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## Structure of ( $\eta^5$ -Indenyl)uranium Tribromide–Bis(tetrahydrofuran), [U(C<sub>9</sub>H<sub>7</sub>)]Br<sub>3</sub>·2C<sub>4</sub>H<sub>8</sub>O

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**Abstract.**  $M_r = 737.1$ , monoclinic,  $P2_1/c$ ,  $a = 9.260(3)$ ,  $b = 15.997(4)$ ,  $c = 14.756(3)$  Å,  $\beta = 108.22(2)^\circ$ ,  $V = 2076(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.358$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 130.960$  cm<sup>-1</sup>,  $F(000) = 1352$ ,  $T = 295(1)$  K,  $R = 0.033$  for 1969 observed reflections. The title compound is isostructural with its chlorine analogue. Coordination about the U atom is pseudo-octahedral with one  $\eta^5$ -C<sub>9</sub>H<sub>7</sub> ligand and one coordinated C<sub>4</sub>H<sub>8</sub>O molecule occupying *trans* axial positions. A second C<sub>4</sub>H<sub>8</sub>O molecule and three Br atoms occupy equatorial positions. The results and conclusions reported for [U(C<sub>9</sub>H<sub>7</sub>)]Cl<sub>3</sub>·2C<sub>4</sub>H<sub>8</sub>O are entirely corroborated by the present structure analysis.

**Introduction.** As part of our investigation on the bonding and coordination geometry in organoactinide complexes, we recently reported the structure of indenyluranium trichloride–bis(tetrahydrofuran), [U(C<sub>9</sub>H<sub>7</sub>)]Cl<sub>3</sub>·2C<sub>4</sub>H<sub>8</sub>O (Rebizant, Spirlet & Goffart, 1983).

The synthesis and characterization of the title compound were undertaken with the aim of establishing whether the halide-ion size could modify the crowding and therefore the geometry of the coordination polyhedron about uranium.

**Experimental.** Brown, prismatic single crystal (0.30 × 0.25 × 0.24 mm), suitable for X-ray analysis, obtained at room temperature by recrystallization from tetrahydrofuran solution and sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo  $K\alpha$  radiation. Cell parameters refined by least squares from angle data of 25 reflections. Space group unequivocally established from systematic absences. 7755 reflections collected ( $\theta$ – $2\theta$  scan mode) in range  $4 \leq 2\theta \leq 50^\circ$ , 5475 considered observed [ $I \geq 1\sigma(I)$ ,  $\pm h, \pm k, \pm l$ ], averaged to 3633 unique reflections ( $R_{\text{int}} = 0.025$ ). Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors range from 38.57 to 99.88%). Structure solved by direct methods and

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Fourier techniques; full-matrix least-squares refinement [minimizing  $\sum w(\Delta F)^2$ ] on 1969 independent reflections with  $F^2 \geq 3\sigma(F^2)$ , index range  $h$  0/10,  $k$  0/18,  $l$  -17/16; unit weights. Anisotropic thermal parameters for non-H atoms; H atoms in calculated positions, included in final structure-factor calculation with  $B_{\text{iso}} = 4.0 \text{ \AA}^2$ .  $R = 0.033$ ,  $R_w = 0.043$ ,  $S = 0.986$ ,  $(\Delta/\sigma)_{\text{max}} = 0.01$ ,  $\Delta\rho$  in final difference Fourier map within  $+1.8$  and  $-1.2 \text{ e \AA}^{-3}$  (around U atom). Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf-Nonius (1981) SDP programs.

**Discussion.** Table 1\* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are listed in Table 2. The molecular structure is illustrated in Fig. 1. H atoms are omitted to simplify the drawing.

The structure analysis shows that the title compound is isostructural with the corresponding chloride derivative  $[\text{U}(\text{C}_9\text{H}_7)]\text{Cl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  (Rebizant *et al.*, 1983). Moreover, the pseudo-octahedral coordination geometry about the U atom as well as the respective orientation of the ligands in the coordination sphere are identical in the two compounds. Even the atomic thermal motions are comparable, the largest r.m.s. amplitudes of vibration being observed for the tetrahydrofuran C atoms ( $0.145$ – $0.738 \text{ \AA}$  in the bromide).

