

dihydrate (Cousson, Stout, Nectoux, Pagès & Gasperin, 1986) indicate a significant shortening in the benzoate complex. The same conclusions can be extended to comparisons with the structure of the diaqua(benzoato)chlorodioxouranium(VI) (Charpin, Keller, Lance & Vigner, 1989). Such shortening is associated with the expansion in the coordination sphere of the U atom (hexagonal bipyramid in the latter cases). According to Evans (1963), the uranyl group tends to coordinate four, five or six donor atoms in the equatorial plane with a strong tendency to arrange these atoms in a planar way. Fourfold and fivefold coordination provide the most stable arrangement. Stable planar sixfold coordination is observed when the coordination sphere contains

highly polarized bidentate anionic groups, otherwise a puckered, less stable structure is formed with a possible expansion in the bond length.

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## Structure of Tris( $\eta^5$ -cyclopentadienyl)phenolatouranium(IV)

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**Abstract.**  $[\text{U}(\text{C}_6\text{H}_5\text{O})(\text{C}_5\text{H}_5)_3]$ ,  $M_r = 526.42$ , orthorhombic,  $P2_12_12_1$ ,  $a = 8.331(3)$ ,  $b = 8.899(3)$ ,  $c = 23.337(5)$  Å,  $V = 1730(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.021$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 88.973$  cm<sup>-1</sup>,  $F(000) = 984$ ,  $T = 295(1)$  K,  $R = 0.025$  for 2190 observed reflections. The three cyclopentadienyl rings are  $\eta^5$ -covalently bonded to uranium to form a distorted tetrahedron with the oxygen of the phenoxide. The most important feature is the presence of the oxo functional group with a U—O distance of 2.119(7) Å and a U—O—C(16) angle of 159.4(5)°.

**Introduction.** The geometry of the large class of compounds of the type  $\text{Cp}_3MY$ , where  $M$  is a lanthanide or an actinide,  $Y$  a monodentate Lewis base,

anion or  $\eta^1$ -bridging Cp ring, is best described as a flattened tetrahedron (Lippard, 1979) in which the Cp rings are shifted towards the sterically less bulky  $Y$  ligand, decreasing the  $Y-M-Cp$  (centroid) angles and increasing the  $Cp-M-Cp$  angles. Among this class, organometallic uranium(IV) compounds have been widely investigated in recent years but little information has been reported on the mixed-ligand complexes  $\text{Cp}_3\text{U}(XR)$  where  $R = \text{alkyl}$  or aryl,  $X = \text{Group VI donor atom}$  (e.g. O or S). The title compound was prepared and its structure determined in order to verify that its geometry was consistent with that of the  $\text{Cp}_3MY$  species.

**Experimental.** The title compound was prepared by reaction of tricyclopentadienyluranium chloride with potassium phenoxide in tetrahydrofuran (von Ammon, Fischer & Kanellakopoulos, 1972). Extraction with  $n$ -pentane followed by crystallization pro-

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duced single crystals suitable for X-ray analysis. Selected specimen (0.25 × 0.25 × 0.20 mm) sealed in a thin-walled glass capillary under an inert atmosphere. Enraf-Nonius CAD-4 X-ray diffractometer, graphite-monochromated radiation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ( $4 < 2\theta < 30^\circ$ ). Space group established from systematic absences. Data were collected ( $\theta$ - $2\theta$  scans) in range  $4 < 2\theta < 46^\circ$ ,  $h - 10 \rightarrow 10$ ,  $k - 10 \rightarrow 10$ ,  $l - 26 \rightarrow 26$ . A total of 9590 reflections were measured to give 2423 unique reflections ( $R_{\text{int}} = 0.027$ ); 2190 were considered observed [ $I > 3\sigma(I)$ ] and used in refinement ( $h 0 \rightarrow 9$ ,  $k 0 \rightarrow 9$ ,  $l - 25 \rightarrow 25$ ). Intensities of three standard reflections were measured at 30 min intervals and showed slight changes during data collection. The data were rescaled to correct for this (minimum correction 0.995, maximum correction 1.057) and corrected for Lorentz-polarization and absorption effects, the latter empirically; maximum and minimum transmission factors were 0.756 and 0.999. Structure was solved by direct methods and refined by full-matrix least squares minimizing  $\sum w(\Delta F)^2$ . Anisotropic temperature factors were used for non-H atoms. A secondary-extinction coefficient was refined to  $g = 7.3 \times 10^{-8}$  ( $F_c = F_o/[1 + g(F_o)^2 \text{ Lp}]$ ). Final  $R = 0.025$ ,  $wR = 0.038$ ,  $S = 1.15$ . Number of variables refined in least squares was 209, maximum shift/e.s.d. in final cycle 0.01. H atoms were included in final structure-factor calculation in idealized positions with  $B_{\text{iso}} = 5 \text{ \AA}^2$ . Largest positive and negative peaks on final difference Fourier synthesis were of height +1.78 and -1.46 e  $\text{\AA}^{-3}$  respectively, with all substantial peaks close to U. A weighting scheme based on counting statistics was used:  $w = 1/[\sigma(F_o)]^2$ ,  $\sigma(F_o) = \sigma(F_o^2)/2F_o$ ,  $\sigma(F_o^2) = [\sigma^2(I) + (PI)^2]^{1/2}$  Lp, where P, the ignorance factor used to downweight intense reflections, is 0.06. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius (Frenz, 1983) SDP programs.

