

Fig. 1. ORTEP (Johnson, 1976) drawing of the polymer [symmetry code: (i) $x, -y, \frac{1}{2} + z$].

and O; scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974 Vol. IV, Tables 2.2B and 2.3.1); H atoms of benzoate groups introduced at calculated positions, not refined but constrained to ride on their C atoms ($C-H = 0.95 \text{ \AA}$ and $B = 6 \text{ \AA}^2$), $R = 0.033$, $wR = 0.0411$ ($w = 1$), $(\Delta/\sigma)_{\max} = 0.10$, $S = 5.02$. In final difference Fourier synthesis, no peak greater than 0.72 e \AA^{-3} except for two peaks (1.3 and 1.03 e \AA^{-3}) in the vicinity of the U atom; calculations carried out on a Digital Computer MicroVAX II using the SDP chain of programs

(Frenz, 1985). The structure belongs clearly to the non-centrosymmetric group and the absolute configuration has been obtained unambiguously.

Atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2.* Fig. 1 shows the polymeric structure and the labelling scheme.

Related literature. The title compound was obtained during the preparation of diaqua(benzoato)chlorodioxouranium(VI) (Charpin, Keller, Lance & Vigner, 1989).

* 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 53189 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Di- μ -oxo-bis[(cyclopentadienyl)(heptafluoropropyl)oxotungsten]

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Abstract. C₈H₅F₇O₂W, $M_r = 449.96$, triclinic, $P\bar{1}$, $a = 6.294$ (4), $b = 12.737$ (9), $c = 14.871$ (11) Å, $\alpha = 67.83$ (5), $\beta = 78.97$ (5), $\gamma = 83.74$ (5)°, $V = 1083$ (1) Å³, $Z = 4$, $D_x = 2.760 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 10.99 \text{ mm}^{-1}$, $F(000) = 824$, $T = 291$ (1) K, final $R = 0.074$ for 2840 unique observed [$F \geq 4.0\sigma(F)$] diffractometer data. The crystal contains two independent centrosymmetric molecular dimers. The central part of these molecules is a planar four-membered W—O—W—O ring [W—O

1.95 (2) Å, O—W—O 74.4 (6)°, W...W 3.102 (3), O...O 2.35 (2) Å]. A cyclopentadienyl ring is attached to each W, with W—C distances in the range 2.33 (2)–2.49 (2) Å and these rings are *trans* to each other with respect to the central ring. If one takes the centers of the four-membered W—O—W—O ring and the cyclopentene ring as coordination points, these two coordination points and the atoms C(*i*1) and O(*i*1) ($i = 1, 2$) bound to W form a distorted tetrahedron around W.

Experimental. The title compound was prepared by exposing $(C_5H_5)(NO)_2WC_3F_7$ (Naumann & Varbelow, 1990) to the air. $(C_5H_5)WO_2(C_3F_7)$ was crystallized slowly from a CH_2Cl_2/n -hexane solution at room temperature. A crystal of size $\sim 0.25 \times 0.10 \times 0.03$ mm was used. D_m was not determined. Intensity data were collected with $\omega/2\theta$ scans, scan speed $3.0\text{--}14.6^\circ \text{ min}^{-1}$ in θ , scan width $1.2^\circ + \text{dispersion}$. A Nicolet R3m/V diffractometer with graphite-monochromated $Mo K\alpha$ radiation was used. The lattice parameters were determined from least-squares fit of 18 reflections with $2\theta_{\text{max}} = 19.19^\circ$. ω scans of low-order reflections along the three crystal axes showed broad and asymmetric reflections. Six standard reflections ($22\bar{2}$, $20\bar{2}$, 020 , $\bar{2}22$, $\bar{2}02$, $0\bar{2}0$) were recorded every 2.5 h, only random deviations were detected during 77.92 h of X-ray exposure; 6377 reflections with $3.0 \leq 2\theta \leq 50.0^\circ$, $-8 \leq h \leq 3$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$ were measured. The data were corrected for Lorentz-polarization but not for absorption effects and averaged ($R_{\text{int}} = 0.071$) to

