Synthesis, ^{95}Mo NMR Spectra and X-ray Crystal Structure of $MoO_2(C_{14}H_{11}N_2O)_2(C_2H_5OH)_1$ and $Mo_2O_5(C_{14}H_{11}N_2O)_2(C_2H_5OH)_1(H_2O)_1$

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Abstract

The crystal structures and ^{95}Mo NMR spectra of two complexes formed between 2-α-hydroxybenzylbenzimidazole ($C_6H_5\cdot CHOH\cdot C_7H_5N_2$ = HOBB), as its sodium salt, and MoO_2Cl_2 are reported. $[MoO_2(OBB)_2]\cdot EtOH$ (OBB = deprotonated HOBB) crystallizes in space group $P2_1/n$, with $a = 12.8441(7)$, $b = 15.917(3)$, $c = 13.314(2)$ Å, $\beta = 97.163(8)°$ and $Z = 4$. The structure was determined from 3096 observed reflections and refined to a final R value of 0.030. This complex is a six coordinate *cis*-dioxo species, the ^{95}Mo spectrum of which shows a single sharp peak at 56 ppm in dimethylformamide (DMF). The second complex, $[Mo_2O_5(OBB)_2]\cdot EtOH\cdot H_2O$, crystallizes in space group *Pbca*, with $a = 22.482(4)$, $b = 16.442(3)$, $c = 18.407(3)$ Å and $Z = 8$. The structure was determined from 2936 observed reflections and refined to a final R value of 0.061. The complex is a binuclear doubly bridged species in which one metal atom is six coordinate while the other is five coordinate. Its ^{95}Mo NMR spectrum in DMF shows a sharp peak at 124 ppm and a second broader much weaker peak at 51 ppm.

Introduction

The synthesis, ^{95}Mo NMR spectrum and a brief description of the crystal structure of $[MoO_2(OBB)_2]\cdot EtOH$ (I) (OBB is the deprotonated form of 2-α-hydroxybenzylbenzimidazole, $C_6H_5\cdot CHOH\cdot C_7H_5N_2$ = HOBB) were reported previously [1].

During the ^{95}Mo NMR study of I, in just one case, a spectrum with a low signal to noise ratio, which had a weak broad peak at *ca.* 120 ppm, was recorded. At the time this result was considered spurious, since a signal at 56 ppm was consistently obtained from all other solutions studied.

However, in view of a recent paper [2] concerning the significance of a signal at *ca.* 120 ppm in the ^{95}Mo NMR spectra of Mo(VI) complexes, it was decided to carry out a reinvestigation on this compound. During this study a new complex, *viz.* $[Mo_2O_5(OBB)_2]\cdot EtOH\cdot H_2O$ (II) was isolated, its ^{95}Mo NMR spectrum recorded and its crystal structure determined.

Experimental

Syntheses

The ligand HOBB was synthesized as described previously [1].

The synthesis and analysis of complex **I** were identical to those reported previously [1].

The synthesis of complex **II** was identical to that above, except that at no stage was recrystallization carried out. The filtrate resulting from the reaction was allowed to stand for a few days after which time crystals suitable for X-ray study were produced. *Anal.* Found: C, 48.1; H, 4.2; N, 6.7. Calc. for $C_{30}H_{30}Mo_2N_4O_9$; C, 46.1; H, 3.9; N, 7.2%.

NMR Data

^{95}Mo NMR spectra were recorded as described previously [1].

X-ray Data Collection and Reduction

Complex I

Complex I crystallizes from ethanol as pale lilac prisms elongated along *c*. A specimen of *ca.* 0.37 × 0.15 × 0.11 mm, bounded by (001), (00$\bar{1}$), (010), (0$\bar{1}$0), (101) and ($\bar{1}$0$\bar{1}$), was used for unit cell and intensity measurements, which were carried out on a Nicolet R3m/Eclipse S140 diffractometer system using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). *Crystal Data*: formula, $C_{30}H_{28}MoN_4O_5$; $M_r = 620.52$, monoclinic, $a = 12.8441(7)$, $b = 15.917(3)$, $c = 13.314(2)$ Å, $\beta = 97.163(8)°$, $V = 2700.8(6)$

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Å^3, space group $P2_1/n$, $Z = 4$, D_m (flotation) = 1.49(2) g cm^{-1}, $D_x = 1.526$ g cm^{-1}, $F(000) = 1272$, μ(Cu Kα) = 44.3 cm^{-1}.

Unit-cell parameters were determined by least-squares refinement of the angular settings of 19 automatically centered reflections (with $39° \leqslant \theta \leqslant 55°$). The space group was uniquely determined from the systematic absences ($h0l$: $h + l = 2n + 1$; $0k0$: $k = 2n + 1$).

