

(Schubert, Werner, Zinner & Werner, 1983) and P=O 1.488, P—O 1.595 Å (Fernanda, Carvalho, Pombeiro, Hughes & Richards, 1987).

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## Structure of Di- $\mu$ -chloro-bis[trichlorobis(tetrahydrofuran)uranium(IV)]

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**Abstract.** [ $\{\text{UCl}_4(\text{C}_4\text{H}_8\text{O})_2\}_2$ ],  $M_r = 1048.12$ , monoclinic,  $P2_1/c$ ,  $a = 10.756$  (5),  $b = 12.372$  (5),  $c = 12.293$  (6) Å,  $\beta = 113.31$  (3)°,  $V = 1502$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.317$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 109.486$  cm<sup>-1</sup>,  $F(000) = 960$ ,  $T = 295$  (1) K,  $R = 0.037$  for 1287 observed unique reflections. The dimeric complex, in which two  $\text{UCl}_4(\text{THF})_2$  moieties are bridged by two Cl atoms, lies on a centre of symmetry. Each U atom of the dimer is seven coordinated in a pentagonal-bipyramidal geometry. The maximum deviation from the best plane through the U atom and its five equatorial ligand atoms [Cl(1), Cl(1)<sup>i</sup>, Cl(4) and the O atoms of the two THF] is 0.05 (1) Å. Cl(2)—U—Cl(3) is almost linear and perpendicular to this plane.

**Experimental.** The title complex was prepared by reaction of uranium tetrachloride with tetrahydrofuran in *n*-pentane at room temperature. Extraction and recrystallization with a 10% THF solution in *n*-pentane gave single crystals. The selected specimen (0.30 × 0.25 × 0.30 mm) was sealed in a thin-walled glass capillary under an inert atmosphere. Enraf-Nonius CAD-4 diffractometer was used with graphite-monochromated radiation. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections in the range 16–30°

( $2\theta$ ). The space group was unequivocally established from systematic absences. Intensity data were collected by  $\theta$ - $2\theta$  scans in the range  $4 < 2\theta < 46^\circ$ ,  $h\ 0 \rightarrow 12$ ,  $k\ -14 \rightarrow 14$ ,  $l\ -14 \rightarrow 14$ . In total 3829 reflections were measured to give 2081 unique reflections ( $R_{\text{int}} = 0.023$ ) of which 1287 were considered observed [ $I \geq 3\sigma(I)$ ] and used in refinement ( $h\ 0 \rightarrow 10$ ,  $k\ 0 \rightarrow 12$ ,  $l\ -12 \rightarrow 11$ ). Intensities of three standard reflections were measured at 30 min intervals, anisotropic decay correction was applied (total decay 3.9%). The data were corrected for Lorentz and polarization effects.  $\psi$  scans were used for the absorption correction (North, Phillips & Mathews, 1968), the min. and max. relative transmission factors were 73.32 and 99.95% respectively. The structure was solved by direct methods and refined by full-matrix least-squares techniques which minimized  $\sum w(\Delta F)^2$ ;  $w = 1/[\sigma(F_o)]^2$  with  $\sigma(F_o) = \sigma(F_o^2)/2F_o$  and  $\sigma(F_o^2) = [\sigma^2(I) + (A/I)^2]^{1/2}/Lp$  where  $A$ , the ignorance factor, is 0.06. Anisotropic temperature factors were used for non-H atoms. A secondary-extinction coefficient was refined to  $g = 8.9 \times 10^{-8} \{F_c = F_c/[1 + g(F_c)^2 Lp]\}$ . The final discrepancy indices were  $R = 0.037$ ,  $wR = 0.066$ ,  $S = 2.09$ . 137 variables were refined with maximum shift/e.s.d. in final cycle 0.03. H atoms were included in final structure factor calculations in idealized positions with  $B_{\text{iso}} = 4$  Å<sup>2</sup>. Largest positive and negative peaks on final  $\Delta\rho$  map had heights +1.16 and -1.39 e Å<sup>-3</sup>, respectively, with all substantial peaks close to U. Atomic scattering factors and

