

## Structure of ( $\eta^7$ -Cycloheptatrienyl)diiodo(tetrahydrofuran)molybdenum

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**Abstract.**  $[\text{Mo}(\eta^7\text{-C}_7\text{H}_7)(\text{C}_4\text{H}_8\text{O})\text{I}_2]$ ,  $\text{C}_{11}\text{H}_{15}\text{I}_2\text{MoO}$ ,  $M_r = 512.98$ , triclinic,  $P\bar{1}$ ,  $a = 10.004$  (3),  $b = 12.191$  (8),  $c = 12.573$  (2) Å,  $\alpha = 98.77$  (4),  $\beta = 104.48$  (2),  $\gamma = 101.74$  (4)°,  $U = 1420$  Å<sup>3</sup>,  $D_c = 2.40$  Mg m<sup>-3</sup> for  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 5.28$  mm<sup>-1</sup>,  $F(000) = 948$ . Final  $R_w = 0.054$  for 2813 observed reflexions. The asymmetric unit contains two crystallographically independent molecules with a quasi-octahedrally coordinated Mo atom. The cycloheptatrienyl ligand occupies one face of the octahedron, the I atoms and the O atom of the tetrahydrofuran occupying the three remaining apices.

**Introduction.** Small black plates (0.5 × 0.3 × 0.1 mm) were supplied by Dr M. L. H. Green and Mr N. Hazel. They were sensitive to air and moisture and were sealed under dry argon in glass capillaries. After a survey by precession photography, the crystal was set up on a Nonius CAD-4F diffractometer and cell dimensions and orientation matrix were obtained from the setting angles of 25 reflexions.

The intensities of reflexions with  $\sin \theta/\lambda < 0.55$  Å<sup>-1</sup> were measured by an  $\omega/2\theta$  scan with a variable scan rate and an  $\omega$  scan angle of  $(1.3 + 0.35 \tan \theta)^\circ$ . Each reflexion was measured at its azimuth angle of minimum absorption using the built-in subroutine *FLAT-MODE*. Mo  $K\alpha$  radiation was used with a graphite monochromator. Reflexions with  $I < 3\sigma(I)$ , where  $\sigma(I)$  is the standard deviation based on simple counting statistics, were not included in subsequent calculations. The data were corrected for Lorentz and polarization effects but not for absorption.

The asymmetric unit contains two molecules of the title compound. The structure was solved by heavy-atom techniques and refined by blocked-matrix least squares [block 1: scale, dummy overall isotropic temperature factor (Rollett, 1965); block 2: positional parameters for molecule (I); block 3: anisotropic temperature factors for (I); block 4: positional parameters for molecule (II); block 5: anisotropic temperature factors for (II)]. All non-H atoms had anisotropic

temperature factors. Difference syntheses showed some evidence for the  $\eta^7$ -cycloheptatrienyl and the tetrahydrofuran H atoms at their expected positions. However, they were positioned geometrically (C–H 1.0 Å,  $U_{\text{iso}} 0.05$  Å<sup>2</sup>), their location being adjusted after each refinement cycle. In the final stages each reflexion was assigned a weight  $w = 1/[1 + (|F_o|/150)^2]$  where  $F_o$  is the observed structure factor. Seven of the strongest reflexions ( $\bar{1}01$ ,  $101$ ,  $\bar{3}23$ ,  $\bar{3}14$ ,  $\bar{3}14$ ,  $406$ ,  $\bar{2}02$ ) were not included in the last refinement cycles because

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors (mean e.s.d. 0.01 Å<sup>2</sup>)

$U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$  where  $U_1, U_2, U_3$  are the mean square displacements (Å<sup>2</sup>) along each of the principal axes of the ellipsoids of vibration.