**Discussion.** Final fractional coordinates with equivalent isotropic thermal parameters for the non-H atoms are given in Table 1\* and Table 2 contains selected bond distances and bond angles. The molecule, with numbering scheme, is depicted in Fig. 1.

The molecular structure consists of one U atom coordinated by three  $\eta^5$ -coordinated cyclopentadienyl rings and by the oxygen of the phenoxide. If the

\* 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 53208 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
U	0.77677 (4)	0.09256 (3)	0.14353 (1)	2.675 (6)
O	0.6321 (9)	-0.0586 (7)	0.0960 (3)	3.8 (1)
C(1)	0.558 (2)	0.133 (1)	0.2292 (5)	6.3 (3)
C(2)	0.467 (2)	0.126 (2)	0.1764 (6)	7.7 (4)
C(3)	0.499 (1)	0.254 (1)	0.1495 (5)	7.1 (3)
C(4)	0.612 (2)	0.342 (1)	0.1765 (5)	7.5 (3)
C(5)	0.651 (2)	0.263 (1)	0.2300 (5)	5.2 (3)
C(6)	0.820 (2)	0.193 (1)	0.0332 (5)	6.0 (3)
C(7)	0.811 (2)	0.326 (2)	0.0663 (5)	6.8 (3)
C(8)	0.947 (2)	0.329 (1)	0.0997 (5)	7.7 (3)
C(9)	1.040 (2)	0.203 (2)	0.0892 (5)	8.4 (3)
C(10)	0.951 (2)	0.113 (1)	0.0444 (5)	7.2 (3)
C(11)	1.036 (1)	-0.086 (1)	0.1656 (6)	5.4 (3)
C(12)	1.039 (1)	0.020 (1)	0.2091 (5)	5.2 (2)
C(13)	0.901 (1)	-0.007 (1)	0.2459 (4)	5.2 (3)
C(14)	0.822 (2)	-0.132 (1)	0.2226 (6)	7.1 (3)
C(15)	0.901 (2)	-0.185 (1)	0.1758 (5)	7.0 (4)
C(16)	0.506 (1)	-0.147 (1)	0.0822 (4)	3.6 (2)
C(17)	0.475 (1)	-0.283 (1)	0.1150 (5)	4.6 (2)
C(18)	0.341 (2)	-0.367 (1)	0.0979 (5)	5.8 (3)
C(19)	0.246 (2)	-0.325 (1)	0.0530 (5)	5.6 (3)
C(20)	0.279 (2)	-0.196 (1)	0.0240 (5)	4.7 (2)
C(21)	0.409 (1)	-0.1050 (9)	0.0398 (4)	3.8 (2)

Table 2. *Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) and short interligand contacts ( $\text{\AA}$ )*

U—O	2.119 (7)	U—C(10)	2.74 (1)
U—C(1)	2.73 (1)	U—C(11)	2.74 (2)
U—C(2)	2.71 (1)	U—C(12)	2.74 (1)
U—C(3)	2.73 (1)	U—C(13)	2.75 (1)
U—C(4)	2.72 (1)	U—C(14)	2.75 (1)
U—C(5)	2.73 (1)	U—C(15)	2.79 (1)
U—C(6)	2.75 (2)	U—Cp I*	2.45 (2)
U—C(7)	2.76 (1)	U—Cp II	2.47 (2)
U—C(8)	2.74 (1)	U—Cp III	2.48 (2)
U—C(9)	2.71 (1)		
O—U—Cp I	97.0 (5)	Cp I—U—Cp II	116.3 (6)
O—U—Cp II	101.7 (5)	Cp I—U—Cp III	115.9 (6)
O—U—Cp III	102.7 (4)	Cp II—U—Cp III	118.0 (5)
U—O—C(16)	159.4 (5)		
O...C contacts	(< 3.1 $\text{\AA}$ )		
O...C(2)	2.85 (2)		
C...C contacts	(< 3.4 $\text{\AA}$ )		
C(1)...C(13)	3.14 (2)	C(4)...C(8)	3.32 (3)
C(1)...C(14)	3.23 (2)	C(5)...C(13)	3.20 (2)
C(2)...C(16)	3.29 (2)	C(9)...C(11)	3.13 (2)
C(3)...C(7)	3.31 (2)	C(9)...C(12)	3.24 (2)
C(4)...C(7)	3.06 (2)	C(10)...C(11)	3.41 (2)