Integrated intensities were collected using the ω scan technique and variable speed (3.9–29.3° min^{-1}) for all reflections up to $\theta = 55°$ within one quadrant. Two reflections (103 and 033), which were monitored every 50 measurements, showed no significant variation in their intensities. A total of 3376 unique reflections were collected, of which 3096 with $F_o > 3\sigma(F_o)$ were used in the structure analysis. The data were scaled using the check reflections and corrected for Lorentz and polarization effects. In the latter stages of refinement a numerical absorption correction was also applied.

Complex II

Complex **II** was obtained as described above as colourless prisms. A specimen of *ca.* 0.5 × 0.27 × 0.15 mm was used for unit cell and intensity measurements, which were carried out on a Philips PW1100 diffractometer system using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). *Crystal Data*: $C_{30}H_{30}Mo_2N_4O_9$, $M_r = 782.47$, orthorhombic, $a = 22.482(4)$, $b = 16.442(3)$, $c = 18.407(3)$ Å, $V = 6804(4)$ Å^3, space group *Pbca* (No. 61), $Z = 8$, $D_x = 1.53$ g cm^{-3}, $F(000) = 3152$, μ(Mo Kα) = 7.4 cm^{-1}.

Unit-cell parameters were obtained from least-squares fit of the setting angles of 25 reflections with 2θ values *ca.* 20°. The space group was uniquely determined from the systematic absences ($0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$).

Intensity data were measured using a θ:2θ scan mode with a constant scan speed of 0.5° s^{-1} and scan width of 0.9°. All reflections within the θ range of 3–25° in one octant were examined. Three standard reflections ($3\bar{3}\bar{2}$, $\bar{3}3\bar{2}$ and $\bar{3}\bar{3}2$), which were monitored every 5 h during data collection, showed no significant variation in their intensities. A total of 3082 unique reflections were collected, of which 2936 with $I > 3\sigma(I)$ were used in the calculations. The data were scaled using the check reflections and corrected for Lorentz and polarization effects. Absorption effects were ignored.

Structure Solution and Refinement

Complex I

The coordinates of the Mo atom were derived from a Patterson map and the positions of the other non-H atoms were located in difference Fourier maps. Least-squares refinement of the coordinates and isotropic thermal parameters for all the 40 atoms in the asymmetric unit gave $R = 0.10$ and when the atoms were allowed to refine anisotropically the discrepancy index was reduced to 0.052.

Hydrogen atoms (except those on ethanol CH_3 and OH groups) were placed at calculated positions using a riding atom model with fixed values of 0.960 Å for C–H and N–H distances and isotropic thermal parameters 1.2 times the equivalent isotropic value of their parent atoms. The OH hydrogen was located from a difference Fourier map and assigned fixed coordinates and isotropic temperature factor, which was allowed to refine. Attempts to introduce the methyl hydrogens gave unsatisfactory results, probably due to rotational disorder, so that these atoms were left out of the structure.

Refinement of the structure incorporating these 25 H atoms gave $R = 0.039$ and the application of a numerical absorption correction to the data reduced this value to 0.030.

During the last cycles of refinement one strong reflection ($\bar{1}01$), thought to be affected by extinction, was omitted and a weighting scheme was applied such that $w = 1/[\sigma^2(F_o) + 0.00020F_o^2]$. For the last cycle $R = 0.030$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{0.5} = 0.038$; the largest shift/e.s.d. ratio for any parameter was 0.12 and the average value was 0.015. The final Fourier difference map was featureless, with no peaks having an electron density larger than 0.29 e Å^{-3}.

Calculations and drawings were made using the SHELXTL program system [3]. Complex neutral-atom scattering factors from ref. 4 were employed.

Complex II

The coordinates of the atoms in the $Mo_2O_5^{2+}$ core were found by direct methods and the positions of the other non-H atoms were located in difference Fourier maps. Least-squares refinement of the coordinates and isotropic thermal parameters for all the 45 atoms in the asymmetric unit gave $R = 0.11$ and when the atoms were allowed to refine anisotropically the discrepancy index was reduced to 0.071.

Hydrogen atoms (except those on the solvent molecules) were introduced in the structure as described for **I**. Refinement of the structure incorporating these 30 H atoms gave $R = 0.066$.

Examination of the residual electron density revealed several peaks of 0.88–1.05 e Å^{-3} around the solvent molecules. To account for this feature, alternative (disordered) positions for O(1w), C(1e) and C(2e) [but not for O(1e)], were introduced in the structure. They were refined with the same (isotropic) temperature factor as the parent atoms and complementary s.o.f.s which refined to final values of 0.28(2) for O(1w′) and 0.50(2) for C(1e′)–C(2e′). At this point the R value was 0.063.

During the last cycles of refinement a weighting scheme was applied such that $w = 1.6064/[\sigma^2(F_o) + 0.001794F_o^2]$. For the last cycle $R = 0.061$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{0.5} = 0.086$; the largest shift/e.s.d. ratio for any parameter was 0.020 and the average value was 0.002. The electron density of the largest peak in the final Fourier difference synthesis was 0.72 e Å^{-3}.