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

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2acc\cos\beta)\beta_{13} + (2bcc\cos\alpha)\beta_{23}].$$

	x	y	z	$B_{\text{eq}}$
U	0.18668 (5)	0.05032 (4)	0.16572 (4)	3.22 (2)
Cl(1)	0.0263 (5)	-0.1236 (3)	0.0379 (4)	6.0 (1)
Cl(2)	0.3314 (5)	0.0315 (4)	0.0452 (4)	5.8 (1)
Cl(3)	0.0347 (4)	0.0728 (4)	0.2799 (4)	5.9 (1)
Cl(4)	0.4010 (5)	0.1001 (4)	0.3520 (4)	6.8 (1)
O(1)	1.1998 (9)	0.2459 (9)	0.1586 (8)	4.9 (3)
O(2)	0.266 (1)	-0.120 (1)	0.2650 (9)	5.2 (3)
C(1)	0.234 (2)	0.305 (2)	0.069 (1)	8.2 (5)
C(2)	0.248 (2)	0.423 (1)	0.117 (1)	5.7 (4)
C(3)	0.275 (2)	0.413 (2)	0.244 (2)	6.4 (5)
C(4)	0.192 (2)	0.318 (1)	0.254 (1)	6.4 (4)
C(5)	0.248 (3)	-0.155 (2)	0.371 (2)	13.1 (9)
C(6)	0.314 (3)	-0.267 (2)	0.402 (3)	10.9 (9)
C(7)	0.355 (3)	-0.285 (2)	0.321 (3)	16.0 (9)
C(8)	0.347 (2)	-0.192 (2)	0.238 (2)	10.7 (8)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

(1) U coordination sphere			
U—Cl(1)	2.816 (3)	U—O(2)	2.415 (9)
U—Cl(1')	2.792 (3)	U—Cl(2)	2.550 (4)
U—O(1)	2.427 (9)	U—Cl(3)	2.556 (4)
U—Cl(4)	2.600 (3)		
Cl(2)—U—Cl(3)	177.8 (1)	O(1)—U—Cl(4)	75.6 (2)
Cl(1)—U—Cl(1')	69.1 (1)	Cl(4)—U—O(2)	75.5 (2)
Cl(1')—U—O(1)	71.5 (2)	O(2)—U—Cl(1)	68.3 (2)
(2) THF			
O(1)—C(1)	1.48 (2)	O(2)—C(5)	1.45 (2)
C(1)—C(2)	1.56 (2)	C(5)—C(6)	1.54 (3)
C(2)—C(3)	1.48 (2)	C(6)—C(7)	1.26 (3)
C(3)—C(4)	1.51 (2)	C(7)—C(8)	1.52 (4)
C(4)—O(1)	1.50 (1)	C(8)—O(2)	1.38 (2)
U—O(1)—C(1)	123.7 (7)	U—O(2)—C(5)	125 (1)
U—O(1)—C(4)	122.8 (7)	U—O(2)—C(8)	125 (1)
C(4)—O(1)—C(1)	113 (1)	C(8)—O(2)—C(5)	110 (2)
O(1)—C(1)—C(2)	101 (1)	O(2)—C(5)—C(6)	106 (2)
C(1)—C(2)—C(3)	105 (1)	C(5)—C(6)—C(7)	104 (2)
C(2)—C(3)—C(4)	106 (1)	C(6)—C(7)—C(8)	117 (2)
C(3)—C(4)—O(1)	101 (1)	C(7)—C(8)—O(2)	102 (2)

Symmetry code: (i)  $-x, -y, -z$ .

anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974, Vol. IV). The Enraf-Nonius SDP (Frenz, 1983) programs were used. Final atomic coordinates are given in Table 1,\* geometrical parameters in Table 2 and a perspective view with numbering scheme in Fig. 1.

