9)	2 665(6)	C(41)	3 582(4)	−1 507(8)	5 662(5)
C(15)	−592(5)	217(9)	1 995(6)	C(42)	5 335(20)	−2 001(33)	689(23)
C(16)	−149(5)	1 043(9)	1 883(6)	C(43)	4 745(32)	−401(63)	1 118(47)
C(17)	373(5)	1 189(9)	2 443(6)	C(44)	5 205(26)	−750(40)	1 682(31)
C(18)	1 217(5)	−376(10)	4 477(5)	C(45)	5 651(21)	−901(37)	1 259(30)

ively and the significant best mean planes in the structures are presented in Table 6. The packing of the molecules in the two compounds are shown in Figures 3 and 4.

In each compound the co-ordination around the uranium is a distorted octahedron with the two oxygen atoms of the PPh_3O and $P(NMe_2)_3O$ ligands respectively in *cis* positions. The cp ligand, considered in these complexes as occupying a single co-ordination position, is *trans* with respect to one oxygen ligand molecule, and three chlorine atoms complete the octahedron in *mer* positions.

The best mean planes passing through Cl(1), Cl(2), Cl(3), and O(2) show that the deviations of the atoms from this plane (here identified as equatorial plane) are between 0.055 and −0.050 Å for (1) and from 0.046 to −0.040 Å for (2). The deviation of the uranium atom is 0.414 Å on the opposite side of the plane to O(1) in (1); and the uranium atom is in

Table 3. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for (2)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	1 614(0)	3 779(0)	4 868(0)	C(3)	6 266(12)	3 837(3)	7 897(13)
Cl(1)	1 498(3)	3 171(1)	2 955(3)	C(4)	7 595(11)	3 197(4)	7 952(16)
Cl(2)	1 151(3)	3 255(1)	6 830(3)	C(5)	4 686(11)	2 797(3)	8 692(9)
Cl(3)	2 645(4)	4 382(1)	6 811(3)	C(6)	3 490(11)	2 492(3)	6 348(11)
O(1)	3 841(7)	3 525(2)	5 716(7)	C(7)	5 480(10)	4 427(4)	3 969(11)
P(1)	4 926(3)	3 192(1)	6 270(3)	C(8)	5 344(12)	4 539(4)	1 431(13)
N(1)	5 331(8)	2 983(2)	4 889(8)	C(9)	2 080(13)	5 001(3)	307(11)
N(2)	6 246(7)	3 421(2)	7 420(9)	C(10)	1 946(12)	5 054(3)	2 794(10)
N(3)	4 503(7)	2 798(2)	7 124(8)	C(11)	1 005(10)	4 024(4)	−226(9)
O(2)	2 601(7)	4 167(2)	3 388(7)	C(12)	3 328(12)	3 720(3)	303(10)
P(2)	2 942(3)	4 334(1)	2 066(3)	C(13)	−503(10)	4 365(3)	4 485(13)
N(4)	4 642(7)	4 379(2)	2 476(7)	C(14)	−916(11)	4 024(4)	5 154(14)
N(5)	2 068(7)	4 773(2)	1 626(7)	C(15)	−1 226(10)	3 695(4)	4 184(17)
N(6)	2 490(7)	4 063(2)	600(7)	C(16)	−1 011(11)	3 834(4)	2 899(14)
C(1)	5 147(11)	3 217(3)	3 541(10)	C(17)	−582(10)	4 237(4)	3 091(13)
C(2)	6 091(15)	2 594(4)	4 962(14)				