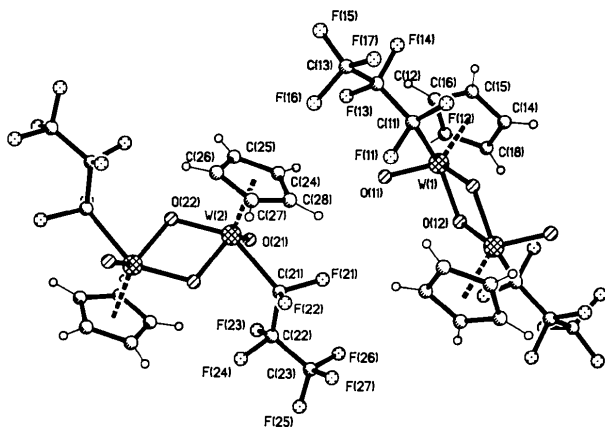


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecules, showing the atom-numbering scheme.

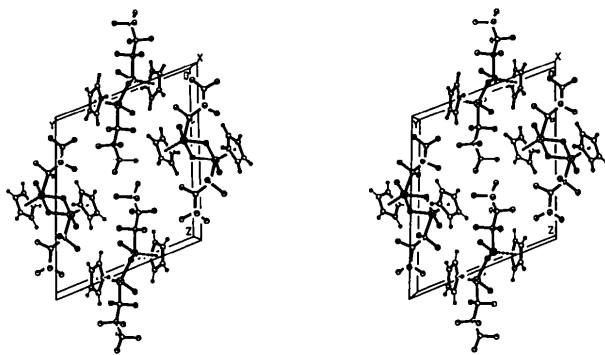


Fig. 2. Stereoscopic view (*SHELXTL-Plus* graphic) of the unit cell.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
W(1)	0.3975 (1)	0.44526 (7)	0.94234 (6)	318
F(11)	0.702 (2)	0.559 (1)	0.763 (1)	549
F(12)	0.827 (2)	0.387 (1)	0.826 (1)	611
F(13)	0.376 (2)	0.460 (1)	0.706 (1)	654
F(14)	0.577 (3)	0.306 (1)	0.749 (1)	678
F(15)	0.667 (4)	0.423 (2)	0.559 (1)	925
F(16)	0.693 (4)	0.576 (2)	0.578 (1)	914
F(17)	0.929 (3)	0.437 (3)	0.631 (2)	1300
O(11)	0.254 (2)	0.543 (1)	0.860 (1)	384
O(12)	0.328 (2)	0.520 (1)	1.038 (1)	443
C(11)	0.635 (4)	0.445 (2)	0.808 (2)	480
C(12)	0.581 (4)	0.418 (2)	0.724 (2)	498
C(13)	0.725 (5)	0.459 (3)	0.620 (2)	706
C(14)	0.431 (3)	0.250 (2)	1.064 (1)	590
C(15)	0.443 (3)	0.245 (2)	0.970 (1)	692
C(16)	0.244 (3)	0.291 (2)	0.936 (1)	452
C(17)	0.109 (3)	0.323 (2)	1.010 (1)	539
C(18)	0.224 (3)	0.298 (2)	1.089 (1)	637
W(2)	0.0497 (1)	0.89467 (7)	0.59030 (6)	293
F(21)	0.165 (2)	0.849 (1)	0.793 (1)	536
F(22)	0.381 (2)	0.974 (1)	0.680 (1)	614
F(23)	-0.166 (3)	1.035 (2)	0.739 (2)	1007
F(24)	0.105 (4)	1.135 (1)	0.667 (2)	1050
F(25)	-0.007 (4)	1.135 (2)	0.845 (2)	1115
F(26)	-0.019 (6)	0.962 (2)	0.910 (2)	1648
F(27)	0.284 (5)	1.043 (3)	0.839 (2)	1620
O(21)	-0.179 (2)	0.854 (1)	0.674 (1)	491
O(22)	-0.103 (2)	0.947 (1)	0.475 (1)	340
C(21)	0.168 (3)	0.944 (2)	0.704 (1)	447
C(22)	0.039 (5)	1.037 (2)	0.736 (2)	660
C(23)	0.076 (8)	1.047 (3)	0.832 (3)	907
C(24)	0.164 (3)	0.703 (1)	0.638 (1)	491
C(25)	0.143 (3)	0.739 (1)	0.538 (1)	534
C(26)	0.307 (3)	0.817 (1)	0.482 (1)	510
C(27)	0.429 (3)	0.829 (1)	0.548 (1)	406
C(28)	0.340 (3)	0.759 (1)	0.645 (1)	606