Calculations were made using SHELX-76 [5] and XANADU [6] programs while for the drawings the ORTEP [7] program was used. Complex neutral-atom scattering factors from ref. 4 were employed.

Results and Discussion

Description of the Structures

Compound I

The final fractional coordinates and isotropic thermal parameters of the non-H atoms are shown in Table I, while the bond lengths and angles are given in Table II.

The crystals contain molecules of [$MoO_2(OBB)_2$] and ethanol molecules of solvation. In the complex molecule (Fig. 1) the metal atom is coordinated to two oxo groups (O_T) and to two bidentate organic ligands, bonded through N and O atoms, in a distorted *cis*-octahedral configuration. Overall the molecule displays approximate C_2 symmetry.

The Mo–O_T distances (1.695(2) and 1.720(2) Å) and the substended O_T–Mo–O_T angle (104.3(1)°) are close to 1.695(4) and 1.710(4) Å and 103.5(2)° found in [$MoO_2(OPB)_2$] (OPB = 2-(*o*-oxyphenyl)-benzimidazolato) [8] and similar to those found in several other *cis*-dioxo Mo(VI) complexes [9, 10]. In the longest of these two bonds the O atom is involved in a hydrogen bond.

The organic ligands are coordinated so that the N atoms are *trans* to the oxo groups. Due to the strong *trans* effect of the terminal oxygens [10, 11] the Mo–N distances of 2.287(2) and 2.361(3) Å are significantly longer than the 'normal' (*i.e.* unaffected by *trans* effect) value of *ca.* 2.13 Å, but are comparable to other Mo–N bond lengths similarly affected by the same *trans* effect [12–14]. As expected, the longest Mo–N distance is *trans* to the shortest Mo–O(oxo) bond.

The Mo–O(OBB) bonds have 'normal' lengths of 1.922(2) and 1.990(2) Å, comparable to 1.938(5) Å found in a similar bond of [$MoO_2(OPB)_2$] and to the ranges of 1.91(3)–1.97(3) Å and 1.952(7)–1.995(8) Å (two independent molecules in both cases) observed in [$MoO_2(OCH_2CH_2)_3N$]$^-$ [15] and in [MoO_2(benzohydroximato)$_2$]$^{2-}$ [16]. Here, again, in the longest Mo–O(OBB) bond the O atom is associated with a hydrogen bond.

TABLE I. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for Compound I

Atom	x	y	z	U_{eq}[a]
Mo	690(1)	1826(1)	4704(1)	33(1)*
O(1a)	59(2)	994(1)	5482(1)	37(1)*
O(1b)	642(2)	2853(1)	3845(2)	40(1)*
O(2)	1689(2)	2228(2)	5548(2)	45(1)*
O(3)	1290(2)	1125(2)	4009(2)	49(1)*
N(1a)	−506(2)	2537(2)	5614(2)	34(1)*
N(1b)	−814(2)	1739(2)	3591(2)	35(1)*
N(2a)	−1394(2)	2421(2)	6935(2)	44(1)*
N(2b)	−1831(2)	2299(2)	2302(2)	41(1)*
C(1a)	73(2)	857(2)	7287(2)	36(1)*
C(2a)	−213(3)	160(2)	7788(3)	54(1)*
C(3a)	372(4)	−96(3)	8681(3)	76(2)*
C(4a)	1253(4)	340(3)	9053(3)	74(2)*
C(5a)	1542(3)	1031(3)	8555(3)	67(2)*
C(6a)	943(3)	1294(3)	7686(3)	55(1)*
C(7a)	−541(2)	1122(2)	6297(2)	36(1)*
C(8a)	−839(2)	2030(2)	6286(2)	35(1)*
C(9a)	−887(2)	3334(2)	5836(2)	36(1)*
C(10a)	−1440(3)	3264(2)	6660(3)	43(1)*
C(11a)	−1930(3)	3949(2)	7061(3)	55(1)*
C(12a)	−1846(3)	4704(2)	6590(3)	55(1)*
C(13a)	−1302(3)	4782(3)	5761(3)	54(1)*
C(14a)	−817(3)	4110(2)	5368(3)	45(1)*
C(1b)	404(3)	3074(2)	2018(2)	39(1)*
C(2b)	566(3)	3835(3)	1576(3)	63(2)*
C(3b)	1058(4)	3870(3)	704(3)	86(2)*
C(4b)	1374(4)	3156(3)	284(3)	80(2)*
C(5b)	1220(3)	2396(3)	719(3)	70(2)*
C(6b)	751(3)	2356(2)	1599(3)	54(1)*
C(7b)	−102(3)	3033(2)	2992(2)	37(1)*
C(8b)	−931(2)	2362(2)	2944(2)	36(1)*
C(9b)	−1682(2)	1222(2)	3368(2)	34(1)*
C(10b)	−2331(2)	1574(2)	2551(2)	37(1)*
C(11b)	−3268(3)	1213(2)	2152(3)	51(1)*
C(12b)	−3539(3)	472(3)	2600(3)	61(1)*
C(13b)	−2889(3)	106(2)	3401(3)	53(1)*
C(14b)	−1952(3)	467(2)	3805(2)	43(1)*
C(1e)	3465(4)	3141(3)	4425(3)	81(2)*
C(2e)	3755(5)	2185(6)	4479(5)	146(4)*
O(1e)	2749(2)	3256(2)	3542(2)	56(1)*

[a]Starred items: U_{eq} defined as one third of the orthogonalized U_{ij} tensor.