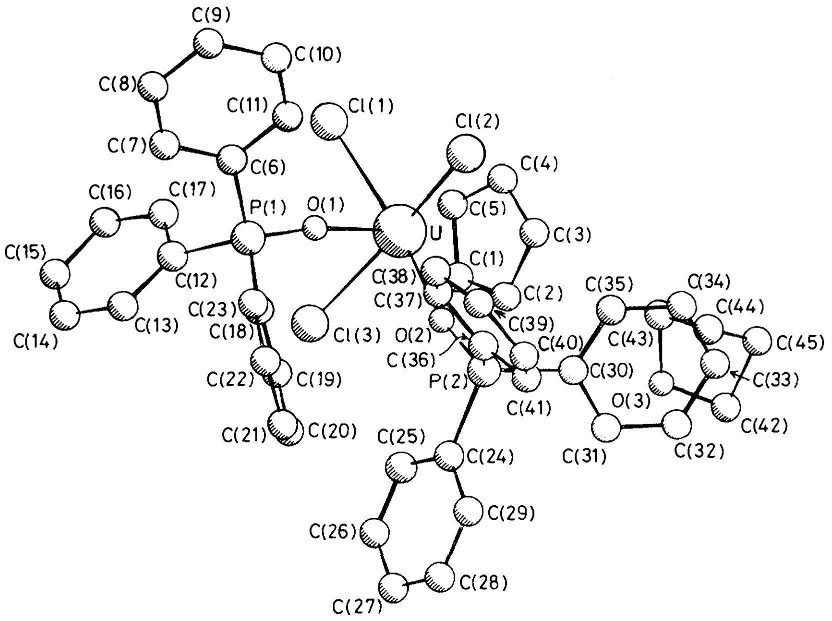

Figure 1. View of the asymmetric unit $[U(cp)Cl_3(PPh_3O)_2]$·thf down *c*

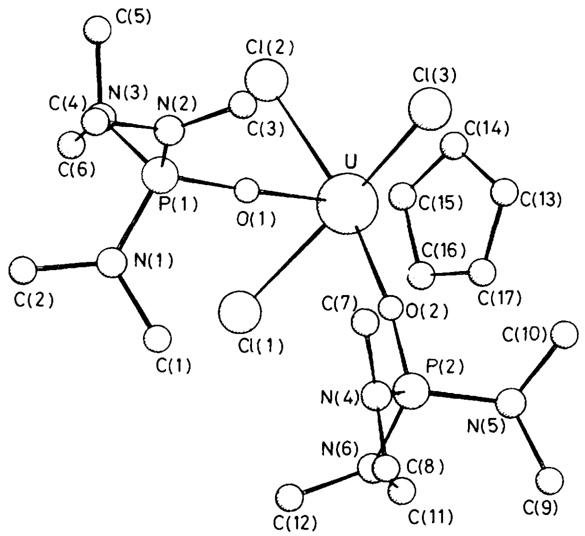

Figure 2. Perspective view of the $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ molecule

the same situation in (2) with a deviation from its equatorial plane of 0.362 Å. In both cases Cl(1), Cl(2), Cl(3), O(2), and U form an ' umbrella ', open in the direction of the neutral ligand PPh_3O in (1) and $P(NMe_2)_3O$ in (2) because of the presence *trans* to O(1) of the bulky cp ligand which is parallel in both cases to the appropriate equatorial plane [within 1° in (1) and 3° in (2)].

Some selected geometrical parameters in parent octahedral compounds are compared in Table 7 from which it can be seen that the U–O bond distances range from 2.23(1) Å in $[UCl_4\{P(NMe_2)_3O\}_2]$ [2] to 2.312(8) Å in $[U(cp)Cl_3(PPh_3O)_2]$; the larger values are in the compounds in which a chlorine atom is replaced by a cp ligand. In particular in the case of $[U(cp)Cl_3(PPh_3O)_2]$ the U–O bond *trans* to cp [2.258(9) Å] is significantly shorter with respect to the equatorial U–O bond [2.312(8) Å], but this is probably due to steric and packing effects. The presence of the cp ligand also affects the U–Cl bond distances, which are also longer with respect to those of the parent tetrachloro-compound, and the angles subtended at the uranium atom of the substituents in the equatorial

