Some Binuclear Molybdenum(VI) Complexes obtained from Condensation Reactions: Their Crystal and Molecular Structures†

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Molybdenum(VI) complexes of three new structural types have been obtained from ethanol solution through use of triethoxymethane as condensing agent. The complex $MoO_3(dmso)_{1.33}$ (dmso = dimethyl sulphoxide) alone yields $[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**), $MoO_3(dmso)_{1.33}$ with 2-amino-1,3-dihydroxy-2-methylpropane (H_2amp) gives $[\{MoO_2(amp)\}_2]\cdot$2dmso (**2**), and two isomeric compounds $[\{MoO(hmmp)(OEt)\}_2]$, (**3a**) and (**3b**), are obtained from $[MoO_2(Hhmmp)]$ (H_3hmmp = 1,3-dihydroxy-2-hydroxymethyl-2-methylpropane). The crystal structures of these compounds have been determined and show that all four contain coplanar di-μ-O_{lb} bridges (O_{lb} = deprotonated ligand-bridging O). The molecules of (**1**), (**2**), and (**3b**) have C_i symmetry, while (**3a**) has C_2 symmetry. The O_{lb}–Mo–O_{lb} angles are 69—72°, the low values being imposed by the bridging ligands. For $[\{MoO_2(amp)\}_2]$ there is the unusual feature that each bridging atom belongs to a five-membered ring, and there is evidence of consequent ligand strain.

Thermally induced condensation reactions using MoO_3 afford an important means of obtaining neutral Mo^{VI} complexes from deprotonated di- or poly-hydroxylic ligands.[1] The method is best suited for ligands which can readily provide both charge balance and six-co-ordination around a molybdenum centre, especially around the *cis*-dioxo MoO_2 core. The use of alternative Mo-containing reactants, with condensing agents to effect reaction at lower temperature, has been reported briefly.[2] We now give three examples of the use of triethoxymethane (teom) in reactions which afford access to new products. Their structural features have been established through *X*-ray crystal analysis. All are to be found to be binuclear through ligand-oxygen (O_{lb}) bridging.

It is shown that triethoxymethane promotes condensation of the dimethyl sulphoxide compound '$MoO_3(dmso)_{1.33}$'[3] with ethanol to give an ethoxy derivative $[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**) in which the two Mo centres are linked through ethoxy bridges. However with the addition of 2-amino-1,3-dihydroxy-2-methylpropane (H_2amp) to the reactants,[2] the product is $[\{MoO_2(amp)\}_2]\cdot$2dmso (**2**) in which the ligand is co-ordinated through both the alkoxy and amino functions. The structure of this derivative shows O_{lb} bridging through an atom of a five-membered ring. In addition the structures of two previously reported isomeric compounds[2] of composition MoO(hmmp)(OEt), (**3a**) and (**3b**), where H_3hmmp = 1,3-dihydroxy-2-hydroxymethyl-2-methylpropane are described. Both isomers are formed from $[MoO_2(Hhmmp)]$[4] using teom in ethanol. As was inferred originally from the i.r. spectra and compositions, the compounds contain the unusual mono-oxomolybdenum core, formally MoO^{4+}. The spectra show only a single ν(Mo–O_t) band, and no ν(O–H) bands. The similarity of their spectra pointed to a close structural relationship.

Experimental

Preparation of Compounds.—$[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**). $MoO_3(dmso)_{1.33}$ (0.8 g) was dissolved in a mixture of dmso (4 cm^3), ethanol (1 cm^3), and teom (2.5 cm^3) with stirring at 80 °C, the solution being maintained at this temperature for 10—15 min. At this concentration a white finely crystalline mass separated on cooling, but with two-fold (or greater) dilution well-formed colourless crystals were obtained. Yellow molybdic acid ($MoO_3\cdot 2H_2O$) can be used in place of $MoO_3(dmso)_{1.33}$ for the preparation. The acid (0.58 g) was dissolved in dmso (4 cm^3) at *ca.* 100 °C. Ethanol (1 cm^3) and teom (2.5 cm^3) were added and the solution heated to 80 °C as before. The compound is rapidly decomposed upon exposure to atmospheric moisture.

In an attempt to obtain the mononuclear complex $[MoO_2(OEt)_2(dmso)_2]$, complex (**1**) (1.5 g) was redissolved in dmso (11 cm^3) with teom (1 cm^3), but it recrystallised unchanged.