The distortion in the octahedral configuration is reflected by the wide range of the *cis* angles (73.1(1)–104.3(1)°) and the departure of the *trans* angles from their nominal value of 180° (152.9(1)°, 161.2(1)° and 164.8(1)°). This distortion is due to the repulsion between the two oxo groups, which causes a well known opening in the corresponding O_T–Mo–O_T angle [10, 17] and, probably, to the steric requirements of the organic ligands. In addition, as indicated above, some degree of asymmetry in the lengths of analogous metal–donor bonds is due to hydrogen bonding.

TABLE II. Bonds Lengths (Å) and Angles (°) in the Coordination Sphere of Compound I

Mo–O(2)	1.720(2)	Mo–O(3)	1.695(2)
Mo–O(1a)	1.922(2)	Mo–O(1b)	1.990(2)
Mo–N(1a)	2.361(3)	Mo–N(1b)	2.287(2)
O(2)–Mo–O(3)	104.3(1)		
O(1a)–Mo–O(1b)	152.9(1)		
N(1a)–Mo–N(1b)	79.1(1)		
O(2)–Mo–O(1a)	103.6(1)	O(3)–Mo–O(1b)	102.2(1)
O(2)–Mo–O(1b)	92.1(1)	O(3)–Mo–O(1a)	95.2(1)
O(2)–Mo–N(1a)	88.1(1)	O(3)–Mo–N(1b)	90.7(1)
O(2)–Mo–N(1b)	161.2(1)	O(3)–Mo–N(1a)	164.8(1)
O(1a)–Mo–N(1a)	73.1(1)	O(1b)–Mo–N(1b)	73.4(1)
O(1a)–Mo–N(1b)	85.9(1)	O(1b)–Mo–N(1a)	85.7(1)
Mo–O(1a)–C(7a)	128.1(2)	Mo–O(1b)–C(7b)	126.5(2)
Mo–N(1a)–C(8a)	110.0(2)	Mo–N(1b)–C(8b)	113.5(2)
Mo–N(1a)–C(9a)	143.9(2)	Mo–N(1b)–C(9b)	140.0(2)

	X···O	X–H	H···O	X–H···O
Hydrogen Bonding				
N(2a)–H(2na)···O(1e)	2.746	0.960	1.787	177.0
N(2b)–H(2nb)···O(2)	2.920	0.960	2.132	138.4
O(1e)–H(1e)···O(1b)	2.858	0.960	1.902	170.7

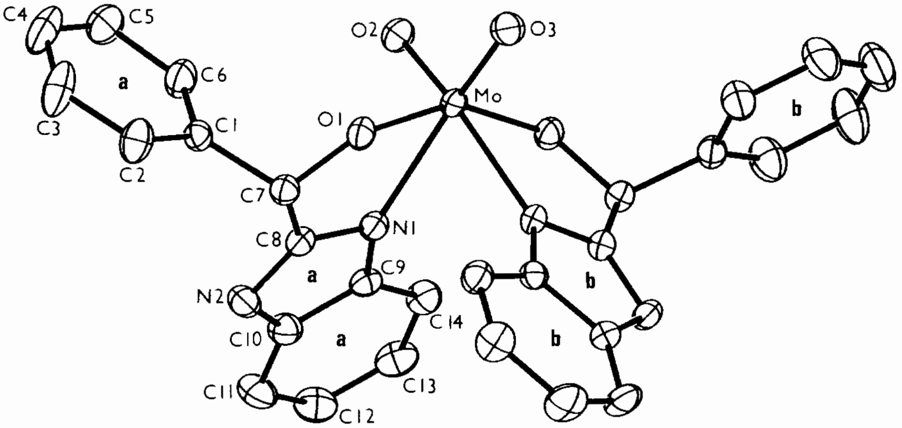


Fig. 1. Molecular structure of $MoO_2(C_{14}H_{11}N_2O)_2$.

