

Air-decomposition of $[\text{Mo}(\mu\text{-Br})\{\text{C}_5(\text{CH}_3)_5\}(\text{CH}_3)(\text{NO})]_2$; crystal structure of $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5\}(\text{O})_2](\mu\text{-O})$

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Abstract

Reaction of $[\text{Mo}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{Br})(\text{CH}_3)(\text{NO})]_2$ (I) with air in sunlight gives a mixture of two oxo complexes: $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5\}(\text{Br})(\text{O})_2]$ (III) and $[\text{Mo}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{O})_2](\mu\text{-O})$ (IV). The X-ray structure of IV shows a space group $P2_1/a$, with a 17.660(1), b 9.238(1), c 21.277(1) Å, β 101.79(1)°, and D_{cal} 1.590 g cm⁻³ for $Z = 6$. A final R value of 0.064 ($R_w = 0.064$), based on 3300 observed reflections was obtained. The dimeric molecule can be regarded as made up of two distorted tetrahedra which share a common oxygen atom. The asymmetric unit in the unit cell contains 1.5 dimeric molecules.

Introduction

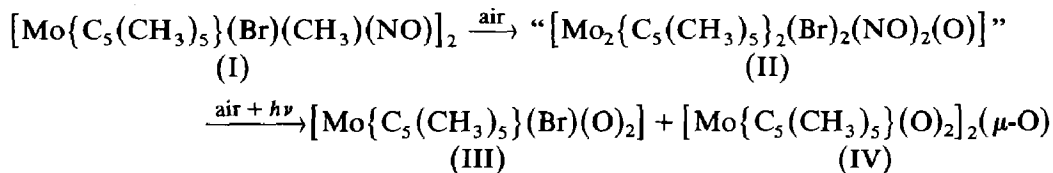
Recently, Legzdins et al. [1] have described the preparation and isolation of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{O})_2\text{R}]$ ($\text{R} = \text{CH}_2\text{SiMe}_3$) by reaction of $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})\text{R}_2]$ with O_2 . The potential interest of this type of oxoalkyl compound led us to investigate the behaviour of $[\text{Mo}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{Br})(\text{CH}_3)(\text{NO})]_2$ in the air.

Results and discussion

Preparative results. We have reported the preparation of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{Br})(\text{CH}_3)(\text{NO})]_2$ [2] and $[\text{Mo}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{Br})(\text{CH}_3)(\text{NO})]_2$ (I) [3] by reaction of the corresponding dihalo derivatives $[\text{MoCp}(\text{Br})_2(\text{NO})]$ with $[\text{Al}_2(\text{CH}_3)_6]$.

Solutions of complex I in toluene show no appreciable decomposition when dry oxygen is bubbled through for 4 h, but decomposition occurs readily when exposed to air. Under these conditions a solution which contains three species, II–IV, is

obtained, according to the ^1H NMR spectrum which shows three different resonances for the pentamethylcyclopentadienyl protons. The first species II ($\delta(\text{H})(\text{C}_5\text{Me}_5)$ 1.79 ppm(s), $\nu(\text{NO})$ 1605 cm^{-1}) (Scheme 1) is the main component when the reaction is carried out in the dark. We could not obtain a pure sample of this complex, which probably is an intermediate oxo- or hydroxo-bromo derivative produced by hydrolysis, which suggests that loss of the methyl group on hydrolysis facilitates further oxidation.



Scheme 1

When the reaction is carried out in the presence of sunlight for a week, $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5(\text{Br})(\text{O})_2]$ (III) ($\delta(\text{H})(\text{C}_5\text{Me}_5)$ 1.55 ppm (s)) and its hydrolysis product $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5(\text{O})_2]_2(\mu\text{-O})$ (IV) ($\delta(\text{H})(\text{C}_5\text{Me}_5)$ 1.62 ppm (s)) were obtained (Scheme 1). Pure samples of both were obtained by fractional crystallization from hexane or column chromatography on Florisil. Similar complexes containing the cyclopentadienyl group have been previously described [4,5], but as far as we know no X-ray structures have been reported.