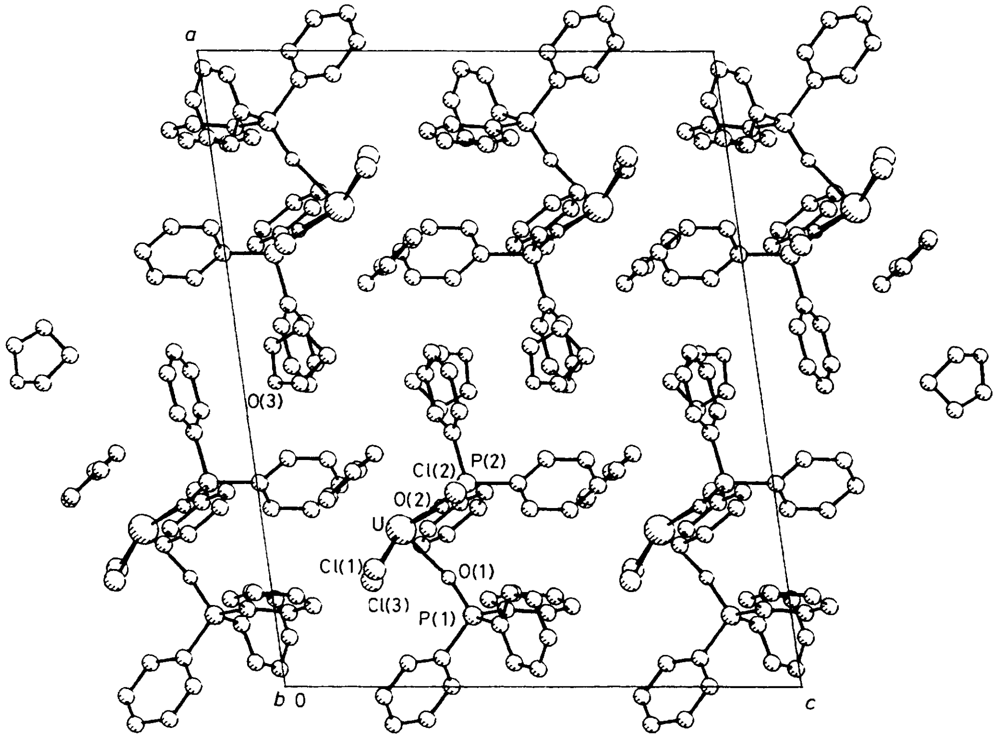

Figure 3. Packing of $[U(cp)Cl_3(PPh_3O)_2]\cdot$thf viewed down the *b* axis

Table 4. Distances (Å) and angles (°) with e.s.d.s in parentheses for $[U(cp)Cl_3(PPh_3O)_2]\cdot$thf

(*a*) Uranium environment

U–Cl(1)	2.652(4)	U–C(1)	2.78(2)	C(1)–C(2)	1.38(3)
U–Cl(2)	2.651(4)	U–C(2)	2.76(2)	C(2)–C(3)	1.44(3)
U–Cl(3)	2.657(4)	U–C(3)	2.73(2)	C(3)–C(4)	1.40(3)
U–O(1)	2.258(9)	U–C(4)	2.74(2)	C(4)–C(5)	1.38(2)
U–O(2)	2.312(8)	U–C(5)	2.74(2)	C(5)–C(1)	1.40(3)
U–M *	2.483	U–C (mean)	2.75	C–C (mean)	1.40

Cl(1)–U–O(1)	81.5(2)	Cl(1)–U–O(2)	162.4(2)	Cl(1)–U–Cl(2)	91.1(1)
Cl(2)–U–O(1)	81.2(2)	Cl(2)–U–O(2)	81.5(2)	Cl(1)–U–Cl(3)	94.9(1)
Cl(3)–U–O(1)	78.9(2)	Cl(3)–U–O(2)	86.7(2)	Cl(2)–U–Cl(3)	158.1(1)
M–U–O(1)	177.9(2)	M–U–O(2)	97.9(2)	O(1)–U–O(2)	81.6(3)
M–U–Cl(1)	99.2(1)	M–U–Cl(2)	100.8(2)	M–U–Cl(3)	99.1(1)

(*b*) Triphenylphosphine oxide

P(1)–O(1)	1.527(10)	P(1)–C(12)	1.801(11)	P(2)–O(2)	1.508(9)	P(2)–C(30)	1.777(12)
P(1)–C(6)	1.778(12)	P(1)–C(18)	1.777(11)	P(2)–C(24)	1.792(9)	P(2)–C(36)	1.780(9)