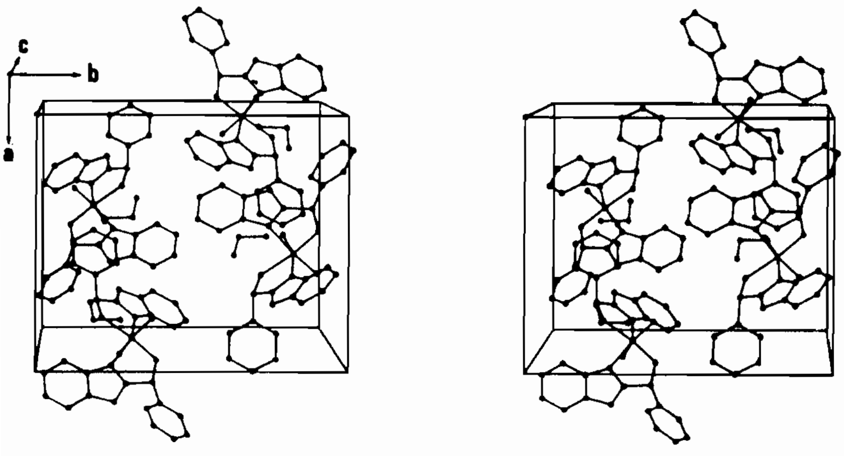


Fig. 2. Stereoscopic drawing of the packing in the crystal structure of $MoO_2(C_{14}H_{11}N_2O)_2(C_2H_5OH)_1$.

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Compound **II**

Atom	*x*	*y*	*z*	$U_{iso}/U_{eq}{}^a$
Mo(1)	−1300(1)	2124(1)	4321(1)	59(1)*
Mo(2)	88(1)	1617(1)	4538(1)	52(1)*
O(12)	−491(3)	2419(4)	4199(3)	59(3)*
O(1a)	−859(3)	1350(4)	4994(3)	45(2)*
O(2a)	−1573(5)	2000(7)	3469(5)	130(5)*
O(3a)	−1646(4)	2933(5)	4698(6)	107(5)*
O(1b)	368(3)	897(4)	5284(3)	55(3)*
O(2b)	710(4)	2112(5)	4238(5)	87(3)*
O(3b)	−27(3)	876(5)	3917(4)	68(3)*
N(1a)	−1924(4)	1238(5)	4675(5)	53(3)*
N(2a)	−2176(4)	106(6)	5251(5)	59(3)*
C(1a)	−1122(4)	844(7)	6190(5)	48(3)*
C(2a)	−1186(5)	1586(7)	6466(6)	64(4)*
C(3a)	−1200(6)	1697(9)	7207(8)	88(6)*
C(4a)	−1162(7)	1041(13)	7663(8)	103(7)*
C(5a)	−1109(6)	280(11)	7411(8)	94(6)*
C(6a)	−1085(5)	177(8)	6656(6)	71(5)*
C(7a)	−1113(4)	688(6)	5370(5)	45(3)*
C(8a)	−1743(5)	632(6)	5108(5)	50(4)*
C(9a)	−2525(5)	1059(7)	4518(6)	61(4)*
C(10a)	−2932(6)	1487(8)	4075(7)	73(3)*
C(11a)	−3489(6)	1140(10)	4037(8)	87(6)*
C(12a)	−3652(6)	419(12)	4395(9)	101(6)*
C(13a)	−3247(6)	25(9)	4829(8)	87(6)*
C(14a)	−2685(5)	361(7)	4882(7)	65(4)*
N(1b)	80(4)	2359(5)	5584(4)	48(3)*
N(2b)	236(4)	2333(5)	6782(4)	53(3)*
C(1b)	1070(5)	889(6)	6268(5)	52(4)*
C(2b)	1534(5)	1373(7)	6058(7)	74(5)*
C(3b)	2112(6)	1209(9)	6293(9)	90(6)*
C(4b)	2231(6)	563(9)	6712(8)	86(6)*
C(5b)	1773(7)	58(11)	6915(8)	104(7)*
C(6b)	1199(6)	201(8)	6699(6)	79(5)*
C(7b)	437(4)	1066(6)	6039(5)	47(4)*
C(8b)	254(4)	1935(6)	6155(6)	44(3)*
C(9b)	−68(5)	3104(7)	5874(6)	53(4)*
C(10b)	−275(5)	3819(7)	5524(6)	63(4)*
C(11b)	−372(6)	4483(7)	5935(7)	75(5)*
C(12b)	−266(6)	4463(8)	6693(8)	83(6)*
C(13b)	−74(6)	3782(6)	7040(6)	67(4)*
C(14b)	20(5)	3092(6)	6635(6)	57(4)*
O(1w)	296(8)	1666(8)	8196(7)	78(4)
O(1w′)	664(19)	1697(19)	8123(17)	78(4)
C(1e)	2201(19)	2913(28)	9195(23)	143(10
C(1e′)	2368(19)	3538(26)	8173(23)	143(10)
C(2e)	2184(18)	2284(25)	8606(24)	142(10)
C(2e′)	2067(20)	2773(26)	7990(23)	142(10)
O(1e)	2172(7)	3653(11)	8973(9)	177(6)

[a] Starred items: U_{eq} defined as one third of the orthogonalized U_{ij} tensor.

Bond lengths and angles in the organic ligands and in the solvent molecule are within normal values. The five-member chelate rings (Mo, O(1), C(7), C(8), N(1)) have slightly puckered conformations, with O(1) out of the mean plane of the other four atoms (0.21 Å in the *a* ligand and 0.10 Å in the *b* ligand).