Table 2. Bond distances (\AA), bond angles ($^\circ$), torsion angles ($^\circ$), least-squares planes and dihedral angles ($^\circ$)

W(1)—O(11)	1.70 (1)	W(2)—O(21)	1.70 (1)
W(1)—O(12)	1.95 (2)	W(2)—O(22)	1.98 (1)
W(1)—O(12a)	1.93 (2)	W(2)—O(22a)	1.92 (2)
W(1)—C(11)	2.26 (3)	W(2)—C(21)	2.28 (3)
W(1)—C(14)	2.48 (2)	W(2)—C(24)	2.34 (1)
W(1)—C(15)	2.42 (2)	W(2)—C(25)	2.38 (2)
W(1)—C(16)	2.33 (2)	W(2)—C(26)	2.47 (2)
W(1)—C(17)	2.34 (2)	W(2)—C(27)	2.49 (2)
W(1)—C(18)	2.44 (2)	W(2)—C(28)	2.41 (2)
W(1)···W(1a)	3.098 (3)	W(2)···W(2a)	3.105 (3)
O(12)···O(12a)	2.34 (2)	O(22)···O(22a)	2.36 (3)

Distance of atom W(*i*) from the least-squares plane through the atoms C(*i*4), C(*i*5), C(*i*6), C(*i*7), C(*i*8): 2.06 (8) \AA (*i* = 1), 2.09 (12) \AA (*i* = 2); dihedral angles between the least-squares plane through C(*i*4), C(*i*5), C(*i*6), C(*i*7), C(*i*8) and the plane through W(*i*), O(*i*2), W(*ia*), O(*i*2a) 35.2 (10) $^\circ$ (*i* = 1), 37.0 (9) $^\circ$ (*i* = 2).

O(12)—W(1)—C(11)	142.1 (9)	O(22)—W(2)—C(21)	146.1 (9)
O(11)—W(1)—C(11)	84.6 (8)	O(21)—W(2)—C(21)	86.3 (8)
O(11)—W(1)—O(12)	94.0 (8)	O(21)—W(2)—O(22)	94.5 (7)
O(12)—W(1)—O(12a)	74.1 (6)	O(22)—W(2)—O(22a)	74.6 (6)
O(11)—W(1)—O(12a)	121.5 (7)	O(21)—W(2)—O(22a)	119.2 (8)
C(11)—W(1)—O(12a)	74.8 (8)	C(21)—W(2)—O(22a)	75.5 (7)
O(11)—W(1)—Z(11)	119 (1)	O(21)—W(2)—Z(21)	119 (2)
O(11)—W(1)—Z(12)	112 (3)	O(21)—W(2)—Z(22)	111 (2)
C(11)—W(1)—Z(11)	107 (2)	C(21)—W(2)—Z(21)	104 (1)
C(11)—W(1)—Z(12)	109 (2)	C(21)—W(2)—Z(22)	112 (2)
Z(11)—W(1)—Z(12)	119 (3)	Z(21)—W(2)—Z(22)	120 (3)
W(1)—O(12)—W(1a)	105.9 (7)	W(2)—O(22)—W(2a)	105.4 (7)
C(15)—C(14)—C(18)	108 (2)	C(25)—C(24)—C(28)	108 (1)
C(14)—C(15)—C(16)	108 (2)	C(24)—C(25)—C(26)	108 (1)
C(15)—C(16)—C(17)	108 (2)	C(25)—C(26)—C(27)	108 (1)
C(16)—C(17)—C(18)	108 (2)	C(26)—C(27)—C(28)	108 (1)
C(14)—C(18)—C(17)	108 (2)	C(24)—C(28)—C(27)	108 (1)

Z(1) is the center of the cyclopentadienyl ring and Z(2) the center of the central ring in molecule *i*.