	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
Mo(1)	0.1358 (1)	0.8719 (1)	0.3379 (1)	0.0360
I(11)	0.3058 (1)	1.08784 (9)	0.46378 (9)	0.0459
I(12)	-0.0457 (1)	0.98858 (9)	0.2158 (1)	0.0519
O(1)	0.257 (1)	0.9023 (9)	0.2121 (8)	0.0470
C(2)	0.409 (2)	0.921 (2)	0.241 (2)	0.0648
C(3)	0.445 (3)	0.923 (3)	0.129 (3)	0.1209
C(4)	0.315 (3)	0.878 (3)	0.043 (2)	0.1013
C(5)	0.199 (3)	0.862 (2)	0.092 (2)	0.0713
C(11)	-0.054 (2)	0.783 (2)	0.384 (2)	0.0618
C(12)	-0.053 (2)	0.717 (2)	0.286 (2)	0.0622
C(13)	0.053 (2)	0.680 (1)	0.259 (2)	0.0547
C(14)	0.196 (2)	0.703 (1)	0.319 (2)	0.0554
C(15)	0.262 (2)	0.763 (2)	0.430 (2)	0.0618
C(16)	0.201 (3)	0.823 (2)	0.504 (2)	0.0613
C(17)	0.059 (3)	0.831 (2)	0.483 (2)	0.0627
Mo(2)	0.3820 (1)	0.3856 (1)	0.1777 (1)	0.0360
I(21)	0.2066 (1)	0.4870 (1)	0.03436 (9)	0.0515
I(22)	0.5378 (1)	0.60858 (9)	0.2935 (1)	0.0502
O(21)	0.232 (1)	0.4084 (9)	0.2804 (9)	0.0505
C(22)	0.268 (2)	0.427 (2)	0.402 (2)	0.0674
C(23)	0.143 (3)	0.438 (2)	0.437 (2)	0.0820
C(24)	0.021 (3)	0.377 (2)	0.333 (2)	0.1010
C(25)	0.079 (2)	0.354 (2)	0.241 (2)	0.0692
C(31)	0.583 (2)	0.333 (1)	0.256 (2)	0.0523
C(32)	0.587 (2)	0.360 (2)	0.150 (2)	0.0599
C(33)	0.481 (2)	0.325 (2)	0.047 (2)	0.0603
C(34)	0.349 (2)	0.253 (1)	0.019 (1)	0.0507
C(35)	0.284 (2)	0.197 (1)	0.088 (2)	0.0518
C(36)	0.335 (2)	0.205 (1)	0.206 (2)	0.0592
C(37)	0.474 (2)	0.264 (2)	0.277 (2)	0.0583

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Table 2. *Interatomic distances (Å) and bond angles (°)*

Molecule (I)		Molecule (II)	
Mo(1)—I(11)	2.808 (2)	Mo(2)—I(21)	2.800 (2)
Mo(1)—I(12)	2.829 (2)	Mo(2)—I(22)	2.805 (2)
Mo(1)—O(1)	2.25 (1)	Mo(2)—O(21)	2.24 (2)
Mo(1)—C(11)	2.24 (2)	Mo(2)—C(31)	2.27 (2)
Mo(1)—C(12)	2.26 (3)	Mo(2)—C(32)	2.24 (2)
Mo(1)—C(13)	2.29 (2)	Mo(2)—C(33)	2.23 (2)
Mo(1)—C(14)	2.25 (2)	Mo(2)—C(34)	2.28 (2)
Mo(1)—C(15)	2.26 (2)	Mo(2)—C(35)	2.29 (2)
Mo(1)—C(16)	2.24 (2)	Mo(2)—C(36)	2.26 (2)
Mo(1)—C(17)	2.23 (2)	Mo(2)—C(37)	2.27 (2)
Mo(1)—cent(1)	1.59 (2)	Mo(2)—cent(2)	1.59 (2)
O(1)—C(2)	1.44 (3)	O(21)—C(22)	1.45 (3)
O(1)—C(5)	1.44 (3)	O(21)—C(25)	1.46 (3)
C(2)—C(3)	1.53 (4)	C(22)—C(23)	1.46 (3)
C(3)—C(4)	1.41 (4)	C(23)—C(24)	1.51 (4)
C(4)—C(5)	1.44 (4)	C(24)—C(25)	1.44 (4)
C(11)—C(12)	1.37 (3)	C(31)—C(32)	1.42 (3)
C(12)—C(13)	1.33 (3)	C(32)—C(33)	1.40 (3)
C(13)—C(14)	1.39 (3)	C(33)—C(34)	1.37 (3)
C(14)—C(15)	1.40 (3)	C(34)—C(35)	1.39 (3)
C(15)—C(16)	1.42 (4)	C(35)—C(36)	1.43 (3)
C(16)—C(17)	1.40 (4)	C(36)—C(37)	1.42 (3)
C(17)—C(11)	1.40 (4)	C(37)—C(31)	1.35 (3)
I(11)—Mo(1)—I(12)	87.46 (3)	I(21)—Mo(2)—I(22)	87.12 (5)
I(11)—Mo(1)—O(1)	85.5 (3)	I(21)—Mo(2)—O(21)	82.2 (3)
I(11)—Mo(1)—cent(1)	128.5 (5)	I(21)—Mo(2)—cent(2)	129.7 (5)
I(12)—Mo(1)—O(1)	83.5 (3)	I(22)—Mo(2)—O(21)	85.6 (3)
I(12)—Mo(1)—cent(1)	129.0 (6)	I(22)—Mo(2)—cent(2)	127.9 (5)
O(1)—Mo(1)—cent(1)	127.6 (7)	O(21)—Mo(2)—cent(2)	128.6 (7)
Mo(1)—O(1)—C(2)	122 (2)	Mo(2)—O(21)—C(22)	126 (2)
Mo(1)—O(1)—C(5)	125 (2)	Mo(2)—O(21)—C(25)	124 (2)
C(2)—O(1)—C(5)	108 (2)	C(22)—O(21)—C(25)	104 (2)
O(1)—C(2)—C(3)	105 (2)	O(21)—C(22)—C(23)	110 (2)
C(2)—C(3)—C(4)	107 (3)	C(22)—C(23)—C(24)	103 (2)
C(3)—C(4)—C(5)	109 (3)	C(23)—C(24)—C(25)	108 (2)
C(4)—C(5)—O(1)	109 (2)	C(24)—C(25)—O(21)	108 (2)
C(17)—C(11)—C(12)	129 (2)	C(37)—C(31)—C(32)	127 (2)
C(11)—C(12)—C(13)	130 (2)	C(31)—C(32)—C(33)	129 (2)
C(12)—C(13)—C(14)	130 (2)	C(32)—C(33)—C(34)	129 (2)
C(13)—C(14)—C(15)	128 (2)	C(33)—C(34)—C(35)	128 (2)
C(14)—C(15)—C(16)	127 (2)	C(34)—C(35)—C(36)	129 (2)
C(15)—C(16)—C(17)	128 (2)	C(35)—C(36)—C(37)	126 (2)
C(16)—C(17)—C(11)	128 (2)	C(36)—C(37)—C(31)	131 (2)

