

Tetrachlorobis(*N,N*-dimethylpivalamide)uranium(IV), $[\text{U}(\text{C}_7\text{H}_{15}\text{NO})_2\text{Cl}_4]$

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Abstract. $M_r = 638.3$, triclinic, $\bar{1}\bar{1}$, $a = 13.484$ (2), $b = 9.917$ (2), $c = 8.443$ (2) Å, $\alpha = 84.6$ (1), $\beta = 93.3$ (1) and $\gamma = 92.3$ (1)° (standard lattice obtainable with transformation matrix from $\bar{1}\bar{1}$ to $P\bar{1}$ 0,1,1/1,0,1/1,1,0: $a = 9.893$, $b = 9.127$, $c = 9.192$ Å, $\alpha = 85.2$, $\beta = 117.5$, $\gamma = 127.5$ °), $U = 1121.5$ (5) Å³, $Z = 2$, $D_x = 1.89$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 7.37$ mm⁻¹, $F(000) = 608$, room temperature. Final R value of 0.034 for 1940 observed reflections. The coordination polyhedron around the U atom is a centrosymmetric distorted octahedron.

Introduction. Complexes of the type ($\eta^5\text{-C}_5\text{H}_5$)- $\text{UCl}_3 \cdot 2L$ ($L =$ triphenylphosphine oxide or hexamethylphosphoramide) have been recently studied (Bagnall, Benetollo, Bombieri & De Paoli, 1983) and compared with the analogous $\text{UCl}_4 \cdot 2L$ complexes in order to ascertain the conformational changes induced by the substitution of a chlorine by the bulkier cyclopentadienyl (cp) ligand. We noticed that in these complexes a *cis* geometry for the neutral ligands is adopted with the oxygen donor ligand *trans* to the η^5 bonded cyclopentadienyl group regardless of the *cis* or *trans* arrangement of the ligands in the corresponding $\text{UCl}_4 \cdot 2L$ compounds. In this context we have examined the title compound* which has as neutral ligand the bulkier dmpva ($\text{Me}_3\text{CCONMe}_2$) molecule (Bagnall, du Preez, Bonner, Cooper & Segal, 1973). The corresponding $\text{U}(\text{cp})\text{Cl}_3(\text{dmpva})_2$ complex is known (Bagnall, Edwards & Tempest, 1978) but all attempts to crystallize it gave a mixture of disproportionation products $\text{U}(\text{cp})_3\text{Cl}$ and $\text{UCl}_4(\text{dmpva})_2$.

Experimental. Green prismatic crystals, preliminary determination of lattice parameters and crystal symmetry ($I1$ or $\bar{1}\bar{1}$ from systematic absences: hkl ,

$h + k + l = 2n$) made with a Weissenberg goniometer, approximate dimensions of crystal $0.5 \times 0.3 \times 0.2$ mm, Philips PW 1100 four-circle diffractometer, graphite monochromator, cell parameters refined by least-squares methods on the basis of 25 independent 2θ values, Mo $K\alpha$ radiation ($20 \leq 2\theta \leq 38$ °, $\lambda = 0.7107$ Å), intensity measurements performed up to $2\theta = 50$ °, θ - 2θ scan mode, scan speed 1.80 ° min⁻¹, scan width 1.2 °, background 10 s, no significant intensity variation for two standard reflections (301 and $2\bar{1}1$) monitored every 180 min; 2300 reflections measured, 1940 intensities with $I \geq 2.5\sigma(I)$ considered observed and used for the structure determination; corrections for Lorentz-polarization and absorption effects (North, Phillips & Mathews, 1968), transmission 0.585 – 0.637 , $R_{\text{int}} = 0.008$ ($hk0$ reflections only); structure solved by Patterson and Fourier methods, refined by full-matrix least squares with anisotropic thermal parameters for all non-H atoms; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1$; no H atoms included; final $R = 0.034$ for 1940 observed reflections; $(\Delta/\sigma)_{\text{max}} = 0.03$, maximum $\Delta\rho$ excursions = 1.43 e Å⁻³ and -1.18 e Å⁻³; scattering factors from *International Tables for X-ray Crystallography* (1974); Cyber 76 computer with *SHELX76* (Sheldrick, 1976). Final atomic parameters are in Table 1, bond distances and angles in Table 2.*

Discussion. A view of the molecule is shown in Fig. 1 with the atom-numbering scheme. The molecule lies on an inversion centre; the two dmpva ligands are in *trans* positions as in the parent compounds $\text{UCl}_4(\text{tppa})_2$ (Caira & Nassimbeni, 1977) (tppa = *N,N,N',N'*-tetramethylphenylphosphoramide) and $\text{UCl}_4(\text{hmpa})_2$ (du

* A preliminary communication has been presented at the '10^e Journées des Actinides', Stockholm, Sweden, 1980, p. 37.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38682 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent U values ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

