μ-Oxo-bis[(η⁵-cyclopentadienyl)iodooxomolybdenum(V)]

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Abstract. $C_{10}H_{10}I_2Mo_2O_3$, $[Mo_2(C_5H_5)_2I_2O_3]$, $M_r = 623.9$, monoclinic, $a = 8.168$ (1), $b = 6.483$ (1), $c = 14.327$ (1) Å, $\beta = 91.48$ (1)°, $U = 758.4$ Å³; systematic extinctions: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$; space group $P2_1/n$ ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$). $D_c = 2.73$ Mg m⁻³ for $Z = 2$. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 5.64$ mm⁻¹. The discrete dimeric molecule consists of two $Mo(\eta^5\text{-}C_5H_5)IO$ moieties which share a linear bridging O atom situated at an inversion centre. The Mo to bridging O atom length is 1.856 (1) Å and to the terminal O atom, 1.684 (6) Å. The Mo–I length is 2.709 (1) Å, and the coordination sphere of the Mo atom is completed by a η^5-cyclopentadienyl ligand.

Introduction. Small green plates of the title compound were supplied by Dr M. L. H. Green and Mr M. J. Bunker. They were sensitive to air and moisture and were sealed under dry nitrogen in glass capillaries. It was not possible to measure their density. After survey photography by Weissenberg and precession techniques, the selected crystal was set up on a Nonius CAD-4F diffractometer; cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions.

The intensities of reflexions with sin $\theta/\lambda < 0.70$ Å⁻¹ were measured by an $\omega/2\theta$ scan, a variable scan rate and an ω scan angle of $(1.00 + 0.35 \tan \theta)°$. 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, polarization and absorption effects (North, Phillips & Mathews, 1968). A final set of 1085 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; $U_{iso} = 0.05$ Å²) and included in the structure factor calculations, their locations being readjusted after each cycle. In the final stages an overall isotropic extinction parameter (87.4) was introduced (Larson, 1967). Each reflexion was assigned a weight $w = 1/\sum_{r=1}^{n} A_r T_r^*(X)$ where n is the

Table 1. *μ-Oxo-bis[(η⁵-cyclopentadienyl)iodooxo-molybdenum(V)]: atomic parameters*

	x	y	z
Mo(1)	0.28516 (7)	0.0723 (1)	0.02356 (4)
I(1)	0.25575 (7)	0.2663 (1)	−0.14354 (4)
O(1)	0.5	0	0
O(2)	0.1699 (8)	−0.1418 (9)	0.0109 (5)
C(1)	0.302 (1)	0.412 (1)	0.0963 (6)
C(2)	0.408 (1)	0.286 (2)	0.1466 (6)
C(3)	0.315 (1)	0.127 (2)	0.1839 (6)
C(4)	0.147 (1)	0.160 (2)	0.1599 (7)
C(5)	0.145 (1)	0.339 (2)	0.0999 (6)
H(1)	0.3350	0.5392	0.0620
H(2)	0.5294	0.3057	0.1548
H(3)	0.3592	0.0090	0.2215
H(4)	0.0513	0.0768	0.1801
H(5)	0.0465	0.3989	0.0670

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

Mo(1)–I(1)	2.709 (1)	Mo(1)–O(2)	1.684 (6)
Mo(1)–O(1)	1.856 (1)		
Mo(1)–C(1)	2.440 (8)	C(1)–C(2)	1.38 (1)
Mo(1)–C(2)	2.441 (8)	C(2)–C(3)	1.40 (1)
Mo(1)–C(3)	2.331 (9)	C(3)–C(4)	1.42 (2)
Mo(1)–C(4)	2.350 (8)	C(4)–C(5)	1.44 (2)
Mo(1)–C(5)	2.359 (9)	C(5)–C(1)	1.37 (1)
I(1)–Mo(1)–O(1)	91.10 (3)	C(5)–C(1)–C(2)	110.7 (8)
I(1)–Mo(1)–O(2)	104.5 (2)	C(1)–C(2)–C(3)	107.0 (9)
O(1)–Mo(1)–O(2)	107.5 (2)	C(2)–C(3)–C(4)	109.3 (9)
Mo(1)–O(1)–Mo(1ⁱ)	180.0	C(3)–C(4)–C(5)	105.2 (7)
		C(4)–C(5)–C(1)	107.7 (8)

Symmetry code: none x,y,z; (i) $1 - x, \bar{y}, \bar{z}$.

number of coefficients, A_r, for a Chebyshev series, T_r^* is the polynomial function, and $X = |F_o|/|F_o|(\text{max})|$. Three coefficients, A_r, were used with values 87.90, 123.14 and 47.11 (Rollett, 1965) and the final R_w was 0.040 for 1085 reflexions.