$[\{MoO_2(amp)\}_2]\cdot$2dmso (**2**). $MoO_3(dmso)_{1.33}$ (1.0 g) and H_2amp (0.75 g) were dissolved in dmso (4.5 cm^3). Triethoxymethane (3.0 cm^3) was added and the temperature raised to 90—100 °C for 3—4 min. The solution became somewhat brown and was decanted from any yellow sediment which separated on cooling. Colourless needle-like crystals appeared after 2—3 d (Found: C, 23.3; H, 4.8; N, 4.5. Calc. for $C_6H_{15}MoO_5S$: C, 23.3; H, 4.85; N, 4.4%).

$[\{MoO(hmmp)(OEt)\}_2]$, (**3a**) *and* (**3b**). An earlier procedure[2] was modified to produce suitable crystals of the two isomers. $[MoO_2(Hhmmp)]$ (0.5 g) was quickly (< 5 min) dissolved in ethanol (5 cm^3) and teom (3 cm^3) with stirring under reflux to give a yellow solution. The solution was held at 80 °C for a further 5 min (but no longer) and set aside to allow slow crystallisation at room temperature (which usually began after *ca.* 30 min). Two types of yellow crystals separated, usually in admixture: diamond-shaped tabloids of (**3a**) and elongated plates grading towards acicular, (**3b**). The latter seemed to predominate when crystallisation was slow. Analyses showed identical compositions [Found for (**3a**): C, 31.0; H, 5.1; Mo, 34.7. Found for (**3b**): C, 30.7; H, 5.5; Mo, 34.6. Calc. for $C_7H_{14}MoO_5$: C, 30.7; H, 5.1; Mo, 35.0%]. Distinctively different features of the i.r. spectra (cm^{-1}) were seen: (**3a**), 1 065s, 1 045ms, 620s, and 607w; (**3b**), 1 068m, 1 040s, 633s, and 606s.

X-Ray Structure Determinations.—These were made on a Nicolet R3M four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) with the crystal at 130 K. Crystals sensitive to atmospheric moisture [(**1**) and (**2**)] were coated with epoxy glue immediately on removal from the mother-liquor and mounted in the cold N_2 stream on the diffractometer within 5 min. The general procedure was as

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Crystal data, experimental conditions, and refinement

Compound	**(1)**	**(2)**	**(3a)**	**(3b)**
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$I2/a^{a}$	$P\bar{1}$
a/Å	8.308(3)	20.869(7)	13.137(2)	7.380(1)
b/Å	8.914(3)	8.083(2)	10.363(1)	8.356(2)
c/Å	9.554(2)	17.333(5)	14.359(2)	8.437(2)
α/°	63.07(2)			111.02(2)
β/°	85.58(2)	128.24(2)	93.24(1)	93.68(2)
γ/°	62.88(2)			100.01(2)
U/Å^3	554.4(2)	2 296(1)	1 951.7(5)	473.7(2)
Z (dimer)	1	4	4	1
Crystal size (mm)	0.4 × 0.36 × 0.20	0.25 × 0.25 × 0.06	0.13 × 0.13 × 0.06	0.28 × 0.06 × 0.04
μ/cm^{-1}	13.3	12.9	13.0	13.4
Scan mode	θ–2θ	ω	θ–2θ	θ–2θ
Range, 2θ	3.5—55	3—50	3—50	3—50
Range, h	0—11	−25—25	−15—15	−8—8
Range, k	−12—12	0—10	0—12	−9—9
Range, l	−13—13	0—21	0—12	0—9
Total reflections	2 743	2 260	1 905	1 814
Unique reflections	2 564	2 028	1 593	1 672
Observed reflections, $I > 3\sigma(I)$	2 534	1 619	1 330	1 365
Parameters refined	127	131	118	118
Weighting g	0.000 17	0.000 82	0.000 11	Unit weights
$R(R')^{b}$	0.0345 (0.0597)	0.0456 (0.0670)	0.0237 (0.0262)	0.0279 (0.0324)

[a] Alternative setting to $C2/c$ (no. 15). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma(w||F_o| - |F_c||^2)/\Sigma(w|F_o|)^2]^{\frac{1}{2}}$.