**Related literature.** The tendency for bridged bonds to be longer than otherwise equivalent terminal bonds

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53616 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

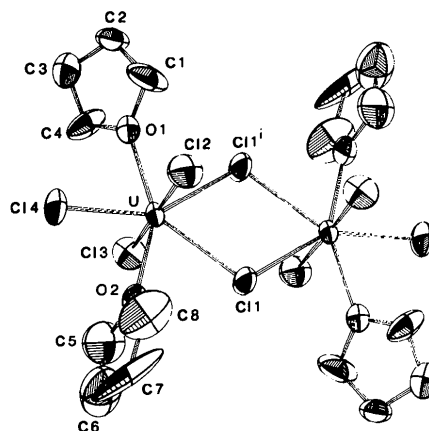


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound with thermal ellipsoids at the 50% probability level.

is also observed here. The U...U' distance of 4.618 (1)  $\text{\AA}$  and the average bridging U—Cl distance of 2.804 (4)  $\text{\AA}$  are comparable to the values in  $\text{UO}_2\text{-Cl}_2(\text{THF})_2$  (Rogers, Green & Benning, 1986), respectively 4.619(5) and 2.82 (2)  $\text{\AA}$ . The pentagonal bipyramidal geometry found for this compound is interesting because it is relatively uncommon in uranium(IV) complexes. Some of them have been characterized in the solid state:  $\text{UBr}_4$  (Taylor & Wilson, 1974), which is a bromine-bridged polymer, the  $[\text{UF}_7]^{3-}$  anion in  $\text{K}_3[\text{UF}_7]$  (Zachariasen, 1954), the  $[\text{UCl}_3\{\text{C}_2\text{H}_5\text{CON}(\text{C}_2\text{H}_5)_2\}_4]^+$  cation in  $[\text{UCl}_3\{\text{C}_2\text{H}_5\text{CON}(\text{C}_2\text{H}_5)_2\}_4][\text{UCl}_5\{\text{C}_2\text{H}_5\text{CON}(\text{C}_2\text{H}_5)_2\}_2]$  (Bagnall, Beddoes, Mills & Xing-fu, 1982), the neutral complexes  $\text{U}(\text{NCS})_4[(\text{CH}_3)_2\text{CHCON}(\text{CH}_3)_2]_3$  (Bagnall, Xing-fu, Bombieri & Benetollo, 1982) and  $\text{U}(\text{NCS})_4[(\text{C}_2\text{H}_5)\text{CON}(\text{C}_2\text{H}_5)_2]_3$  (Al-Daher, Bagnall, Benetollo, Polo & Bombieri, 1986). The reduction in the coordination number around the uranium from eight ( $\text{UCl}_4$ ) to seven (here) would result from the hindrance of the additional THF ligands with respect to Cl ligands.

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## Structure of Aqua-hexakis( $\mu_2$ -benzoato)-bis(methanol)- $\mu_3$ -oxo-triiron(III) Benzoate Ethanol Methanol Solvate

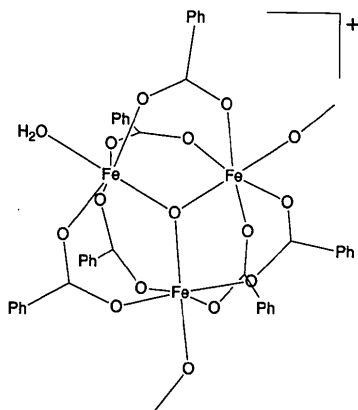
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**Abstract.**  $[\text{Fe}_3(\text{O})(\text{C}_7\text{H}_5\text{O}_2)_6(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})][\text{C}_7\text{H}_5\text{O}_2]\cdot\text{C}_2\text{H}_5\text{OH}\cdot\text{CH}_3\text{OH}$  (1/1/1),  $M_r = 1191.56$ , triclinic,  $P\bar{1}$ ,  $a = 11.591$  (3),  $b = 13.308$  (2),  $c = 20.154$  (3) Å,  $\alpha = 96.910$  (12),  $\beta = 96.95$  (2),  $\gamma = 114.10$  (2)°,  $V = 2767.1$  (9) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.43$  g cm<sup>-3</sup>,  $\mu = 8.471$  cm<sup>-1</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $F(000) = 1234$ ,  $T = 198$  K,  $R = 0.0522$  for 6252 reflections [ $F_o \geq 4\sigma(F_o)$ ]. The complex has nearly  $D_{3h}$  symmetry with two coordinated  $\text{CH}_3\text{OH}$  molecules and one coordinated  $\text{H}_2\text{O}$  molecule. The coordination around the Fe atoms is essentially octahedral. Each Fe atom lies slightly out of the plane of the O atoms of the bridging benzoates and is directed towards the  $\mu_3\text{-O}$  atom. The average Fe—O distances are 1.907 (2) Å for the  $\mu_3\text{-O}$  atom and 2.010 (1) Å for the benzoate O atoms.