IR spectra for complexes III, IV show the expected [4–7] IR absorptions for asymmetric and symmetric $\nu(\text{Mo}-\text{O})$ terminal bond vibrations at 915 and 883 cm^{-1} for complex III and at 915 and 885 cm^{-1} for complex IV. The asymmetric vibration $\nu(\text{Mo}-\text{O}-\text{Mo})$ for IV appears at 770 cm^{-1} whereas no symmetric Mo–O–Mo vibration is observed, which is consistent with the linear nature of the bridge [4] found in the X-ray diffraction study. The $\nu(\text{MoO})$ absorption frequencies are lower than those for the cyclopentadienyl derivatives $\nu(\text{M}=\text{O})$ 930 (asym), 898 (sym), $\nu(\text{Mo}-\text{O}-\text{Mo})$ 770 (asym) cm^{-1} for $[\text{Mo}(\text{C}_5\text{H}_5)(\text{O})_2(\mu\text{-O})_2]$ [4], and $\nu(\text{M}=\text{O})$ 920 (asym) and 885 (sym) cm^{-1} for $[\text{Mo}(\text{C}_5\text{H}_5)(\text{Br})(\text{O})_2]$ [5], because the increased electron donation from the pentamethylcyclopentadienyl group decreases the π -donation from the oxygen to the metal.

An X-ray study for a single crystal of IV was made to confirm its structure.

Crystal structure of $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5\}(\text{O})_2]_2(\mu\text{-O})$ (IV). An ORTEP drawing of the molecule based on the X-ray structural analysis is shown in Fig. 1, along with the numbering scheme. Atomic parameters for the non-hydrogen atoms are listed in Table 1. Important bond distances and bond angles are listed in Table 2.

The structure contains discrete dimeric molecules. The asymmetric unit in the unit cell contains 1.5 dimeric molecules, leading to the maximum monoclinic symmetry. There are three different Mo atoms in the asymmetric unit, three $\{\text{C}_5(\text{CH}_3)_5\}$ rings, seven oxygen atoms in a general position, and one oxygen atom at a symmetric centre which links two half dimeric molecules to produce the other dimers 2. There are no significant differences between the two crystallographically different dimers.

The dimeric molecule 1, can be regarded as two distorted octahedra which share a common oxygen atom situated on a pseudo inversion center if the η^5 -pentamethylcyclopentadienyl ring is considered to occupy three coordination sites. The unidentate ligands are disposed about the Mo atoms with a fairly regular geometry, the

O–Mo–O angle ranging from 102.7(7) to 107.0(5)°. The Mo(1)–O(2)–Mo(2) bridge is linear 179.1(6)° and the Mo–O terminal bonds are *trans*. The dimer **2** is similar to **1**, but the bridging oxygen, is situated at an inversion centre.

The Mo–O bridge bond lengths range from 1.886(8) to 1.852(8) Å, whereas the Mo–O terminal bonds lengths are between 1.659(16) and 1.693(12) Å, showing that there is important multiple-bond character, and at least a double bond [8]. These values are comparable with those found for [Mo₂(C₅H₅)₂I₂O₃] [9], [Mo₂(η⁵-