In the crystal structure (Fig. 2) the complex molecules are linked directly to each other by N–H···O_T hydrogen bonds and indirectly, through the solvent molecules, by means of N–H···O(ethanol)–H···O-(OBB) bonds.

Complex II

The final fractional coordinates and isotropic thermal parameters of the non-H atoms are shown in Table III while the bond lengths and angles are given in Table IV.

The crystals contain molecules of the complex $[Mo_2O_5(OBB)_2]$ (Fig. 3) and water and ethanol molecules of solvation. In the binuclear complex each molybdenum is coordinated to two terminal oxygens (O_T) and to one bidentate organic ligand, bonded through N and O atoms. The metal atoms are linked by two asymmetric oxygen bridges, one formed by a μ-oxo ligand (O_B) while the other arises from the sharing of the oxygen atom of one OBB ligand (O_{LB}). Therefore, one of the metal atoms is five-coordinate whereas the other is six-coordinate.

The $Mo_2O_7N_2$ core displays all the four types of Mo–O bonds enumerated by Knobler *et al.* [17], *viz.* terminal (Mo–O_T), ligand (Mo–O_L), core-bridging (Mo–O_B) and ligand-bridging (Mo–O_{LB}) bonds. Its geometry is essentially identical to that of the previously reported $[Mo_2O_5(\text{n-POBB})_2]$ (n-POBB = 1-n-propyl-2-α-hydroxybenzylbenzimidazole, deprotonated) [18] the largest differences between them being 0.028 Å in Mo(2)–O(1a) and Mo(2)–O(2b), 0.026 Å in Mo(1)–O(12) and 3.1° in O(12)–Mo(2)–O(2b). These differences are probably not significant and, at least in part, due to packing forces, since O(12) and O(2b) are involved in hydrogen bonding.

The Mo–O_T distances are in the range 1.690(10)–1.711(9) Å, similar to that observed in I and to the average of 1.705 Å compiled by Schroder [19] over a large number of *cis*-dioxo Mo(VI) complexes. In the longest of these bonds the O atom participates in a hydrogen bond. The O_T–Mo–O_T angle in the six-coordinate Mo(2) (104.5(4)°) is also similar to that found in **I**, while in the five-coordinate Mo(1) the less crowded environment allows a larger angle opening (108.0(5)°).

In the asymmetric Mo–O_B–Mo bridge the O_B atom is closer to five-coordinate Mo(1). The O_B atom takes part in a hydrogen bond and, accordingly, the mean Mo–O_B distance, 1.927 Å, is slightly longer than the mean of 1.916 Å found in $[Mo_2O_5(\text{n-POBB})_2]$ [18]. On the other hand, this value is significantly longer than the average of *ca.* 1.89 Å observed in several single-bridged O_2Mo–O_B–MoO_2 complexes [20]. The Mo–O_B–Mo angle (115.3(4)°) is much smaller than those observed in single-bridged compounds [20] because of the existence of a second bridge.

TABLE IV. Bonds Lengths (Å) and Angles (°) in the Coordination Sphere of Compound II

Mo(1)–O(12)	1.898(7)	Mo(2)–O(12)	1.955(7)
Mo(1)–O(1a)	2.033(6)	Mo(2)–O(1b)	1.919(7)
Mo(1)–O(2a)	1.697(9)	Mo(2)–O(2b)	1.711(9)
Mo(1)–O(3a)	1.690(10)	Mo(2)–O(3b)	1.691(8)
Mo(1)–N(1a)	2.124(8)	Mo(2)–N(1b)	2.279(8)
		Mo(2)–O(1a)	2.330(6)
Mo(1)–O(12)–Mo(2)	115.3(4)		
Mo(1)–O(1a)–Mo(2)	96.2(2)		
O(12)–Mo(1)–O(1a)	76.4(3)	O(12)–Mo(2)–O(1b)	149.7(3)
O(12)–Mo(1)–O(2a)	105.5(4)	O(12)–Mo(2)–O(2b)	96.9(4)
O(12)–Mo(1)–O(3a)	106.8(4)	O(12)–Mo(2)–O(3b)	99.7(3)
O(12)–Mo(1)–N(1a)	147.7(3)	O(12)–Mo(2)–N(1b)	84.5(3)
O(1a)–Mo(1)–O(2a)	131.6(4)	O(1b)–Mo(2)–O(2b)	104.9(4)
O(1a)–Mo(1)–O(3a)	117.8(4)	O(1b)–Mo(2)–O(3b)	95.1(3)
O(1a)–Mo(1)–N(1a)	72.9(3)	O(1b)–Mo(2)–N(1b)	74.2(3)
O(2a)–Mo(1)–O(3a)	108.0(5)	O(2b)–Mo(2)–O(3b)	104.5(4)
O(2a)–Mo(1)–N(1a)	87.9(4)	O(2b)–Mo(2)–N(1b)	91.4(4)
O(3a)–Mo(1)–N(1a)	96.4(4)	O(3b)–Mo(2)–N(1b)	162.9(3)
		O(1a)–Mo(2)–O(12)	68.6(3)
		O(1a)–Mo(2)–O(1b)	85.7(3)
		O(1a)–Mo(2)–O(2b)	162.4(3)
		O(1a)–Mo(2)–O(3b)	88.2(3)
		O(1a)–Mo(2)–N(1b)	77.8(3)
Mo(1)–O(1a)–C(7a)	125.8(5)	Mo(2)–O(1b)–C(7b)	127.8(6)
Mo(1)–N(1a)–C(8a)	119.5(7)	Mo(2)–N(1b)–C(8b)	112.8(6)
Mo(1)–N(1a)–C(9a)	135.3(7)	Mo(2)–N(1b)–C(9b)	143.6(7)
		Mo(2)–O(1a)–C(7a)	133.7(5)