they were recorded at a count rate for which the dead-time of the counter was very significant. Final  $R = 0.042$  and  $R_w = 0.054$  for 2813 reflexions.

All calculations were performed with *CRYSTALS* (Carruthers & Watkin, 1979) on the Oxford University ICL 2980 computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final positional parameters are given in Table 1.\* Table 2 lists interatomic distances and bond angles for the non-H atoms, with e.s.d.'s calculated from the variance-covariance matrix.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36634 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The very similar molecules (I) and (II) of  $(\text{cht})\text{MoI}_2 \cdot \text{H}_4\text{F}$  (cht = cycloheptatrienyl,  $\text{H}_4\text{F}$  = tetrahydrofuran) are shown in Fig. 1. The environment of the metal atom is octahedral with the cht ligand occupying one face and the I atoms and the O atom of the  $\text{H}_4\text{F}$  rings occupying the remaining apices. The Mo atoms have a 17-electron configuration.

The C atoms of the  $\eta^7\text{-cht}$  group are coplanar within experimental errors and the cht rings can be described as essentially regular heptagons with C—C bonds in the range 1.33 (3)–1.43 (3) Å (mean 1.39 Å) and internal ring angles 126 (2)–131 (2)° (mean 129°). The Mo atoms are 1.59 (2) Å from the cht plane and the perpendiculars to the cht rings at the Mo atoms meet the rings close to their centroids (within 0.04 Å). Mo—C distances [range 2.23 (2)–2.29 (2) Å, mean 2.25 Å] compare well with those in the 17-electron cation  $[\text{Mo}(\text{acac})(\text{H}_2\text{O})(\eta^7\text{-cht})]^+$  (Green, Kirsch, Stone & Welch, 1977) [mean 2.265 (15) Å] and are on average shorter than the corresponding values observed in the 18-electron compounds  $[\text{Mo}(\sigma\text{-C}_6\text{F}_5)(\text{CO})_2(\eta^7\text{-cht})]$ , mean 2.316 Å (Churchill & O'Brien, 1969),  $[\text{MoX}(\text{CO})_2(\eta^7\text{-cht})]$  with  $X = \text{Cl}$  or  $\text{Br}$ , mean 2.321 and 2.337 Å respectively (Ziegler, Sasse & Nuber, 1975). It is not possible to relate the slight variations in Mo—C bond lengths to a *trans* influence of the I atoms.

The Mo—I bond lengths [2.800 (2)–2.829 (2) Å, mean 2.810 Å] are in the expected range, shorter than in 18-electron complexes such as  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{CNPh})\text{I}]$  [2.858 (1) Å] (Sim, Sime, Woodhouse & Knox, 1979),  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}\text{I}]$  [2.858 (3) Å] (Bush, Hardy, Manojlović-Muir & Sim, 1971),  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{I})_2\text{MoI}_2]$  [2.849 (1) Å] (Gourdon & Prout, 1981) but longer than in the 16-electron complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}_2(\text{CH}_3)_2\text{N}_2]$  [2.735 (1) and 2.767 (1) Å] (Mallinson, Sim & Woodhouse, 1980). The distances between the two I atoms within a molecule are surprisingly short [3.897 (1) and 3.862 (2) Å] if compared with the sum of the van der Waals radii (4.30 Å). The difference between the Mo—I and Mo—O [2.25 (1) and 2.24 (2) Å] bond lengths of ca 0.56 Å is significantly less than the difference between the tetrahedral covalent radii of I and O, 0.70 Å, which is not surprising since the O