The U–Br bond lengths, ranging from  $2.759$  (1) to  $2.791$  (1)  $\text{\AA}$ , compare favorably with the U–Br (non-bridging apical Br atom) distance of  $2.78$  (3)  $\text{\AA}$  in uranium tetrabromide (Taylor & Wilson, 1974). The mean plane through Br(1), Br(2), Br(3) and O(1) [coplanar within  $0.028$  (9)  $\text{\AA}$ ] corresponds to the

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, intramolecular bond lengths, atomic displacements from selected least-squares mean planes and shortest intramolecular and intermolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39849 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

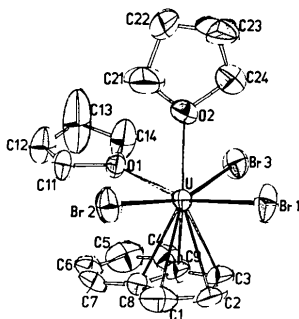


Fig. 1. The molecule of  $[\text{U}(\text{C}_9\text{H}_7)]\text{Br}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$ . Thermal ellipsoids are at the 50% probability level.

equatorial plane of the coordination polyhedron and is within  $5.4$  (1) $^\circ$  of being parallel to the indenyl mean plane. The U atom is located  $0.496$  (1)  $\text{\AA}$  below this four-atom mean plane towards the indenyl ligand. All U–C and U–O distances and all bond angles at U (Table 2) are in remarkably good agreement with the corresponding distances and angles in  $[\text{U}(\text{C}_9\text{H}_7)]\text{Cl}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$  (Rebizant *et al.*, 1983).

Table 1. Atomic positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

	$B_{\text{eq}} = \frac{1}{3} \text{trace } \bar{B}$			$B_{\text{eq}}(\text{\AA}^2)$
	x	y	z	
U	0.30927 (5)	0.39254 (3)	0.23020 (3)	2.784 (8)
Br(1)	0.0172 (2)	0.4026 (1)	0.1056 (1)	5.50 (4)
Br(2)	0.2176 (2)	0.4609 (1)	0.37745 (9)	4.58 (3)
Br(3)	0.3899 (2)	0.2726 (1)	0.11892 (9)	5.42 (4)
C(1)	0.363 (2)	0.560 (1)	0.229 (1)	6.3 (5)
C(2)	0.299 (2)	0.535 (1)	0.132 (1)	6.8 (5)
C(3)	0.396 (2)	0.482 (1)	0.102 (1)	5.7 (4)
C(4)	0.673 (2)	0.441 (1)	0.189 (1)	5.6 (4)
C(5)	0.784 (2)	0.449 (1)	0.276 (1)	8.0 (6)
C(6)	0.765 (2)	0.496 (1)	0.351 (1)	5.9 (4)
C(7)	0.632 (2)	0.534 (1)	0.345 (1)	5.2 (4)
C(8)	0.512 (2)	0.5268 (9)	0.2594 (9)	4.4 (3)
C(9)	0.528 (2)	0.478 (1)	0.1779 (9)	4.6 (4)
O(1)	0.5216 (9)	0.3352 (6)	0.3616 (5)	3.7 (2)
C(11)	0.569 (1)	0.362 (1)	0.4636 (9)	4.3 (3)
C(12)	0.709 (2)	0.314 (1)	0.511 (1)	6.4 (4)
C(13)	0.712 (3)	0.246 (1)	0.455 (1)	16.6 (7)
C(14)	0.613 (2)	0.265 (1)	0.353 (1)	8.3 (5)
O(2)	0.201 (1)	0.2681 (6)	0.2785 (6)	4.5 (2)
C(21)	0.190 (4)	0.249 (1)	0.370 (1)	17.1 (9)
C(22)	0.134 (3)	0.159 (1)	0.361 (1)	15.2 (7)
C(23)	0.015 (2)	0.165 (1)	0.271 (1)	9.5 (6)
C(24)	0.105 (2)	0.205 (1)	0.212 (1)	8.4 (6)

Table 2. Bond distances ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and polyhedral edge lengths ( $\text{\AA}$ ) in the coordination sphere of  $[\text{U}(\text{C}_9\text{H}_7)]\text{Br}_3 \cdot 2\text{C}_4\text{H}_8\text{O}$

E.s.d.'s are given in parentheses.			
U–Br(1)	2.759 (1)	U–C(3)	2.68 (2)
U–Br(2)	2.791 (1)	U–C(8)	2.79 (2)
U–Br(3)	2.775 (2)	U–C(9)	2.75 (2)
U–O(1)	2.466 (8)	U–C(4)	3.69 (2)
U–O(2)	2.432 (9)	U–C(5)	4.33 (2)
U–C(1)	2.73 (2)	U–C(6)	4.36 (2)
U–C(2)	2.69 (2)	U–C(7)	3.70 (2)
U...Ind*	2.450 (1)	Br(2)...Ind*	2.950 (2)
Br(1)...Br(2)	3.968 (3)	Br(3)...O(1)	3.55 (1)
Br(1)...Br(3)	3.981 (3)	Br(3)...O(2)	3.343 (9)
Br(1)...O(2)	3.36 (1)	Br(3)...Ind*	2.920 (2)
Br(1)...Ind*	2.710 (2)	O(1)...O(2)	3.03 (1)
Br(2)...O(1)	3.53 (1)	O(1)...Ind*	3.197 (9)
Br(2)...O(2)	3.40 (1)		
Br(1)–U–Br(2)	91.29 (5)	Br(3)–U–O(2)	79.6 (2)
Br(1)–U–Br(3)	92.01 (6)	Br(3)–U–Ind*	99.76 (6)
Br(1)–U–O(2)	80.5 (2)	O(1)–U–O(2)	76.5 (3)
Br(1)–U–Ind*	95.43 (6)	O(1)–U–Ind*	107.6 (3)
Br(2)–U–O(1)	84.0 (2)	Br(1)–U–O(1)	156.9 (2)
Br(2)–U–O(2)	80.8 (2)	Br(2)–U–Br(3)	159.23 (6)
Br(2)–U–Ind*	100.33 (5)	O(2)–U–Ind*	175.9 (2)
Br(3)–U–O(1)	85.0 (2)		