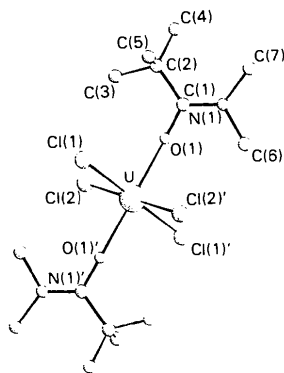
	x	y	z	U_{eq}
U	2500	2500	2500	33.8 (2)
Cl(1)	3463 (2)	4182 (2)	522 (2)	52 (1)
Cl(2)	2898 (2)	456 (2)	931 (3)	58 (1)
O(1)	3917 (4)	2173 (6)	3997 (6)	43 (3)
N(1)	4702 (5)	2395 (7)	6336 (8)	45 (4)
C(1)	4730 (5)	2319 (7)	4805 (9)	35 (4)
C(2)	5685 (6)	2408 (8)	3884 (10)	45 (4)
C(3)	5451 (7)	1712 (12)	2317 (12)	71 (6)
C(4)	6567 (7)	1686 (12)	4807 (13)	74 (6)
C(5)	5906 (8)	3951 (10)	3438 (13)	73 (6)
C(6)	3735 (7)	2204 (10)	7077 (10)	59 (5)
C(7)	5556 (8)	2772 (11)	7446 (11)	68 (6)

Table 2. Bond lengths (\AA) and angles ($^\circ$) and their e.s.d.'s in parentheses

Primed atoms are at $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$.

U—Cl(1)	2.609 (2)	N(1)—C(6)	1.48 (1)
U—Cl(2)	2.614 (2)	N(1)—C(7)	1.50 (1)
U—O(1)	2.246 (5)	C(1)—C(2)	1.54 (1)
O(1)—C(1)	1.268 (9)	C(2)—C(3)	1.56 (1)
C(1)—N(1)	1.30 (1)	C(2)—C(4)	1.55 (1)
		C(2)—C(5)	1.56 (1)
Cl(1)—U—Cl(2)	91.2 (1)	C(1)—N(1)—C(6)	118.8 (6)
Cl(1)—U—Cl(2)'	88.8 (1)	C(1)—N(1)—C(7)	126.4 (7)
O(1)—U—Cl(1)	89.4 (1)	C(6)—N(1)—C(7)	114.6 (7)
O(1)—U—Cl(2)	89.2 (2)	C(1)—C(2)—C(4)	113.6 (7)
U—O(1)—C(1)	165.2 (5)	C(1)—C(2)—C(3)	107.6 (7)
O(1)—C(1)—N(1)	118.5 (7)	C(1)—C(2)—C(5)	105.9 (7)
O(1)—C(1)—C(2)	116.7 (7)	C(3)—C(2)—C(4)	107.9 (8)
N(1)—C(1)—C(2)	124.8 (6)	C(3)—C(2)—C(5)	108.6 (7)
		C(4)—C(2)—C(5)	113.1 (7)

Preez, Gellatly, Jackson, Nassimbeni & Rodgers, 1978) (hmpa = hexamethylphosphoramide), and differ from $\text{UCl}_4(\text{tppo})_2$ (Bombieri, Brown & Graziani, 1975) (tppo = triphenylphosphine oxide) in which the neutral ligands are *cis* related. The U—Cl distances of 2.609 (2) and 2.614 (2) \AA , equal within the limits of the errors, are usual values for these complexes regardless of their *cis* or *trans* geometry. The U—O distance, 2.246 (5) \AA , is in agreement with the values observed in UCl_4 -

Fig. 1. View of the molecule down b . The primed atoms are centrosymmetrically related to those without primes through the U atom.

(hmpa) $_2$ [2.23 (1) \AA], UCl_4 (tppa) $_2$ [2.226 (6) \AA] and in UCl_4 (tppo) $_2$ [2.242 (7) \AA].

The dimensions of the neutral ligands are not unusual. The crystal packing is mainly determined by van der Waals forces and all intermolecular contacts agree with those predicted from the sums of the ionic radii.

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trans-Hydrido(phenyl)bis(triisopropylphosphine)platinum(II), $[\text{Pt}(\text{C}_6\text{H}_5)(\text{C}_9\text{H}_{21}\text{P})_2\text{H}]$

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Abstract. $M_r = 593.7$, triclinic, $P\bar{1}$, $a = 15.997$ (6), $b = 19.803$ (5), $c = 10.109$ (3) \AA , $\alpha = 116.48$ (1), β

$= 106.28$ (1), $\gamma = 82.62$ (1) $^\circ$, $U = 2751.5$ \AA^3 , $Z = 4$, $D_x = 1.43$ Mg m^{-3} , $F(000) = 1200$, $\text{Mo K}\alpha$, $\mu = 5.00$ mm^{-1} , $T = 293$ (2) K , $R = 0.078$ for 7153 unique reflections from four rapidly degrading crystals. Independent molecules are dimensionally similar but

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