Table 2. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Complex (**1**)				Complex (**3a**)			
Mo	3 123(1)	2 277(1)	4 342(1)	Mo	2 189(1)	5 577(1)	6 155(1)
O(1)	1 632(3)	1 875(3)	3 609(3)	O(1)	1 083(2)	5 543(3)	6 703(2)
O(2)	1 911(3)	3 210(3)	5 527(3)	C(1)	4 194(3)	7 307(4)	6 252(3)
O(3)	2 901(3)	4 414(3)	2 390(3)	C(2)	4 333(3)	6 454(4)	5 395(3)
C(31)	1 651(6)	5 385(5)	969(4)	O(2)	3 458(2)	5 664(2)	5 154(2)
C(32)	108(5)	7 225(5)	783(5)	C(3)	3 243(3)	8 142(4)	6 095(3)
O(4)	5 468(3)	373(7)	3 706(2)	O(3)	2 338(2)	7 403(2)	6 110(2)
C(41)^{a}	5 243(7)	546(7)	2 125(5)	C(4)	4 114(3)	6 499(4)	7 137(2)
C(42)^{a}	6 385(7)	1 459(8)	1 153(5)	O(4)	3 289(2)	5 607(3)	7 062(2)
C(43)^{b}	6 055(13)	917(13)	2 092(11)	C(5)	5 130(3)	8 184(4)	6 374(3)
C(44)^{b}	5 046(16)	509(16)	1 211(14)	O(6)	2 414(2)	3 794(3)	6 066(2)
O(5)	5 327(3)	2 715(3)	5 022(3)	C(6)	3 335(3)	3 065(4)	6 053(3)
S	7 161(1)	2 433(1)	4 452(1)	C(7)	3 173(3)	1 694(4)	6 335(3)
C(51)	8 427(4)	2 173(6)	6 039(4)				
C(52)	6 750(5)	4 758(5)	3 009(4)				
Complex (**2**)				Complex (**3b**)			
Mo	658(1)	6 269(1)	4 932(1)	Mo	1 389(1)	4 686(1)	3 364(1)
O(1)	1 649(3)	5 963(7)	5 389(4)	O(1)	3 427(4)	5 780(4)	3 114(4)
O(2)	272(3)	7 670(6)	4 004(4)	C(1)	−2 713(6)	3 238(6)	1 290(6)
N	−301(3)	5 762(7)	6 149(4)	C(2)	−2 954(6)	2 884(6)	2 940(6)
C(1)	−440(4)	7 471(9)	5 755(5)	O(2)	−1 307(4)	3 724(4)	4 203(4)
C(2)	−936(5)	8 522(9)	5 956(6)	C(3)	−2 081(7)	5 211(6)	1 728(6)
C(3)	−918(4)	7 330(10)	4 643(5)	O(3)	−198(4)	5 836(4)	2 531(4)
O(3)	−594(3)	5 970(6)	4 458(3)	C(4)	−1 317(6)	2 264(6)	308(6)
C(4)	380(4)	8 295(9)	6 213(6)	O(4)	474(4)	2 707(4)	1 297(4)
O(4)	841(3)	7 502(7)	5 982(4)	C(5)	−4 602(7)	2 586(7)	144(6)
S	3 048(1)	9 175(3)	6 359(1)	O(6)	2 323(4)	3 094(4)	4 117(4)
O(11)	3 756(3)	10 384(7)	6 855(4)	C(6)	1 475(7)	1 399(6)	4 065(7)
C(12)	3 504(5)	7 184(10)	6 723(7)	C(7)	2 955(7)	460(7)	4 355(7)
C(13)	2 700(4)	9 278(11)	7 073(5)				

[a] Site of major occupancy. [b] Site of minor occupancy.

follows: space group from systematic absences; cell parameters determined using least-squares refinement on 25 accurately-centred reflections; crystal stability monitored using three standard reflections every 100 reflections, but no significant variations; Lorentz-polarisation correction applied, empirical absorption corrections included for (**1**) and (**2**); Mo atoms located from Patterson map and the remaining non-hydrogen atoms from difference Fourier syntheses; least-squares refinement with anisotropic thermal parameters through minimisation of $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + gF_o^2]^{-1}$; H

Table 3. Bond lengths (Å) and angles (°)[a]