3841 unique reflections, 2840 of which had $F \geq 4.0\sigma(F)$. The structure was solved *via* direct methods in space group $P\bar{1}$ and $\Delta\rho$ maps. It was refined (on F) using full-matrix least squares with anisotropic displacement parameters for all non-H atoms and for each molecule a common isotropic one for the H atoms, which were placed in geometrically calculated positions (C—H 0.96 Å). 309 parameters were refined. Weights $w = 1.0/[\sigma^2(F) + (0.004849F^2)]$ led to a featureless analysis of variance in terms of $\sin\theta$ and F_o . The refinement converged to $S = 1.16$, $R = 0.074$, $wR = 0.077$, $(\Delta/\sigma)_{\max} = 0.018$ (no extinction correction). The largest peaks in final $\Delta\rho$ map were $\pm 3.7(9) \text{ e \AA}^{-3}$, near W. The poor quality of the weakly reflecting crystal could be a reason for the high R value. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were: *PARST* (Nardelli, 1983), *SHELXTL-Plus* (Sheldrick, 1987), *PCK83* (Williams, 1984), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987). The two independent molecules and the numbering scheme are shown in Fig. 1 and a stereoscopic view of the unit-cell contents is in Fig. 2. Positional parameters and the

equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths and bond angles are given in Table 2.

Related literature. For the preparation of the compound see Naumann & Varbelow (1990).

* 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 53190 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Trinuclear Rhodium(I) Complex, [*cis*-Rh(CO)(PPh₃)₃(μ₃-O)(μ₃-OCMe₃)

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Abstract. μ_3 -*tert*-Butoxy-1,2,3-tricarbonyl- μ_3 -oxo-1,2,3-tris(triphenylphosphine)trirrhodium, $[\text{Rh}_3(\text{CO})_3(\text{O})(\text{C}_4\text{H}_9\text{O})(\text{C}_6\text{H}_5)_3\text{P}]_3$, $M_r = 1268.7$, monoclinic, $P2_1/n$, $a = 12.728(6)$, $b = 21.392(6)$, $c = 21.741(11)$ Å, $\beta = 100.29(4)^\circ$, $V = 5824(4)$ Å³, $Z = 4$, $D_x = 1.45 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.710730$ Å, $\mu = 9.5 \text{ cm}^{-1}$, $F(000) = 2560$, $T = 296 \text{ K}$, $R(F) = 5.3$, $R(wF) = 6.6\%$ for 5466 data with $|F_o| > 4.0\sigma(|F_o|)$. The molecule consists of three *cis*-Rh(CO)(PPh₃) units which are linked together symmetrically by a capping μ_3 -oxo ligand (*trans* to the three CO ligands) and a capping μ_3 -*tert*-butoxy ligand (*trans* to the three PPh₃ ligands). Bond lengths are

Rh—PPh₃ = 2.231(3)–2.236(3) Å, Rh—CO = 1.796(13)–1.818(12) Å, Rh—(μ₃-O) = 2.045(5)–2.053(6) Å and Rh—(μ₃-OCMe₃) = 2.144(6)–2.163(6) Å; non-bonding Rh···Rh distances are 2.888(2)–2.995(2) Å. Each rhodium(I) center is in a slightly distorted square-planar coordination environment. The [Rh(CO)P]₃(μ₃-O)(μ₃-OCC₃) core of the molecule possesses approximate C_{3v} symmetry.

Experimental. The title compound, [*cis*-Rh(CO)(PPh₃)₃(μ₃-O)(μ₃-OCMe₃)], was obtained, in low yield, as an unexpected product during attempts to synthesize *trans*-Rh(PPh₃)₂(CO)(OCMe₃) [from