Table 1

Atomic parameters for [Mo(C₅(CH₃)₅)(O)₂](μ-O), coordinates and thermal parameters as $U_{\text{Eq}} = \frac{1}{3}\Sigma(U_{ij}a_i^*a_j^*a_i a_j \cos(a_i a_j)) \times 10^4$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
Mo(1)	0.0507(1)	0.0257(1)	0.6700(1)	571(4)
Mo(2)	0.2594(1)	−0.0126(1)	0.6624(1)	580(4)
Mo(3)	0.3927(1)	0.4796(1)	0.9841(1)	729(5)
O(1)	0.5000(0)	0.5000(0)	1.0000(0)	861(52)
O(2)	0.1558(4)	0.0070(9)	0.6655(5)	983(41)
O(3)	0.0123(6)	0.1349(10)	0.6081(6)	1061(53)
O(4)	0.0484(7)	0.1280(11)	0.7356(6)	1105(56)
O(5)	0.2980(6)	−0.1248(10)	0.7227(6)	1164(56)
O(6)	0.2607(7)	−0.1105(11)	0.5960(6)	1196(58)
O(7)	0.3761(8)	0.3519(12)	1.0360(10)	1708(93)
O(8)	0.3668(8)	0.3975(14)	0.9136(8)	1703(76)
C(21)	0.3158(8)	0.1791(13)	0.6093(6)	610(51)
C(22)	0.2575(6)	0.2450(11)	0.6350(7)	514(45)
C(23)	0.2754(7)	0.2370(12)	0.7016(7)	534(48)
C(24)	0.3455(8)	0.1695(13)	0.7196(6)	615(49)
C(25)	0.3708(6)	0.1263(12)	0.6636(8)	675(55)
C(31)	0.3872(7)	0.7425(11)	0.9723(7)	570(49)
C(32)	0.3850(8)	0.7092(14)	1.0394(7)	657(54)
C(33)	0.3166(9)	0.6339(15)	1.0368(8)	761(61)
C(34)	0.2791(7)	0.6129(13)	0.9717(8)	754(59)
C(35)	0.3220(8)	0.6866(13)	0.9343(6)	655(53)
C(211)	0.3223(11)	0.1639(20)	0.5415(8)	1152(87)
C(221)	0.1874(8)	0.3196(14)	0.5959(8)	923(66)
C(231)	0.2280(10)	0.3002(18)	0.7457(8)	1049(79)
C(241)	0.3905(11)	0.1380(19)	0.7872(9)	1243(86)
C(251)	0.4446(8)	0.0482(15)	0.6618(11)	1362(102)
C(311)	0.4488(10)	0.8279(17)	0.9499(9)	1033(79)
C(321)	0.4474(11)	0.7528(19)	1.0946(9)	1333(93)
C(331)	0.2889(13)	0.5792(25)	1.0951(11)	1627(122)
C(341)	0.2026(8)	0.5400(18)	0.9469(12)	1509(109)
C(351)	0.2984(13)	0.6985(22)	0.8627(8)	1310(98)
C(11)	0.0570(8)	−0.2366(14)	0.6867(11)	821(73)
C(12)	0.0219(13)	−0.2112(15)	0.6237(10)	910(87)
C(13)	−0.0483(10)	−0.1396(16)	0.6250(10)	920(71)
C(14)	−0.0505(9)	−0.1214(13)	0.6875(11)	800(70)
C(15)	0.0122(12)	−0.1829(17)	0.7246(8)	834(74)
C(111)	0.1308(10)	−0.3149(21)	0.7085(18)	2421(209)
C(121)	0.0543(22)	−0.2540(26)	0.5662(14)	2725(241)
C(131)	−0.1062(14)	−0.0901(27)	0.5681(13)	2393(151)
C(141)	−0.1161(17)	−0.0533(20)	0.7120(19)	2833(246)
C(151)	0.0266(22)	−0.1899(29)	0.7963(11)	2496(213)