Complex (1)				Complex (2)			
Mo–O(1)	1.708(3)	O(1)–Mo–O(2)	102.9(1)	Mo–O(1)	1.715(8)	O(1)–Mo–O(2)	105.1(4)
Mo–O(2)	1.703(3)	O(1)–Mo–O(3)	95.4(1)	Mo–O(2)	1.708(8)	O(1)–Mo–O(3)	164.8(3)
Mo–O(3)	1.912(2)	O(1)–Mo–O(4)	92.3(1)	Mo–O(3)	2.213(9)	O(1)–Mo–O(3′)	94.4(3)
Mo–O(4)	2.187(2)	O(1)–Mo–O(4′)	99.1(1)	Mo–O(3′)	2.142(8)	O(1)–Mo–O(4)	99.4(3)
Mo–O(4′)	2.062(2)	O(1)–Mo–O(5)	171.2(1)	Mo–O(4)	1.895(9)	O(1)–Mo–N′	87.8(3)
Mo–O(5)	2.234(3)	O(2)–Mo–O(3)	105.7(1)	Mo–N′	2.244(9)	O(2)–Mo–O(3)	87.9(3)
O(3)–C(31)	1.415(4)	O(2)–Mo–O(4)	156.9(1)	N–C(1)	1.488(11)	O(2)–Mo–O(3′)	152.7(3)
O(4)–C(41)[b]	1.466(6)	O(2)–Mo–O(4′)	90.9(1)	O(3)–C(3)	1.427(12)	O(2)–Mo–O(4)	104.7(3)
O(4)–C(43)[c]	1.508(10)	O(2)–Mo–O(5)	85.7(1)	O(4)–C(4)	1.406(14)	O(2)–Mo–N′	88.8(3)
C(31)–C(32)	1.490(5)	O(3)–Mo–O(4)	89.8(1)	C(1)–C(2)	1.538(16)	O(3)–Mo–O(4)	84.5(3)
C(41)–C(42)[b]	1.519(9)	O(3)–Mo–O(4′)	154.8(1)	C(1)–C(3)	1.530(12)	O(3)–Mo–N′	84.5(3)
C(43)–C(44)[c]	1.486(22)	O(3)–Mo–O(5)	80.4(1)	C(1)–C(4)	1.522(12)	O(3′)–Mo–O(4)	90.4(3)
O(5)–S	1.526(2)	O(4)–Mo–O(5)	80.0(1)	S–O(11)	1.517(7)	O(3′)–Mo–N′	72.8(3)
S–C(51)	1.779(5)	O(4′)–Mo–O(5)	82.2(1)	S–C(12)	1.774(10)	O(4)–Mo–N′	162.2(3)
S–C(52)	1.775(3)	Mo–O(3)–C(31)	128.0(3)	S–C(13)	1.784(13)	Mo–O(4)–C(4)	138.3(4)
Mo ··· Mo	3.496	Mo–O(5)–S	130.8(2)	Mo ··· Mo	3.550	Mo′–N–C(1)	115.2(5)

[a] Values for angles given in Table 5 are omitted. [b] Within site of major occupancy by bridging group. [c] Within site of minor occupancy.

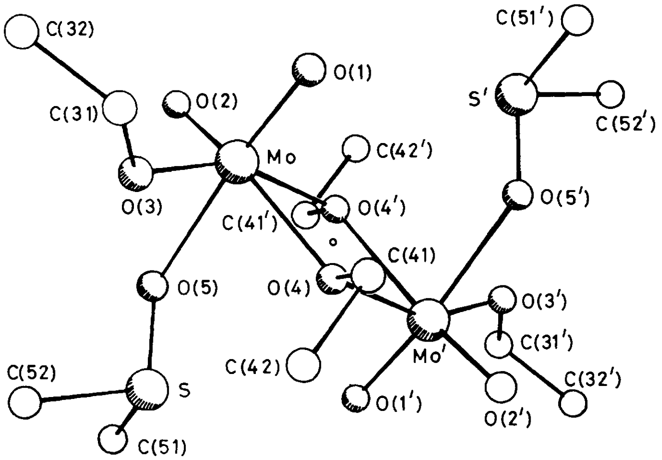

Figure 1. Molecular structure of $[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**). The atoms C(41) and C(42) of the ethyl groups are shown in the positions of major occupancy

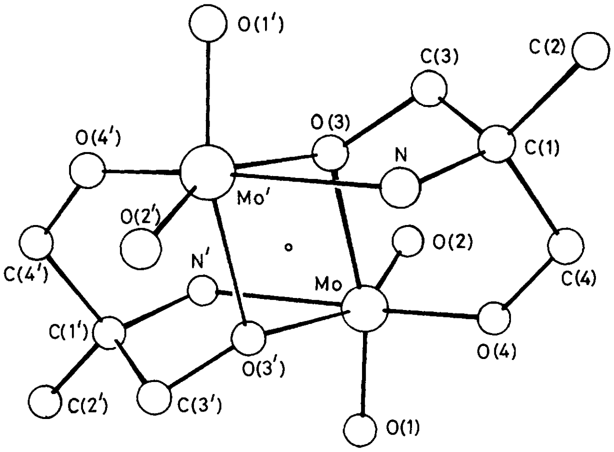

Figure 2. Molecular structure of $[\{MoO_2(amp)\}_2]$, showing the relationship between the five-membered ring Mo′NC(1)C(3)O(3) and the six-membered ring MoO(4)C(4)C(1)C(3)O(3)