\* Ind denotes the intersection of the perpendicular from the U atom to the indenyl plane with that plane.

The U atom is  $\eta^5$  covalently bonded to the planar [within 0.06 (2) Å] indenyl ring. The slight lengthening of U–C(8) and U–C(9) in comparison with U–C(2) and U–C(3) may result from the fact that the negative charge of the indenyl anion primarily resides on the three non-bridging C atoms. Examination of short interligand contacts reveals that it cannot be attributed to steric effects.

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### Structure of 1,1,2,2,3,3-Hexacarbonyl-1,2;2,3;3,1-tris( $\mu$ -diphenylphosphido)-triangular-cobalt(I)(3Co–Co) Acetonitrile Solvate, $[\text{Co}_3\{\text{P}(\text{C}_6\text{H}_5)_2\}_3(\text{CO})_6] \cdot \text{C}_2\text{H}_3\text{N}$

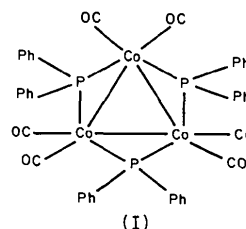
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**Abstract.**  $M_r = 941.5$ , triclinic,  $P\bar{1}$ ,  $a = 12.448$  (2),  $b = 16.234$  (4),  $c = 11.656$  (4) Å,  $\alpha = 98.34$  (3),  $\beta = 110.19$  (2),  $\gamma = 103.54$  (2)°,  $V = 2082.2$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.502$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 112.3$  cm<sup>-1</sup>,  $F(000) = 956$ ,  $T = 293$  K, final  $R = 0.043$  for 2749 observed reflections. The cobalt atoms form an approximate equilateral triangle with each edge being bridged by a diphenylphosphido ligand. Each of the cobalt atoms is, in addition, coordinated to two terminal carbonyl groups. The mean values for the Co–Co, Co–P, Co–C and C≡O bond lengths are 2.60 (3), 2.172 (3), 1.75 (1) and 1.148 (8) Å respectively.

**Introduction.** During an investigation of the chemistry of cobalt complexes of the cationic tertiary phosphine  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3^+$  (as the iodide salt) (Smith, Ungar, Sanderson & Baird, 1983), green crystals of the title compound (I) were obtained. A similar compound,  $[\text{Co}_3(\mu\text{-PMe}_2)_3(\text{CO})_6]$ , was known (Keller & Vahrenkamp, 1978, 1979) to contain non-equivalent dimethylphosphido ligands. Since such compounds are currently of considerable interest because of their potential catalytic properties (Harley, Guskey & Geoffroy, 1983), it was decided to investigate the structure of the diphenylphosphido analogue for purposes of comparison. It was later discovered that a single-crystal X-ray diffraction study had previously been carried out on the title compound (Huntsman, 1973), for which, to our knowledge, the results have not been published.



**Experimental.** Dark-green crystal, specimen 0.17 × 0.17 × 0.06 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu  $K\alpha$ ; cell parameters from least squares applied to 25 reflections with  $5.7 \leq \theta \leq 27.2^\circ$ ; 4673 unique reflections, 2749 considered observed at  $3\sigma(I)$  level,  $h$  0→12,  $k$  -16→16,  $l$  -11→10,  $\theta \leq 52^\circ$ ,  $\theta$ - $2\theta$  scans, three standard reflections monitored after every 7200 s of exposure, max. variation in intensity -7.6%, Lp correction, decay correction, numerical absorption correction, min., max. and av. transmission 0.3308, 0.6562 and 0.5258. Structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier methods. Full-matrix least-squares refinement minimizing  $\sum w|F_o| - |F_c|^2$ , where  $w = 4F^2/[\sigma^2(F^2) + (0.06 F^2)^2]$ , anisotropic temperature factors for non-hydrogen atoms. Acetonitrile molecule located from difference Fourier map, atoms refined with isotropic temperature factors. Hydrogen atoms, calculated and assigned isotropic temperature factor equal to 1.2 times equivalent isotropic value of parent atom, included in calculations but not refined. Scattering factors those of Cromer & Waber (1974), anomalous-dispersion coefficients from Cromer (1974).

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