All calculations were performed on the Oxford University ICL 1906A computer with the Oxford *CRYSTALS* package (Carruthers, 1975). 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 interbond angles for the non-hydrogen atoms, with e.s.d.'s calculated from the full variance–covariance matrix.

Discussion. If the η^5-cyclopentadienyl ring is considered to occupy three coordination sites, the molecule consists of two distorted octahedra which share a common O atom situated on the space-group inversion centre (Fig. 1). The Mo(1)–O(1)–Mo(1^i) bridge is linear and the Mo(1)–O(2)(terminal) bonds are *trans*, as required by crystal symmetry. The arrangement is similar to that found in $[Mo_2\{(C_2H_5O)_2PS_2\}_4O_3].2C_6H_4Cl_2$ (Knox & Prout, 1969). The unidentate ligands are disposed about the Mo atom with a fairly regular geometry [I(1)–Mo(1)–O(1) 91·10 (3), I(1)–Mo(1)–O(2) 104·5 (2), O(1)–Mo(1)–O(2) 107·5 (2)°]. They also have pseudo threefold symmetry relative to the η^5-cyclopentadienyl ligand where the angles are Cp–Mo(1)–I(1) 114·2, Cp–Mo(1)–O(1) 113·4, Cp–

Mo(1)–O(2) 121·6° (Cp is the centroid of the five-membered ring).

The Mo(1)–O(1)(bridge) length is 1·856 (1) Å, whereas the Mo(1)–O(2)(terminal) bond is 1·684 (6) Å, showing considerable multiple-bond character. These values are comparable to those found in, for example, μ-oxo-bis[bis(isopropylthioxanthato)oxo-molybdenum(V)] (Zubieta & Maniloff, 1976) and $[Mo_2\{(C_2H_5O)_2PS_2\}_4O_3].2C_6H_4Cl_2$ (Knox & Prout, 1969). The Mo(1)–I(1) length [2·709 (1) Å] is shorter than that calculated by summing the covalent radii of Mo (1·61 Å) and I (1·33 Å) (Churchill & Fennessey, 1968).

In the η^5-cyclopentadienyl ring the average bond length is 1·40 Å, similar to that found in other complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974), and the average bond angle is 108·0°. The ring is planar within experimental error. The Mo–C distances are in the range 2·331 (9)–2·441 (8) Å, the perpendicular distance from the Mo atom to the ring is 2·060 Å, and the perpendicular to the ring at the Mo atom meets the ring close (0·14 Å) to its centroid.
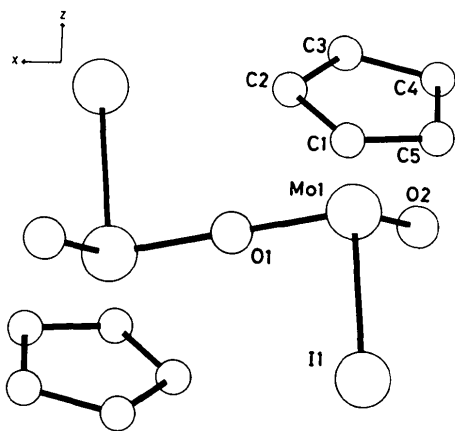
Fig. 1. The molecular structure of μ-oxo-bis[(η⁵-cyclopentadienyl)-iodooxomolybdenum(V)] projected down b.

References

CARRUTHERS, J. R. (1975). *CRYSTALS User Manual.* Oxford Univ. Computing Laboratory, Oxford.

CHURCHILL, M. R. & FENNESSEY, J. P. (1968). *Inorg. Chem.* 7, 953–959.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KNOX, J. R. & PROUT, C. K. (1969). *Acta Cryst.* B25, 2281–2285.

LARSON, A. C. (1967). *Acta Cryst.* 23, 664–665.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.

PROUT, K., CAMERON, T. S., FORDER, R. A., CRITCHLEY, S. R., DENTON, B. & REES, G. V. (1974). *Acta Cryst.* B30, 2290–2304.

ROLLETT, J. S. (1965). Editor, *Computing Methods in Crystallography.* Oxford: Pergamon Press.

ZUBIETA, J. A. & MANILOFF, G. B. (1976). *Inorg. Nucl. Chem. Lett.* 12, 121–126.