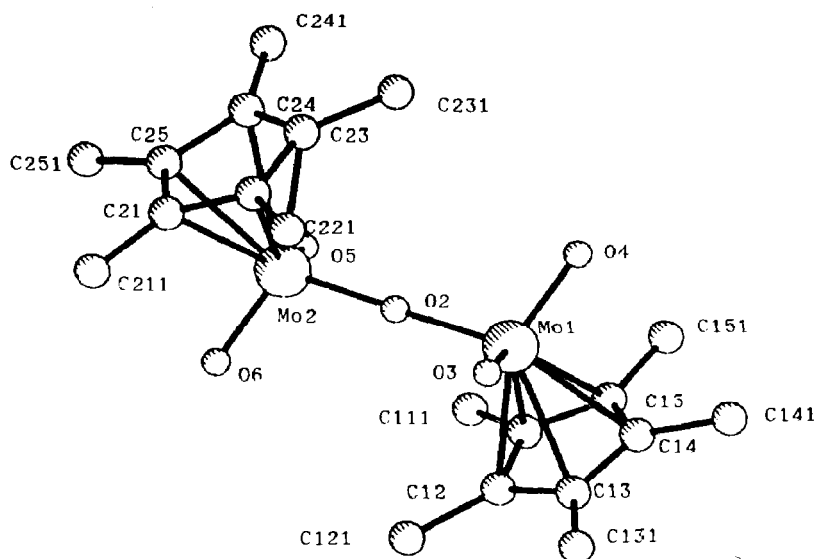


Fig. 1. The molecular structure of $[\text{Mo}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{O})_2]_2(\mu\text{-O})$ showing the atom numbering scheme. For sake of clarity the half molecule in the asymmetric unit cell is omitted.

$\text{C}_5\text{H}_5)_2\text{O}_4]$ [10] and $[\text{Mo}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{O}_4]$ [11].

The cyclopentadienyl rings form essentially parallel planes. The angle between the two planes in the same molecule in dimer 1 is $0.6(5)^\circ$, in good agreement with the 0° crystallographically imposed in dimer 2. C atoms of the methyl groups are in the same plane of the C atoms on the ring, with a maximum deviation of $0.06(2)$ Å. The distances of the Mo atoms from these planes range from $2.100(1)$ to $2.089(1)$ Å.

In the η^5 -pentamethylcyclopentadienyl rings, the average bond length is 1.389 , similar to that in other complexes, and the angles are normal. The Mo–C(cyclopentadienyl) bond lengths show normal values, from $2.323(12)$ to $2.449(10)$ Å.

Table 2

Important bond distances (Å) and bond angles ($^\circ$) with their e.s.d.'s

Mo(1)–O(2)	1.886(8)	Mo(1)–O(4)	1.693(12)
Mo(2)–O(2)	1.852(8)	Mo(2)–O(5)	1.682(11)
Mo(3)–O(1)	1.865(1)	Mo(2)–O(6)	1.682(12)
Mo(1)–O(3)	1.687(11)	Mo(3)–O(7)	1.683(17)
Mo(3)–O(8)	1.659(16)	Mo(1)–C(11)	2.448(13)
Mo(1)–C(12)	2.411(15)	Mo(1)–C(13)	2.371(16)
Mo(1)–C(14)	2.335(16)	Mo(1)–C(15)	2.419(17)
Mo(2)–C(21)	2.421(13)	Mo(2)–C(22)	2.449(10)
Mo(2)–C(23)	2.448(11)	Mo(2)–C(24)	2.422(12)
Mo(2)–C(25)	2.344(11)	Mo(3)–C(31)	2.441(10)
Mo(3)–C(32)	2.443(14)	Mo(3)–C(33)	2.391(16)
Mo(3)–C(34)	2.323(12)	Mo(3)–C(35)	2.408(12)
O(2)–Mo(1)–O(3)	104.96(49)	O(2)–Mo(1)–O(4)	106.44(50)
O(3)–Mo(1)–O(4)	103.64(49)	O(2)–Mo(2)–O(5)	106.40(50)
O(2)–Mo(2)–O(6)	105.38(53)	O(5)–Mo(2)–O(6)	103.68(51)
O(1)–Mo(3)–O(7)	104.99(51)	O(1)–Mo(3)–O(8)	107.03(50)
O(7)–Mo(3)–O(8)	102.74(67)	Mo(1)–O(2)–Mo(2)	179.07(66)

Experimental

The IR spectra were recorded in Nujol mulls over the range 4000–200 cm^{-1} on a Perkin–Elmer 599 Spectrophotometer. The ^1H NMR spectra were recorded on a Varian FT 80 A spectrometer with C_6D_6 as solvent. The C, H, and N analysis were carried out with a Perkin–Elmer 240B microanalyzer. Methane was determined by GLC using a Perkin–Elmer sigma 3B instrument fitted with a Carbobax column and a flame ionization detector.