**Experimental.** As a by-product of ongoing research related to the respiratory protein hemerythrin (Sessler, Sibert & Lynch, 1990; Sessler, Hugdahl, Lynch & Davis, 1990), complex (1),  $[\text{Fe}_3(\text{O})(\text{O}_2\text{CC}_6\text{H}_5)_6(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})][\text{O}_2\text{CC}_6\text{H}_5]\cdot\text{CH}_3\text{OH}\cdot\text{C}_2\text{H}_5\text{OH}$ , was synthesized. Orange crystals were obtained by slow evaporation of a methanol–ethanol (5:1) solution. The crystals quickly decomposed when taken out of the mother liquor, presumably due to the loss of methanol and/or ethanol solvate molecules.



The data crystal was an orange needle of approximate dimensions 0.13 × 0.20 × 0.41 mm. The data

were collected on a Nicolet P3 diffractometer, using graphite-monochromatized Mo  $K\alpha$  radiation, and a Nicolet LT-2 low-temperature delivery system. Lattice parameters were obtained from the least-squares refinement of 42 reflections with  $24.4 < 2\theta < 30.0^\circ$ . Data were collected using the  $\omega$ -scan technique (10 318 reflections, 9788 unique,  $R_{\text{int}} = 0.0134$ ), with a  $2\theta$  range from  $4.0\text{--}50^\circ$  in  $2\theta$ , over a  $1.3^\circ$   $\omega$  scan at  $4\text{--}8^\circ \text{min}^{-1}$  ( $h = 0 \rightarrow 12$ ,  $k = -15 \rightarrow 15$ ,  $l = -23 \rightarrow 23$ ). Four reflections ( $233$ ;  $232$ ;  $332$ ;  $30\bar{1}$ ) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these four reflections was used to scale the data. The scaling factor ranged from 0.968–1.03. The data were also corrected for Lp effects and absorption. The absorption correction was based on crystal-face measurements with a minimum and maximum transmission factor range of 0.8291–0.9147. The data reduction, absorption and decay correction were performed using *SHELXTL-Plus* (Sheldrick, 1987). Reflections having  $F_o < 4\sigma(F_o)$  were considered unobserved (3536 reflections). The structure was solved by the direct methods and refined by full-matrix least squares (Sheldrick, 1987). The non-H atoms were refined with anisotropic thermal parameters. The H atoms were obtained from a  $\Delta F$  map and refined with isotropic thermal parameters. During the latter stages of refinement, the H atoms of the methanol C atoms (C60, C62, C2B) and the C atoms of the ethanol molecule (C2A, C3A) were idealized (C—H 0.96 Å) with isotropic thermal parameters fixed at  $1.2 \times U_{\text{eq}}$  of the relevant C atom. In all, a total of 858 parameters were refined in blocks of 394 and 465 parameters with the scale factor being refined in each block. The function  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $w = 1/[\sigma(F_o)]^2$  and  $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)^2 + (0.02I)^2]\}^{1/2}$ . The intensity,  $I$ , is given by  $(I_{\text{peak}} - I_{\text{background}}) \times$  (scan rate); 0.02 is a factor to downweight intense reflections and to account for instrument instability and  $k$  is the correction due to Lp effects, absorption and decay.  $\sigma(I)$  was estimated from counting statistics;  $\sigma(I) = [(I_{\text{peak}} + I_{\text{background}})]^{1/2} \times$  (scan rate). Final  $R = 0.0522$  for 6252 reflections,  $wR = 0.0533$  ( $R_{\text{all}} = 0.0863$ ,  $wR_{\text{all}} = 0.0583$ ) and a goodness of fit = 1.43.