

## Di- $\mu$ -oxo-bis[oxo( $\eta^5$ -cyclopentadienyl)molybdenum(V)]

BY CLAIRE COULDWELL AND KEITH PROUT

*Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England*

(Received 21 October 1977; accepted 5 November 1977)

**Abstract.** ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>4</sub>, C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>Mo<sub>2</sub>,  $M_r = 386.1$ , orthorhombic,  $a = 18.500$  (3),  $b = 8.993$  (2),  $c = 6.731$  (1) Å,  $U = 1119.8$  Å<sup>3</sup>. Systematic extinctions:  $0kl$ ,  $k + l = 2n + 1$ ;  $hk0$ ,  $h = 2n + 1$ . Space group  $Pnma$  or  $Pn2_1a$ ;  $Pnma$  from structure analysis.  $D_c = 2.29$  g cm<sup>-3</sup> for  $Z = 4$ ; Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 22$  cm<sup>-1</sup>. The structure contains discrete molecules of crystallographic point group symmetry  $C_s$ , the mirror plane passing through the two *cis* terminal oxo ligands, the two Mo atoms and the centroid of each  $\eta^5$ -cyclopentadienyl ring. The two bridging O atoms complete the distorted octahedral coordination of each Mo atom.

**Introduction.** Small brown hexagonal plates of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>4</sub> were kindly supplied by Dr M. L. H. Green and Mr M. Bunker. They were sensitive to air and moisture and were sealed under dry nitrogen in glass capillary tubes. It was not possible to measure their density. After survey precession photography, the selected crystal was set up on a Nonius CAD-4F PDP8-controlled  $\kappa$  geometry diffractometer; cell dimensions and the orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflexions.

The intensities of reflexions with  $\sin \theta/\lambda < 0.70$  Å<sup>-1</sup> were measured by an  $\omega/2\theta$  scan, a variable scan rate and an  $\omega$ -scan angle of  $(1.00 + 0.35 \tan \theta)^\circ$ . 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. Corrections were made for Lorentz and polarization effects, but not for absorption. A set of 1512 independent structure amplitudes was obtained.

The structure was solved by Patterson and Fourier techniques, with full-matrix least-squares refinement. All non-H atoms had anisotropic temperature factors. Difference syntheses permitted the location of the H atoms in their expected positions. They were positioned geometrically ( $C-H = 1.0$  Å;  $U_{iso} = 0.05$  Å<sup>2</sup>) and included in the structure factor calculations, their location being readjusted after each cycle. In the final stages an overall isotropic extinction parameter (109.5) was introduced (Larson, 1967). Each reflexion was assigned a weight  $w^{-1} = 1 + (0.1|F_o| - 1.5)^2$ , chosen to minimize the variation of  $w(|F_o| - |F_c|)^2$  with  $F_o$ .

The final  $R_w$  was 0.038 for 1512 reflexions. All calculations were performed on the Oxford University ICL 1906A computer with the Oxford CRYSTALS package (Carruthers, 1975). Complex neutral-atom

Table 1. *Fractional atomic coordinates, with estimated standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Mo(1)	0.20457 (2)	0.2500	0.09131 (7)
Mo(2)	0.07013 (2)	0.2500	-0.02220 (7)
O(1)	0.2025 (2)	0.2500	0.3441 (6)
O(2)	0.0210 (2)	0.2500	0.1904 (6)
O(3)	0.1430 (1)	0.4060 (3)	-0.0103 (4)
C(1)	0.2861 (4)	0.2500	-0.180 (1)
C(2)	0.3035 (3)	0.1262 (7)	-0.057 (1)
C(3)	0.3308 (3)	0.1770 (8)	0.115 (1)
C(4)	0.0594 (4)	0.2500	-0.373 (1)
C(5)	0.0227 (3)	0.3764 (7)	-0.3029 (8)
C(6)	-0.0381 (2)	0.3273 (5)	-0.1995 (7)
H(1)	0.2664	0.2500	-0.3179
H(2)	0.2966	0.0192	-0.0934
H(3)	0.3484	0.1131	0.2266
H(4)	0.1037	0.2500	-0.4580
H(5)	0.0374	0.4826	-0.3228
H(6)	-0.0755	0.3921	-0.1361