atoms introduced at idealised positions with thermal parameters held at 1.2 U of their carrier atoms. With (**1**), the bridging ethoxy groups were found to be disordered through alternative orientations which place the ethyl groups on either side of the $MoO_{lb}Mo'O_{lb}'$ plane of the molecule. Site occupancy for these carbon atoms was therefore included in the refinement. Other details for the individual compounds are given in Table 1.

The SHELXTL (version 4) package used[5] included atomic scattering factors and all programs required for data reduction and structure solution.

Results and Discussion

Atomic co-ordinates are listed in Table 2 and bond lengths and angles in Tables 3 and 4. The molecular structures are shown in Figures 1—4. It is not coincidental that all four complexes are binuclear. The use of a condensing agent promotes deprotonation of the hydroxyl groups and consequent alkoxo co-ordination. Charge balance is therefore attained with a low ligand: Mo ratio. But since this can disfavour six-co-ordination in a mononuclear complex, it should promote O_{lb} bridging across Mo centres, as is found.

For complexes having planar di-μ-oxo bridges, isomers having C_i or C_2 symmetry should in general be theoretical possibilities.* The present and other structure determinations[6,7] show a predominance of the former type, with only compound (**3a**) representative of the latter type. For the common case of molecules with a pair of *cis*-dioxo MoO_2 cores, C_i symmetry requires that the symmetry-related Mo–O_t dipoles be opposed in direction, as with Mo–O(1), Mo′–O(1′) and Mo–O(2), Mo′–O(2′) in Figure 1. This minimises intramolecular dipole repulsions and favours the C_i isomer. For a C_2 isomer, on the other hand, one symmetry-related pair would have the same orientation. However, in the isomers (**3a**) and (**3b**) there is only one Mo–O_t pair (see below) and they are necessarily opposed in direction in each case. Hence there is no dipole destabilisation of either isomer.

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* However, a corresponding C_2 structure is not possible in the special case of (**2**) since the Mo–N′ and Mo′–N bonds lie on opposite sides of the bridging plane. Alternative isomers with Mo–N and Mo′–N′ bonds would involve greater ligand strain.

Structure of $[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**).—Although methoxo,[8] isopropoxo and t-butoxo[9] analogues of Mo^{VI} have all been described, this seems to be the first derivative in which ethoxo groups alone are responsible for charge balance. With its binuclear structure it stands in contrast to the compounds $[MoO_2(OBu^t)_2]$, $[MoO(OPr^i)_4]$, and $[MoO(OBu^t)_4]$ which are apparently mononuclear. In these three complexes it appears that the bulky isopropoxo and t-butoxo groups inhibit bridging.

As is usual in Mo–O_{lb}–Mo′ bridges the two bonds are non-equivalent. The disorder of the $O_{lb}Et$ ethyl groups (see above) through their lying symmetrically on either side of the MoO_{lb}-$Mo'O_{lb}'$ bridging plane [MoO(4)Mo′O(4′) in Figure 1] can thus be described as due to development of right- and left-handed forms around the O_{lb} atoms. Through non-equivalence of intra- and inter-molecular approaches for the two forms, they appear in unequal (0.62:0.38) proportions.

The non-appearance of the alternative mononuclear complex $[MoO_2(OEt)_2(dmso)_2]$ emphasises the stability of di-μ-alkoxo bridges. It is evident that dmso co-ordination cannot compete with bridge formation by the highly basic ethoxo group. In (**1**), where O_l (ligand O from dmso) and O_{lb} (*via* the longer bridging arm) are both *trans* to O_t atoms, Mo–O_l (2.234 Å) remains longer (and weaker) than Mo–O_{lb} (2.187 Å). In (**2**) bridge formation is sufficiently strong to impose strain on the chelated ligand (see below).