U–O(1)–P(1)	165.9(5)	U–O(2)–P(2)	167.9(6)
O(1)–P(1)–C(6)	108.6(5)	O(2)–P(2)–C(24)	109.2(5)
O(1)–P(1)–C(12)	112.7(5)	O(2)–P(2)–C(30)	111.4(5)
O(1)–P(1)–C(18)	109.1(5)	O(2)–P(2)–C(36)	111.1(5)
C(6)–P(1)–C(12)	108.1(5)	C(24)–P(2)–C(30)	108.3(4)
C(6)–P(1)–C(18)	111.0(5)	C(24)–P(2)–C(36)	111.2(5)
C(12)–P(1)–C(18)	107.4(5)	C(30)–P(2)–C(36)	105.6(5)

* M = centre of cyclopentadienyl ring.

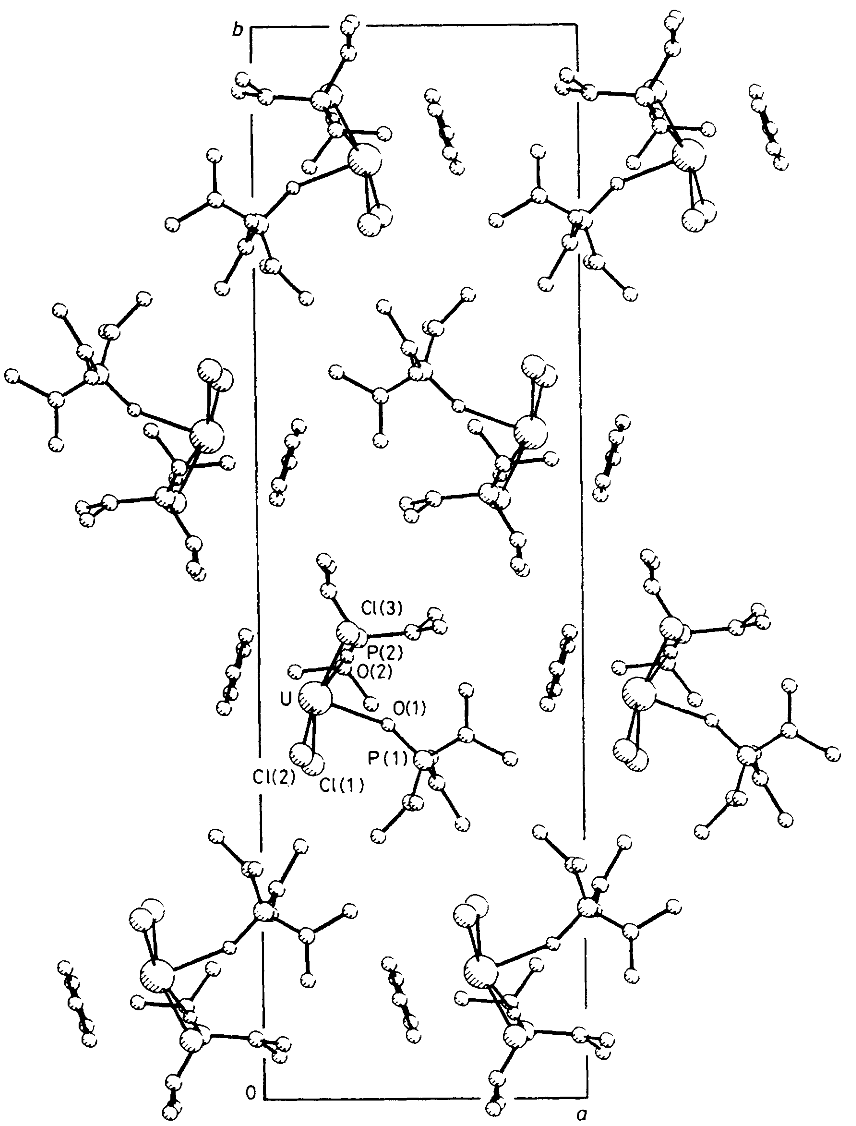

Figure 4. Packing of $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ viewed down the *c* axis

plane. In fact the deviations from linearity of the *trans* substituents are of the order of 20°.