\* Cp I denotes centre of cyclopentadienyl ring I, etc.

coordination polyhedron is considered to be formed by the centres of the Cp rings and the oxygen, the coordination about the uranium can be considered to have approximate  $C_{3v}$  symmetry, with the Cp rings at the base and the oxygen at the apex of a flattened tetrahedron (Fig. 1). Thus the  $Cp_3MY$  geometry is maintained in this compound, the Cp—U—Cp angles are nearly identical and greater than  $109^\circ$

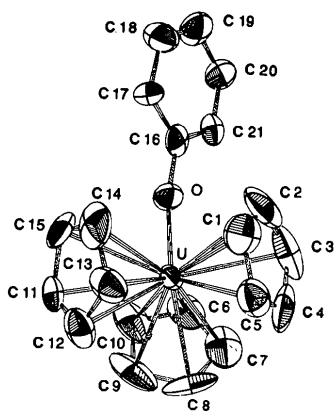


Fig. 1. ORTEP drawing (Johnson, 1965) of the title molecule, with thermal ellipsoids at the 50% probability level.

while the O—U—Cp angles are less than  $109^\circ$  (Table 2). The extent of deviation of the structure from a regular tetrahedron is also shown by the distance of the U atom from the plane defined by the centres of the three Cp rings. If one assumes a tetrahedral geometry about the U atom and an average uranium to ring-centre distance of 2.463 Å, then the U atom should be located 0.821 Å above the plane. This distance here is 0.449 Å and measures the trigonal distortion from a tetrahedral geometry.

The phenyl ring and the Cp rings are planar with average deviations from their least-squares planes of 0.008 (11), 0.016 (13), 0.002 (13) and 0.011 (12) Å. The O atom lies in the phenyl plane and the U—O—C(16) angle is  $159.4(5)^\circ$ . The phenyl C—C distances and the Cp C—C distances average 1.39 (2) and 1.41 (2) Å, respectively, and the internal angles are  $120(1)$  and  $108(1)^\circ$ . The placement of the phenyl ring divides the Cp rings into two classes. Cp II and Cp III are non-parallel with the phenyl moiety [the angles are  $60.9(4)$  and  $74.5(4)^\circ$ ] while Cp I is nearly parallel to the phenyl moiety [ $13.8(1.6)^\circ$ ]. In addition the angle at U from the Cp I centre to the oxygen is less than for the other two Cp rings. There are several short intramolecular contacts which may result from steric hindrance in the coordination sphere of uranium (Table 2c).

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## Structural Characterization of the Ru<sup>III</sup> Benzonitrile Complexes (Bu<sub>4</sub>N)[RuCl<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>] and [RuCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>CN)<sub>3</sub>]

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**Abstract.** Tetrabutylammonium *trans*-bis-(benzonitrile)tetrachlororuthenate(III), C<sub>12</sub>H<sub>28</sub>N<sup>+</sup>·[RuCl<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>N)<sub>2</sub>]<sup>-</sup>, *M<sub>r</sub>* = 691.60, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 15.627 (2), *b* = 13.936 (2), *c* = 17.319 (1) Å, β = 113.66 (1)°, *V* = 3454.7 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.330 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.78 mm<sup>-1</sup>, *F*(000) = 1436, *T* = 298 K, *R* = 0.039 for 4478

observed reflections. There are two independent anions to the asymmetric unit, each with  $\bar{1}$  symmetry. In one molecule Ru—Cl = 2.356 (2) and 2.348 (1) Å and Ru—N = 2.024 (3) Å; in the other Ru—Cl = 2.354 (1) and 2.356 (1) Å and Ru—N = 2.002 (3) Å.

*mer*-Tris(benzonitrile)trichlororuthenium(III) hemibenzenonitrile solvate, [RuCl<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>N)<sub>3</sub>].0.5C<sub>6</sub>H<sub>5</sub>N, *M<sub>r</sub>* = 568.36, triclinic, *P* $\bar{1}$ , *a* = 9.981 (5), *b* = 10.895 (5), *c* = 11.563 (5) Å, α = 80.86 (5), β = 87.60 (5), γ = 88.64 (5)°, *V* = 1240.2 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.522 Mg m<sup>-3</sup>, λ(Mo *K*α) =

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