Structure of $[\{MoO_2(amp)\}_2]\cdot 2dmso$ (**2**).—The structure determination showed the dmso molecules to be fulfilling a solvate role. As will be seen from Figure 2, all three functional groups of the ligand are co-ordinated despite their close spacing. With the O_{lb} bridging, each ligand develops a five-membered ring on one Mo centre and a six-membered ring on the other. It is unusual for an O atom of a five-membered ring to provide Mo ⋯ Mo bridging,[4] although it is known elsewhere.[10] In the present complex this bridging destroys any approach to ring planarity. The four ring atoms Mo′NC(1)C(3) all lie close to their mean-plane (0.022, 0.046, 0.054, 0.034 Å respectively), but the bridging O(3) lies 0.73 Å from that plane.

Both 'arms' of the Mo–O_{lb}–Mo′ bridge lie opposite O_t atoms. The arms are therefore more similar in length than usual (2.142,

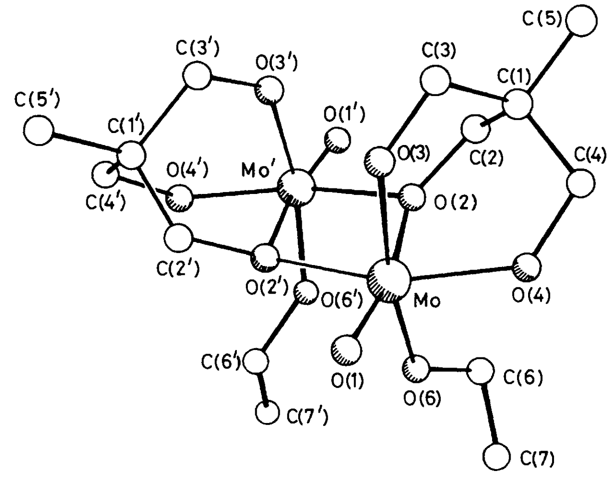

Figure 3. The structure of isomer (**3a**) of $[\{MoO(hmmp)(OEt)\}_2]$, showing the favourable disposition of the ligand for bridge formation. The existence of a C_2 axis perpendicular to the bridging plane MoO(2)Mo′O(2′) is evident

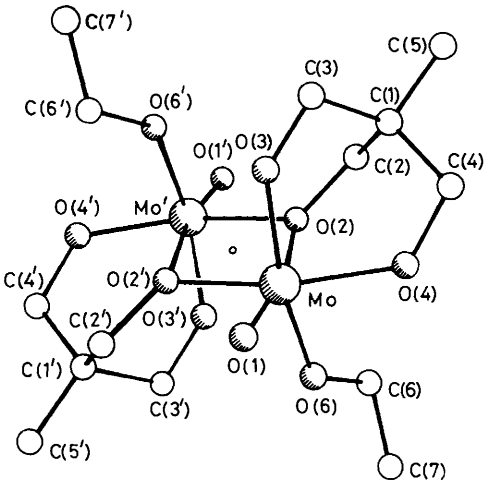

Figure 4. The structure of isomer (**3b**) showing the C_i molecular symmetry. Co-ordinated groups (to the right) around Mo are in the same orientation as for isomer (**3a**) in Figure 3

Table 4. Bond lengths (Å) and angles (°) for isomers (**3a**) and (**3b**)*

	(**3a**)	(**3b**)
Mo–O(1)	1.691(2)	1.686(3)
Mo–O(2)	2.263(2)	2.267(3)
Mo–O(2′)	2.021(2)	2.017(3)
Mo–O(3)	1.904(3)	1.886(4)
Mo–O(4)	1.890(2)	1.903(3)
Mo–O(6)	1.877(3)	1.876(4)
O(2)–C(2)	1.437(4)	1.451(5)
O(3)–C(3)	1.415(4)	1.427(5)
O(4)–C(4)	1.423(4)	1.431(5)
O(6)–C(6)	1.427(5)	1.429(6)
C(1)–C(2)	1.534(5)	1.538(8)
C(1)–C(3)	1.527(5)	1.532(7)
C(1)–C(4)	1.530(5)	1.525(7)
C(1)–C(5)	1.531(5)	1.536(6)
C(6)–C(7)	1.496(6)	1.507(8)
Mo ⋯ Mo	3.455	3.471