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

Mo(1)–Mo(2)	2.602 (1)		
Mo(1)–O(1)	1.702 (4)	Mo(2)–O(2)	1.695 (4)
Mo(1)–O(3)	1.932 (3)	Mo(2)–O(3)	1.948 (3)
Mo(1)–C(1)	2.366 (7)	Mo(2)–C(4)	2.370 (7)
Mo(1)–C(2)	2.364 (5)	Mo(2)–C(5)	2.373 (5)
Mo(1)–C(3)	2.430 (5)	Mo(2)–C(6)	2.433 (4)
C(1)–C(2)	1.422 (9)	C(4)–C(5)	1.406 (7)
C(2)–C(3)	1.345 (10)	C(5)–C(6)	1.394 (7)
C(3)–C(3 <sup>i</sup> )	1.313 (14)	C(6)–C(6 <sup>i</sup> )	1.390 (10)
Mo(1)–O(3)–Mo(2)	84.2 (1)		
O(1)–Mo(1)–O(3)	109.9 (1)	O(2)–Mo(2)–O(3)	109.7 (1)
O(3)–Mo(1)–O(3 <sup>i</sup> )	93.1 (2)	O(3)–Mo(2)–O(3 <sup>i</sup> )	92.2 (2)
C(1)–C(2)–C(3)	108.6 (5)	C(4)–C(5)–C(6)	107.6 (5)
C(2)–C(3)–C(3 <sup>i</sup> )	109.9 (4)	C(5)–C(6)–C(6 <sup>i</sup> )	108.5 (3)
C(2 <sup>i</sup> )–C(1)–C(2)	103.1 (7)	C(5 <sup>i</sup> )–C(4)–C(5)	107.9 (6)
Symmetry code			
None	<i>x, y, z</i>	(i) <i>x, ½ - y, z</i>	

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 interbond angles for the non-hydrogen atoms, with estimated standard deviations calculated from the full variance-covariance matrix.

**Discussion.** The structure contains discrete dimeric molecules of crystallographic point-group symmetry  $C_s$  (as shown in Fig. 1), the mirror plane passing through the two *cis* terminal oxo ligands, the two Mo atoms and the centroid of each  $\eta^5$ -cyclopentadienyl ring. The successful refinement in *Pnma*, which requires the molecule to have the mirror plane of symmetry, was taken as confirmation of this space group and no calculations were made in *Pn2<sub>1</sub>a*.

If the  $\eta^5$ -cyclopentadienyl ring is considered to occupy three coordination sites, a  $\eta^5$ -cyclopentadienyl ring, a *cis* terminal oxo ligand, and the bridging O

atoms are coordinated with each Mo atom to form two distorted octahedra sharing a common edge of O atoms. The bonding to Mo may be described as seven-coordination, for there is a direct Mo–Mo bond (2.602 Å), not unlike the Mo–Mo distances ranging from 2.552 to 2.569 Å in related di- $\mu$ -oxo complexes (Cotton & Morehouse, 1965; Knox & Prout, 1969; Delbaere & Prout, 1971; Drew & Kay, 1971).

The Mo(1)–O(3)–Mo(2) angle is 84.2°, and the Mo<sub>2</sub>O<sub>4</sub> bridge system is folded about O(3)···O(3<sup>i</sup>) with an angle of 152° between the two MoO<sub>2</sub> planes. Similar foldings (144 to 153°) are present in related complexes, and were said to allow the formation of the Mo–Mo bond without distorting the angles in the bridge, which range from 83.0 to 83.5°. The terminal oxo distances of 1.695 and 1.702 Å, and the bridging oxo distances of 1.932 and 1.948 Å are consistent with other Mo<sub>2</sub>O<sub>4</sub> structures.

In the  $\eta^5$ -cyclopentadienyl rings the average bond length is 1.38 Å, similar to that found in other complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974); the average bond angle is 108°. Mo–C distances lie in the range 2.36–2.43 Å and the normals to the rings at the Mo atoms are 2.08 and 2.09 Å.

We thank the Rhodes Trust for a Rhodes Visiting Fellowship at Somerville College (to CC).

#### References

- CARRUTHERS, J. R. (1975). In *CRYSTALS User Manual*. Oxford Univ. Computing Laboratory.
- COTTON, F. A. & MOREHOUSE, S. M. (1965). *Inorg. Chem.* **4**, 1377–1381.
- DELBAERE, L. T. J. & PROUT, C. K. (1971). *Chem. Commun.* p. 162.
- DREW, M. G. B. & KAY, A. (1971). *J. Chem. Soc. A*, pp. 1846–1850.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KNOX, J. R. & PROUT, C. K. (1969). *Acta Cryst.* **B25**, 1857–1866.
- LARSON, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- PROUT, C. K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* **B30**, 2290–2304.

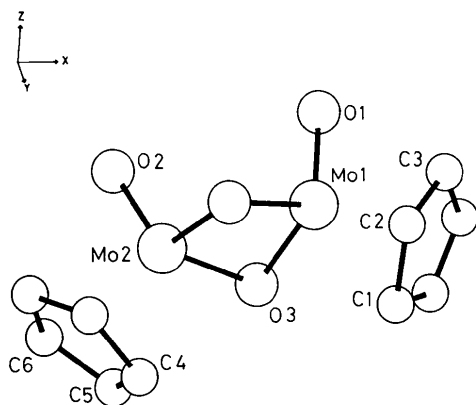


Fig. 1. The molecular structure of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>4</sub>.

\* Lists of structure factors and anisotropic thermal parameters for the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33150 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.