The *cis* disposition of the phosphine oxide ligands in the complex $[U(cp)Cl_3(PPh_3O)_2]$ is similar to that reported[1] for $[UCl_4(PPh_3O)_2]$, although in the latter the *cis* octahedral arrangement involves a significant graphite-type interaction between one phenyl ring of each molecule of the ligand in the complex with another phenyl ring from each of two adjacent molecules of the complex, a result ascribed to improved packing of the molecules of the complex in the crystal.[1] However, the *cis* arrangement of the $P(NMe_2)_3O$ ligands in the structure of $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ is unexpected in view of the *trans* octahedral geometry reported[2] for $[UCl_4\{P(NMe_2)_3O\}_2]$. A *cis* octahedral geometry has also been reported for the complex $[U(\eta^5\text{-}C_5H_4Me)Cl_3(thf)_2]$[11] and for the oxygen donor ligands in the analogous indenyl complex $[U(\eta^5\text{-}C_9H_7)Br_3(PPh_3O)(thf)]$.[12]

The consistent appearance of *cis* geometry in these complexes, with the requirement for an oxygen donor ligand to be *trans* to the η^5-bonded cyclopentadienyl or indenyl ring, infers that a *trans* effect, perhaps of the kind which is observed in platinum(II) complexes, is operative in these species. Thus, if the π-bonded ligands were *trans* to an electron-withdrawing substituent, such as a halogen atom, then one might expect the metal–ring bond to be weakened, whereas if the π-bonded ligand were *trans* to an oxygen donor ligand, as in the instances noted above, the metal–ring bond might be reinforced, particularly if there was some degree of interaction between the filled uranium 5*f* orbitals and the ring π-system. There is, as yet, no evidence to support this view, but other, analogous actinide(IV) systems are being investigated in an attempt to obtain such evidence.

We have also investigated the consequences of using bulky ligands which would so crowd the $[U(cp)Cl_3L_2]$ molecule that the adoption of *cis* geometry would be difficult, if not impossible. The bulky amide ligand $Me_3CCONMe_2$, which forms a *trans* octahedral bis complex with UCl_4,[13,14] forms[15] complexes of composition $[U(cp)X_3(Me_3CCONMe_2)_2]$ ($X =$ Cl or Br), but all attempts to recrystallize the chloride complex lead to a mixture of disproportionation products, $[U(cp)_3Cl]$ and $[UCl_4(Me_3CCONMe_2)_2]$. Similar results have been observed[16] with $[Np(cp)Cl_3(Me_3CCONMe_2)_2]$. It could be argued from these results that there might be transient formation of the *trans* form of $[M(cp)Cl_3(Me_3CCONMe_2)_2]$

Table 5. Distances (Å) and angles (°) with e.s.d.s in parentheses for $[\mathrm{U(cp)Cl_3\{P(NMe_2)_3O\}_2}]$

(*a*) Uranium environment

U–Cl(1)	2.653(3)	U–C(13)	2.765(9)	C(13)–C(14)	1.38(2)
U–Cl(2)	2.653(3)	U–C(14)	2.721(9)	C(14)–C(15)	1.38(2)
U–Cl(3)	2.677(3)	U–C(15)	2.727(10)	C(15)–C(16)	1.38(2)
U–O(1)	2.284(6)	U–C(16)	2.764(10)	C(16)–C(17)	1.35(2)
U–O(2)	2.301(7)	U–C(17)	2.780(9)	C(17)–C(13)	1.38(2)
U–M *	2.491	U–C (mean)	2.751	C–C (mean)	1.37
Cl(1)–U–O(1)	80.5(2)	Cl(1)–U–O(2)	85.1(2)	Cl(1)–U–Cl(2)	92.4(1)
Cl(2)–U–O(1)	82.3(2)	Cl(2)–U–O(2)	165.0(2)	Cl(1)–U–Cl(3)	160.5(1)
Cl(3)–U–O(1)	82.3(2)	Cl(3)–U–O(2)	83.8(2)	Cl(2)–U–Cl(3)	94.1(1)
M–U–O(1)	177.9(2)	M–U–O(2)	99.1(2)	O(1)–U–O(2)	82.7(2)
M–U–Cl(1)	98.6(1)	M–U–Cl(2)	95.9(1)	M–U–Cl(3)	99.0(1)