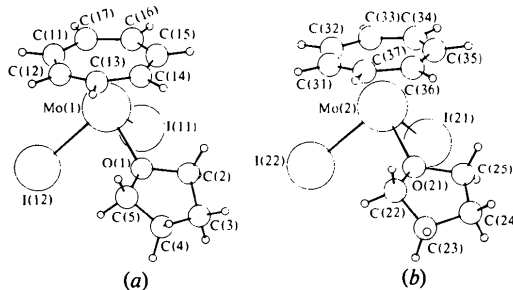


Fig. 1. Perspective view of  $[(\eta^7\text{-C}_7\text{H}_7)\text{MoI}_2(\text{C}_4\text{H}_8\text{O})]$ . (a) Molecule (I); (b) molecule (II).

atom is three-coordinate. The I—Mo—I angles [87.46 (5) and 87.12 (5)°] and the I—Mo—O angles [82.2 (3)—85.6 (3)°] are significantly smaller than 90° and the angles between the normal of the cht plane and the Mo—I and Mo—O bonds [127.6 (5)—129.7 (5)°] are larger than expected for a tetrahedral arrangement of ligands around the Mo atom (109.47°).

The O atom of the H<sub>4</sub>F ligand is pyramidally bonded as shown by the *ca* 20° angle formed by the Mo—O vector with the C—O—C plane. The dihedral angles of 165 and 157° between the planes C—O—C and C—C—C—C compare well with the 149.0 and 149.8° reported in coordinated H<sub>4</sub>F (Brauer & Krüger, 1972, 1975).

The C—O bond lengths (mean 1.45 Å) are slightly longer than the 1.430 Å reported for H<sub>4</sub>F in the gas phase by Geise, Adams & Bartell (1969), whereas the average C—C distance, 1.46 Å, is smaller (1.538 Å in the gas phase). Brauer & Krüger (1975) have explained these differences between coordinated H<sub>4</sub>F and H<sub>4</sub>F in the gas phase by a second-order hybridization.

It is of interest to compare  $(\eta^7\text{-cht})\text{MoI}_2 \cdot \text{H}_4\text{F}$  with the similar molecule  $(\eta^8\text{-cot})\text{ZrCl}_2 \cdot \text{H}_4\text{F}$  (cot = cyclo-octatetraenyl) described by Brauer & Krüger (1975). Although the difference of 0.22 Å between the average metal—carbon distances [2.472 (15) Å in the Zr complex] reflects the difference in covalent radii between Zr and Mo, the metal—O bond lengths are comparable, and the difference between Mo—I and Zr—Cl bond lengths is equal to the difference between the covalent radii of I and of Cl. These features have been observed in numerous Mo and Zr 'sandwich' complexes and may be due to the difference in energy between the Zr and the Mo orbitals (Atwood, Hunter, Alt & Raush, 1976). The Zr *d* orbitals mainly involved in bonding with the cot ligand are too high in energy to be used as effectively as the Mo *d* orbitals with the cht

ligand, but the Zr *s* and *p* orbitals, mainly used in the formation of the  $\sigma$  bonds with the O and Cl atoms, are only slightly higher in energy than the Mo *s* and *p* orbitals used in the formation of the bonds with O and I, thus explaining the similarities in pattern of  $\sigma$ -bond lengths.

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## Dibromodicarbonylbis(triphenylphosphine)tungsten(II)

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**Abstract.** C<sub>38</sub>H<sub>30</sub>Br<sub>2</sub>O<sub>2</sub>P<sub>2</sub>W, triclinic, *M<sub>r</sub>* = 923.85, *a* = 9.417 (11), *b* = 10.008 (9), *c* = 19.837 (9) Å,  $\alpha$  = 89.7 (1),  $\beta$  = 112.8 (1),  $\gamma$  = 88.0 (1)°, *U* = 1721.9 Å<sup>3</sup>, *d<sub>m</sub>* = 1.77, *d<sub>c</sub>* = 1.78 g cm<sup>-3</sup>, *F*(000) = 896, *Z* = 2, Mo

*K* $\alpha$  radiation,  $\lambda$  = 0.7107 Å,  $\mu$  = 61.3 cm<sup>-1</sup>, space group *P*1̄ from the successful structure solution. 3094 independent reflections have been refined to *R* = 0.079. The structure is made up of individual