	(**3a**)	(**3b**)
O(1)–Mo–O(2)	168.3(1)	168.0(1)
O(1)–Mo–O(2′)	96.1(1)	97.1(1)
O(1)–Mo–O(3)	97.4(1)	98.0(2)
O(1)–Mo–O(4)	108.8(1)	108.4(1)
O(1)–Mo–O(6)	98.8(1)	97.9(2)
O(2)–Mo–O(3)	81.9(1)	80.0(1)
O(2′)–Mo–O(3)	87.9(1)	90.5(1)
O(2)–Mo–O(4)	82.8(1)	83.4(1)
O(2)–Mo–O(6)	82.7(1)	85.2(1)
O(2′)–Mo–O(6)	92.3(1)	91.3(1)
O(2′)–Mo–O(4)	154.9(1)	154.5(1)
O(3)–Mo–O(4)	86.1(1)	86.4(1)
O(3)–Mo–O(6)	163.7(1)	163.6(1)
O(4)–Mo–O(6)	86.9(1)	84.9(1)
Mo–O(3)–C(3)	128.8(2)	129.6(3)
Mo–O(4)–C(4)	127.7(2)	126.6(3)
Mo–O(6)–C(6)	131.2(2)	131.6(3)

* Values for angles given in Table 5 are omitted.

Table 5. Bridging bond lengths and angles

Compound	$Mo–O_{lb}$/Å	$Mo–O_{lb}–Mo$/° ($Mo–O_{lb}–R$/°)[a]	$O_{lb}–Mo–O_{lb}$/°
$[\{MoO_2(OEt)_2(dmso)\}_2]$ (**1**)	2.062, 2.187	110.7 (120.5, 117.4)	69.3
$[\{MoO_2(amp)\}_2]$·2dmso (**2**)	2.142, 2.213	109.2 (110.9, 116.5)	70.8
$[\{MoO(hmmp)(OEt)\}_2]$ (**3a**)	2.021, 2.263	107.6 (122.6, 118.5)	72.2
$[\{MoO(hmmp)(OEt)\}_2]$ (**3b**)	2.017, 2.267	108.8 (122.9, 119.2)	71.2
$[\{MoO_2(Hpin)(OMe)\}_2]$[b]	2.00, 2.22	111 (122.8, 116.5)	69
$[\{MoO_2(npg)(H_2O)\}_2]$[c]	2.014, 2.219	109.3 (126.1, 119.2)	70.7

[a] The $Mo–O_{lb}–R$ sequence in parentheses matches the $Mo–O_{lb}$ sequence in column 2. [b] H_2pin = pinacol (ref. 6). [c] H_2npg = 'neopentylglycol' (1,3-dihydroxy-2,2-dimethylpropane) (ref. 7).

2.213 Å), with neither particularly weak through the strength of the other. The Mo–N bond is not weakened by any *trans* effect and it must contribute to the Mo ··· Mo′ positioning.

Structure of $[\{MoO(hmmp)(OEt)\}_2]$, (**3a**) *and* (**3b**).—The structure determinations confirm the presence of only one O_t atom per Mo. The molecule of (**3a**) has C_2 symmetry and (**3b**) C_i symmetry (Figures 3 and 4). One of the alkoxy atoms, O(2), from the 'tripod' ligand provides the bridging in each case. The remaining co-ordination position is occupied by the ethoxy group. The disposition of the C_2 molecules in the centrosymmetric cell produces a racemic crystal. The C_i molecules are necessarily *meso* with Δ and Λ conformations about the Mo pair, along with opposite handedness around C(5) and C(5′). The crystallisation of these isomers points to the formation of Δ and Λ forms of MoO(hmmp)(OEt)(solv) in solution (solv = solvent) before the binuclear structure develops.

Corresponding bond lengths and angles within the two structures are closely similar (Table 4), and show no evidence of ligand strain. Angles adjacent to the $Mo–O_t$ [Mo–O(1)] multiple bond average 100.3°, with correspondingly smaller angles (av. 79.0°) around the weak (*trans*) Mo–O(2) bond.

The yellow colour of (**3a**) and (**3b**) calls for comment, as this is common to other Mo^{VI} compounds having MoO or Mo_2O_3 cores,[11] including yellow molybdic acid.[12] A ligand to metal (L → M) charge-transfer band lies just beyond the visible region,[13] typically at (27—31) × 10^3 cm^{-1}. A small shift of this band, with tailing into the visible, evidently occurs. This can be correlated with a reduction in the aggregate demand upon the Mo π* orbitals for $Mo–O_t$ π bonding on passing from $Mo(O_t)_2$ to $(MoO_t)_2O_b$ or $Mo(O_t)$ cores, and the consequent increased availability of such an orbital for electron promotion.