(*b*) Hexamethylphosphoramide

P(1)–O(1)	1.504(7)	N(1)–C(2)	1.45(1)	P(2)–O(2)	1.497(6)	N(4)–C(8)	1.46(1)
P(1)–N(1)	1.630(7)	N(2)–C(3)	1.40(1)	P(2)–N(4)	1.631(7)	N(5)–C(9)	1.46(1)
P(1)–N(2)	1.632(7)	N(2)–C(4)	1.48(1)	P(2)–N(5)	1.644(6)	N(5)–C(10)	1.47(1)
P(1)–N(3)	1.622(7)	N(3)–C(5)	1.46(1)	P(2)–N(6)	1.604(6)	N(6)–C(11)	1.47(1)
N(1)–C(1)	1.46(1)	N(3)–C(6)	1.45(1)	N(4)–C(7)	1.45(1)	N(6)–C(12)	1.45(1)

U–O(1)–P(1)	155.0(4)	U–O(2)–P(2)	161.8(4)
O(1)–P(1)–N(1)	108.7(2)	O(2)–P(2)–N(4)	107.0(2)
O(1)–P(1)–N(2)	106.4(3)	O(2)–P(2)–N(5)	107.0(2)
O(1)–P(1)–N(3)	117.9(2)	O(2)–P(2)–N(6)	118.2(2)
N(1)–P(1)–N(2)	113.4(4)	N(4)–P(2)–N(5)	115.4(4)
N(1)–P(1)–N(3)	104.3(4)	N(4)–P(2)–N(6)	106.0(3)
N(2)–P(1)–N(3)	106.4(4)	N(5)–P(2)–N(6)	103.9(3)
P(1)–N(1)–C(1)	120.5(6)	P(2)–N(4)–C(7)	121.2(6)
P(1)–N(1)–C(2)	123.9(7)	P(2)–N(4)–C(8)	121.8(7)
C(1)–N(1)–C(2)	114.8(8)	C(7)–N(4)–C(8)	112.8(8)
P(1)–N(2)–C(3)	125.5(7)	P(2)–N(5)–C(9)	121.1(6)
P(1)–N(2)–C(4)	119.7(7)	P(2)–N(5)–C(10)	118.7(5)
C(3)–N(2)–C(4)	114.7(8)	C(9)–N(5)–C(10)	112.0(7)
P(1)–N(3)–C(5)	122.9(6)	P(2)–N(6)–C(11)	120.5(6)
P(1)–N(3)–C(6)	120.5(6)	P(2)–N(6)–C(12)	123.0(6)
C(5)–N(3)–C(6)	113.2(7)	C(11)–N(6)–C(12)	112.1(8)

* M = centre of cyclopentadienyl ring.

Table 6. Least-squares planes * with deviations (Å) of the relevant atoms in square brackets. The equation of a plane in direct space is given by $pX + qY + rZ = s$

	p	q	r	s
Compound (1)				
Plane 1: C(1)—C(5) [C(1) 0.021, C(2) −0.005, C(3) −0.014, C(4) 0.027, C(5) −0.029]	17.3947	−0.4490	−12.1292	3.4949
Plane 2: Cl(1), Cl(2), Cl(3), O(2) [Cl(1) 0.040, Cl(2) −0.050, Cl(3) −0.046, O(2) 0.055, U 0.414, O(1) −1.844]	17.1837	−0.3619	−12.3321	0.5015
Compound (2)				
Plane 1: C(13)—C(17) [C(13) −0.003, C(14) 0.003, C(15) −0.001, C(16) −0.001, C(17) 0.003]	−8.9468	9.8187	−0.4349	4.5439
Plane 2: Cl(1), Cl(2), Cl(3), O(2) [Cl(1) −0.040, Cl(2), 0.034, Cl(3) −0.040, O(2) 0.046, U 0.362, O(1) −1.921]	−8.7003	10.8641	−0.8228	1.9390

* Angles between planes 1 and 2 are 1° for compound (1) and 3° for compound (2).