	X···O	X–H	H···O	X–H···O
Hydrogen Bonding				
N(2a)–H(2na)···O(1e)	2.782	0.960	1.831	170.3
N(2b)–H(2nb)···O(1w)	2.827	0.960	1.905	160.2
N(2b)–H(2nb)···O(1w′)	2.848	0.960	1.892	173.6
O(1w)–H(11w)···O(12)	2.965			
O(1w)–H(12w)···O(2b)	2.930			
O(1w′)–H(12w)···O(2b)	2.838			

As in other ligand-bridged complexes, the Mo–O_{LB}–Mo bridge is quite asymmetric, with the oxygen nearer to the five-coordinate Mo(1). The Mo–O_{LB} bond lengths (2.033(6) and 2.330(6) Å) are significantly longer than those in the Mo–O_B–Mo bridge, and their range is wider than *ca.* 2.00–2.22 Å observed in other *cis*-dioxo ligand-bridged Mo(VI) complexes [17, 21, 22].

The bridging moiety $Mo_2(\mu\text{-}O)_2$ is puckered, with an interplanar angle of 17.2° between the two O–Mo–O planes.

In the octahedral polyhedron about Mo(2) the Mo–N and Mo–O(OBB) bonds are *trans* to O_T and O_B atoms respectively and, therefore, their lengths (2.279(8) and 1.919(7) Å) are comparable to those observed in the analogous bonds of **I**. Since the Mo(1)–N bond is approximately *trans* to O_B, its length has a 'normal' value (2.124(8) Å), significantly shorter than that of Mo(2)–N.

Although the Mo···Mo distance (3.254(1) Å) is just at the longer end of the range observed in single Mo–Mo bonds [23], the +6 oxidation state of molybdenum rules out any metal-to-metal interaction.

The environment of Mo(1) can be described as a distorted trigonal bipyramid with O_B and N in the apical positions, both tilted towards O_{LB} (O_B–Mo(1)–N 147.7(3)°). The metal atom is displaced 0.167 Å from the equatorial plane, towards O_B.

The octahedral configuration about Mo(2) is somewhat more distorted than that of **I**, as shown by the wider range of the *cis* angles (68.6(3)–104.9(4)°) and the non-linearity of the *trans* angles (149.7(3)°, 162.4(3)° and 162.9(3)°). This greater distortion is obviously due to the strain imposed by the double bridge.

Bond lengths and angles in the organic ligands are within normal values. The five-member chelate ring (Mo, O(1), C(7), C(8), N(1)) has a slightly

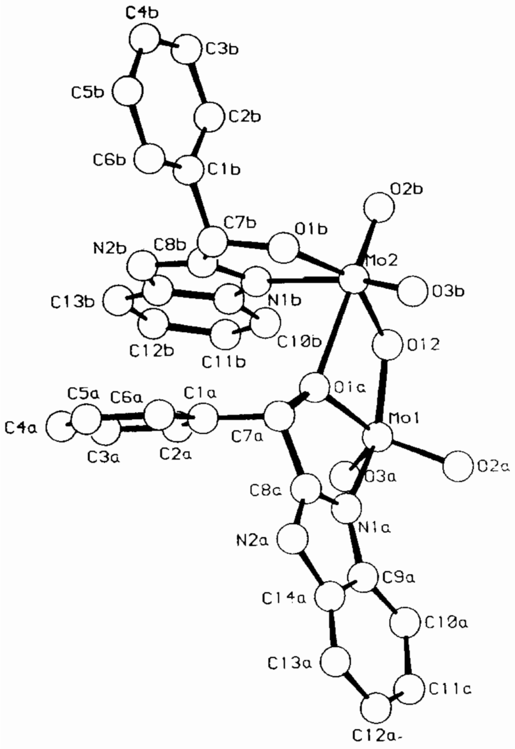


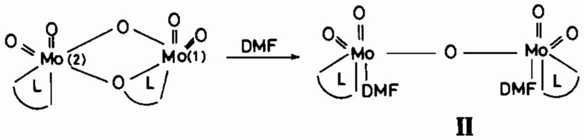
Fig. 3. Molecular structure of $Mo_2O_5(C_{14}H_{11}N_2O)_2(C_2H_5OH)_1(H_2O)_1$ with (C_2H_5OH) and (H_2O) omitted.

puckered conformation in the *a* ligand (C(8) is 0.074 Å out of the mean plane of the other four atoms), but is planar in the *b* ligand.