Bond Angles and Bridging.—The four structures provide precise information on the geometry of $MoO_{lb}Mo'O'_{lb}$ bridging systems. It can be seen from Table 5 that for all cases except (**2**) the larger of the $Mo–O_{lb}–R$ and $Mo'–O_{lb}–R$ angles is adjacent to the shorter $Mo–O_{lb}$ bond. This accords with the valence-shell electron-pair repulsion principle that inter-atomic repulsions increase with bonding electron density,[14] but (**2**) is anomalous. Again, for all molecules except (**2**) the sums of the three O_{lb} bond angles fall in the range 348—351°. For (**2**) the value is lower at 336.6°. There are thus several indications of structural abnormality due to strain in the chelate system of (**2**).

We now consider the angles within the bridging systems, where values for $O_{lb}–Mo–O_{lb}$ (69—72°) are particularly small (see Table 5). These values are best viewed in relation to the small Mo bond angles found in other situations. (*i*) In mononuclear *cis*-dioxo compounds $Mo(O_t)_2A_2L_2$ (A = anionic ligand, L = dative ligand *trans* to O_t), L–Mo–L is typically 76—77°.[15,16] The small angle is due to electrostatic repulsion from the $Mo–O_t$ bonds. (*ii*) Five-membered chelate rings (of which there can be up to three converging on Mo) subtend O–Mo–O and O–Mo–N angles of 74—76°.[17,18] These values are largely independent of the position of the ring in relation to the O_t atoms and are clearly imposed by the ring geometry. In the 1,2-dihydroxyethane complex $[MoO_2(OCH_2CH_2OH)_2]$ for example,[18] the average values at successive atoms in the $\overline{MoOCCO}H$ rings are 74.5, 118.8, 109, 107, 111.7°. The retention of large angles at O at the expense of a small angle at Mo is significant. (*iii*) The still smaller angles subtended by di-μ-O_{lb} bridges, as in the present structures (Table 5), are again insensitive to the disposition of the bridge in relation to O_t atoms. These angles too must therefore be imposed by a large $Mo–O_{lb}–Mo'$ angle between strongly-directed bonds developed at the O_{lb} centre. This implies that there is considerable charge redistribution from O_{lb} towards Mo′ with bridge formation. As evidence of this it is significant that in (**1**) the O(4)–C(41) bond length in the bridging ethoxy group has increased to as much as 1.466 Å, compared with 1.415 Å for O(3)–C(31) in the terminal ethoxo group. The distance between the two O_{lb} atoms in these planar bridges will be such as to maximise $Mo–O_{lb}$ bond strength. This could lead to a 'bent-bond' situation, with the real valence angles at both Mo and O_{lb} greater than the measured values.

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References

1 H. Schultheis, G. P., 1,022,205/1958; 1,162,849/1964; *Chem. Abstr.*, 1960, **54**, 4390; 1964, **60**, 15909.
2 R. N. Hider and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1984, 495.
3 E. M. McCarron and R. L. Harlow, *J. Chem. Soc., Chem. Commun.*, 1983, 90.
4 C. B. Knobler, B. R. Penfold, W. T. Robinson, C. J. Wilkins, and S. H. Yong, *J. Chem. Soc., Dalton Trans.*, 1980, 284.
5 G. M. Sheldrick, SHELXTL, Integrated System for Solving, Refining and Displaying Crystal Structures for Diffraction Data, version 4, Nicolet, Madison, Wisconsin, 1985.
6 C. B. Knobler, B. R. Penfold, W. T. Robinson, and C. J. Wilkins, *Acta Crystallogr., Sect. B*, 1981, **37**, 942.
7 C. K. Chew and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1975, **5**, 413.
8 E. M. McCarron, R. H. Staley, and A. W. Sleight, *Inorg. Chem.*, 1984, **23**, 1043.
9 M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.
10 G. E. Taylor and J. M. Waters, *Tetrahedron Lett.*, 1981, **22**, 1277.
11 R. A. Sheldon, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 367; A. J. Matheson and B. R. Penfold, *Acta Crystallogr., Sect. B*, 1979, **35**, 2707.
12 B. Krebs, *Acta Crystallogr., Sect. B*, 1972, **28**, 2222.
13 F. W. Moore and R. E. Rice, *Inorg. Chem.*, 1968, **7**, 2150.

14 R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.
15 L. R. Florian and E. G. Corey, *Inorg. Chem.*, 1968, **7**, 722.
16 R. J. Butcher, B. R. Penfold, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1979, 668.
17 L. O. Atovmyan and O. N. Krasochka, *Chem. Commun.*, 1970, 1670.
18 F. A. Schröder, J. Scherle, and R. G. Hazell, *Acta Crystallogr., Sect. B*, 1975, **31**, 531.

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