(M = U or Np) in these cases, and that the metal–ring bond is so weakened by the electron-withdrawing effect of the Cl atom *trans* to the ring as to facilitate disproportionation. On the other hand, all complexes of the type $[\mathrm{U(cp)Cl_3L_2}]$ are kinetically labile,[17] so that disturbance of the equilibrium in disproportionation reactions will depend on which of the species involved in the equilibrium in solution has the largest crystal energy, because removal of one product by precipit-

Table 7. Comparison between some geometrical parameters in related uranium compounds

	$[UCl_4(PPh_3O)_2]$ [a]	$[U(cp)Cl_3(PPh_3O)_2]$ [b]	$[UCl_4\{P(NMe_2)_3O\}_2]$ [c]	$[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ [b]	$[UCl_4(Me_3CCONMe_2)_2]$ [d]
Stereochemistry	*cis*	*cis*	*trans*	*cis*	*trans*
U–O(1)/Å	2.242(7)	2.258(9)	2.23(1)	2.284(6)	2.246(5)
U–O(2)/Å	—	2.312(8)	—	2.301(7)	—
U–Cl(1)/Å	2.609(4)	2.652(4)	2.615(6)	2.653(3)	2.609(2)
U–Cl(2)/Å	2.626(3)	2.651(4)	2.614(4)	2.653(3)	2.614(2)
U–Cl(3)/Å	—	2.657(4)	—	2.677(3)	—
U–M [e]/Å	—	2.483	—	2.491	—
Cl–U–Cl(*trans*)/°	168.7(1)	158.1(1)	180	160.5(1)	180
Cl–U–O/°	174.3(2)	162.4	—	165.0(2)	—

[a] Ref. 1. [b] This work. [c] Ref. 2. [d] Ref. 13. [e] M = centre of cyclopentadienyl ring.

ation will disturb the equilibrium appropriately. Thus the high crystal energy of $[UCl_4\{P(NMe_2)_3O\}_2]$ may provide the driving force for the disproportionation, in which case the formation of either $[U(cp)Cl_3\{P(NMe_2)_3O\}_2]$ or $[U(cp)Cl_3\{P(NMe_2)_3O\}(\text{solvent})]$ would be unfavourable. It is interesting to note that in the indenyl complexes $[M(\eta^5\text{-}C_9H_7)X_3L_2]$ (M = Th or U; X = Cl or Br), the bis-PPh_3O complexes are relatively unstable with respect to disproportionation to $[M(\eta^5\text{-}C_9H_7)_3X]$ and $[MX_4L_2]$, the latter being very insoluble in all of the organic solvents used in the reported work.[12]

References

1 G. Bombieri, D. Brown, and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1975, 1893.
2 J. F. de Wet and S. F. Darlow, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 1041.
3 G. Bombieri, G. De Paoli, A. Del Pra, and K. W. Bagnall, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 359.
4 F. Benetollo, G. Bombieri, G. De Paoli, and P. Zanella, Proc. 9th Int. Conf. Organomet. Chem., Dijon (France), 1979, p. 63.
5 A. C. T. North, D. C. Phillips, and F. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
6 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
7 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4, p. 101.
8 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
9 R. F. Stewart, *J. Chem. Phys.*, 1965, **42**, 3175.
10 G. Sheldrick, SHELX 76 system of crystallographic computer programs, University of Cambridge, 1976.
11 R. D. Ernst, W. J. Kennelly, C. S. Day, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, 1979, **101**, 2656.
12 J. Goffart, J. Piret-Meunier, and G. Duyckaerts, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 233.
13 F. Benetollo, G. Bombieri, G. De Paoli, and P. Zanella, '$10^{ème}$ Journées des Actinides,' B. Johansson and A. Rosengren, Stockholm, Sweden, 1980, p. 37.
14 K. W. Bagnall, J. G. H. du Preez, L. Bonner, H. Copper, and G. Segal, *J. Chem. Soc., Dalton Trans.*, 1973, 2682.
15 K. W. Bagnall, J. Edwards, and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, 1978, 295.
16 K. W. Bagnall, M. J. Plews, and D. Brown, unpublished work.
17 K. W. Bagnall, 'Organometallics of the f-elements,' Proc. N.A.T.O. Advanced Study Institutes, 1978, D. Reidel, Dordrecht, 1979, p. 221.

Received 6th April 1983; *Paper* 3/525