Preparation of $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5\}(\text{Br})(\text{CH}_3)(\text{NO})]_2$ (I). Al_2Me_6 (0.90 mmol) was added to a solution of 1.50 g (1.80 mmol) of $[\text{Mo}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{Br})_2(\text{NO})]_2$ [3] in 40 ml of toluene at -68°C . Complex I (1.18 g, 93%) was isolated from the solution by a previously described procedure [2].

Reaction of I with air. A solution of 1.0 g (1.4 mmol) of $[\text{Mo}\{\text{C}_5(\text{CH}_3)_5\}(\text{Br})(\text{CH}_3)(\text{NO})]_2$ (I) in 50 ml of toluene was exposed to air in the presence of sunlight. The reaction was allowed to continue until the NMR signal corresponding to complex II [$\delta(\text{H})$ 1.79 ppm] had disappeared (ca. 1 week). The solution was filtered and evaporated to dryness. The residue contained a mixture of complexes III and IV.

Yellow crystals of complex IV were obtained by slow evaporation of hexane solutions of the residue. Anal. Found: C, 43.9; H, 5.4]. $\text{C}_{20}\text{H}_{30}\text{Mo}_2\text{O}_5$ calcd.: C, 44.3; H, 5.6%.

An analytically pure sample of complex III was obtained extracting the residue with 100 ml of hexane, evaporating the solution to dryness, and extracting the solid with 10 ml of toluene. The extract was chromatographed on a 15×1 cm column of Florisil with hexane, toluene, dichloromethane, and acetone used successively as eluents. The green complex III was obtained from the acetone solution. Anal. Found: C, 34.6; H, 4.9. $\text{C}_{10}\text{H}_{15}\text{BrMoO}_2$ calcd.: C, 35.0; H, 4.4%.

Crystal structure of complex $[\text{Mo}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}(\text{O})_2](\mu\text{-O})$ (IV). $\text{C}_{20}\text{H}_{30}\text{O}_5\text{Mo}_2$, $M = 542.334$ monoclinic, space group $P2_1/a$, a 17.660(1), b 9.238(1), c 21.277(1) Å, β 101.79(1) $^\circ$, V 3398.1(1) Å³, D_{cal} 1.590 g cm^{-3} for $Z = 6$, $F(000) = 1644$, Mo- K_α radiation (λ 0.7107 Å), $\mu(\text{Mo-}K_\alpha)$ 11.03 cm^{-1} .

Intensity data collection and refinements. A yellow crystal was mounted on a Enraf–Nonius, CAD-4 four circle diffractometer with graphite-monochromated Mo- K_α radiation; lattice parameters were determined by least-squares refinement of values for 25 reflections. Reflections were recorded by the $\omega/2\theta$ scan technique in the range ($2^\circ < \theta < 29^\circ$) and h -24 to 24 , k 0 to 12 , and l 0 to 29 .

Two standard reflections ($4\ 4\ 1$) and ($\bar{4}\ \bar{4}\ 1$) were measured after every 100 reflections and no significant change in intensities was detected. A total of 8995 unique reflections were collected, but only 3300 were considered observed with ($I > 3\sigma(I)$) and used in further calculations.

Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption nor extinction corrections were made. The structure was solved by a combination of heavy atom, direct methods, and Fourier synthesis.

The structure was refined on F by full matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. In the later stages of the refinement, H atoms, were included at fixed calculated positions, and with the temperature factors of the atoms to which they were attached to. Final R values of 0.064 and $R_w = 0.064$ (weighting scheme, empirical fit as to give no trends in $\langle w\Delta^2F \rangle$ vs.

$\langle F_o \rangle$ and vs. $\langle \sin \theta / \lambda \rangle$, were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from International Tables for X-ray Crystallography [12]. Calculations performed with X-ray System 80 [13], DIRDIF [14], PARST [15] and Pesos [16] on a VAX 11750 computer.

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