There is one water and one ethanol molecule of solvation per complex molecule, and both are disordered. The H_2O molecule is split in two positions, 0.84(4) Å apart, of which that with the larger s.o.f., 0.72(2), takes part in one more hydrogen bond than the other. The C–C moiety of EtOH is also disordered in two positions, both with the same occupancy and bonded to a single (*i.e.* non-disordered) oxygen, which is hydrogen bonded.

In the crystal structure of **II** the complex molecules are linked indirectly to each other, through the water molecules, by means of $N{-}H\cdots O(w){-}H\cdots O_T/O_B$ hydrogen bonds and also to the ethanol of solvation, by $N{-}H\cdots O$(ethanol) bonds.

As can be seen above the structure of $Mo_2O_5(OBB)_2(C_2H_5OH)_1(H_2O)_1$ is very similar to that of Mo_2O_5(n-POBB)$_2$ and this is also true of their ^{95}Mo NMR spectra in DMF, Table V. If a sufficiently concentrated solution of $Mo_2O_5(OBB)_2(H_2O)_1(C_2H_5OH)_1$ in DCM had been obtained then it is claimed that its ^{95}Mo NMR spectrum would have been similar to that of Mo_2O_5(n-POBB)$_2$, Table V. A suggested explanation of the ^{95}Mo NMR data for Mo_2O_5(n-POBB)$_2$ has been given [2] and involves the conversion in DMF of the ligand-bridged dimer into a single oxo-bridged species similar to that reported for $Mo_2O_5(C_{13}H_9N_2O)_2(C_3H_7NO)_2(H_2O)_{1.5}$ [20]. A similar mechanism to explain the ^{95}Mo NMR data of $Mo_2O_5(OBB)_2$ is suggested *viz.*



II

The long Mo(2)–O(1) bond (2.330 Å) is broken and the vacant site on Mo(2) occupied by a DMF molecule; the vacant site on the five-coordinate Mo(1) is filled by a second DMF molecule to give the species **II**, which is structurally analogous to $Mo_2O_5(C_{13}H_9N_2O)_2(C_3H_7NO)_2(H_2O)_{1.5}$ [20]. It is species **II** which, it is claimed, gives rise to the ^{95}Mo NMR signal at 124 ppm. Attempts to isolate **II** were not successful, only $MoO_2(OBB)_2$ could be crystallized from DMF solutions.

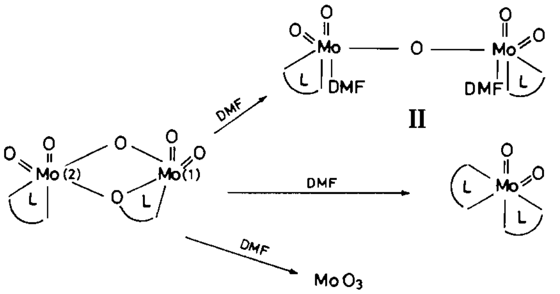
The weak signal at 51 ppm is probably due to a monomeric species; $MoO_2(OBB)_2(C_2H_5OH)_1$ and

TABLE V. ^{95}Mo NMR Spectral Data

Complex	Solvent[a]	Chemical shift (ppm)	Relative signal intensity	Linewidth (Hz)
MoO_2(n-POBB)$_2$	DCM[b]	50		170
Mo_2O_5(n–POBB)$_2$	DMF[c]	125	very strong	147
		59	weak	
	DCM[d]	76	equal	196
		47	equal	196
$MoO_2(OBB)_2(C_2H_5OH)_1$	DMF[b]	56		374
	DCM	insoluble		
	DMF	124	very strong	163
$Mo_2O_5(OBB)_2(H_2O)_1(C_2H_5OH)_1$		51	weak	
	DCM	insoluble		

[a] All solutions were saturated. [b] Ref. 24. [c] Ref. 2. [d] Ref. 18.

$MoO_2(OBB)_2(CH_3COCH_3)_1$ are known to give signals at 56 and 55 ppm respectively in DMF [24]. A more complete scheme would therefore be



with, perhaps, a complex equilibrium between all species. The above scheme rests on the assumption that the peak at 124 ppm is due to an $Mo_2O_5^{2+}$ core species as exemplified by $Mo_2O_5(C_{13}H_9N_2O)_2(C_3H_7NO)_2(H_2O)_{1.5}$ [20]. However, recent work by us has shown that the complex $Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2(C_3H_7ON)_2$ which is tetrameric with alternating Mo–O bonds gives a ^{95}Mo NMR signal at 125 ppm [25].

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