Isolation and Crystal Structure of a Dimeric Oxomolybdenum(V) Complex containing Two Ethoxy Bridges and One Ethanol Bridge†

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Reaction of $MoCl_5$ with EtOH in $CHCl_3$ has given the complex $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** in essentially quantitative yield. Slow removal of the volatile material from the reaction mixture gives orange crystals of an unsolvated orthorhombic phase [$C_6H_{16}Cl_4Mo_2O_5$, $P2_12_12_1$, $a = 8.186(2)$, $b = 8.319(2)$, $c = 24.114(4)$ Å, $Z = 4$, $R = 0.0809$, $R' = 0.0784$], while recrystallisation from CH_2Cl_2 gives a monoclinic phase incorporating partially occupied disordered CH_2Cl_2 of crystallisation and containing two molecules of **1** in the asymmetric unit [$C_{12}H_{32}Cl_8Mo_4O_{10}\cdot 0.45CH_2Cl_2$, $P2_1/c$, $a = 8.449(1)$, $b = 22.127(2)$, $c = 19.526(2)$ Å, $\beta = 96.06(1)°$, $Z = 4$, $R = 0.0427$, $R' = 0.0452$]. Compound **1** is of structural interest because it exhibits the unusual feature of two Mo^V centres bridged by three oxygen atoms, while at the same time furnishing the first example of a bridging ethanol molecule. Compound **1** has been further characterised by IR, ^1H NMR and chemical analyses, while magnetic susceptibility measurements showed it to be diamagnetic. This result is consistent with the crystal structures which imply the presence of a Mo–Mo single bond (length *ca.* 2.69 Å).

The growing interest in organooxometal compounds[1] has provided the impetus for us to explore the chemistry of molybdenum with the ambition of preparing and characterising derivatives of this type. Despite the potential importance of organooxomolybdenum systems containing molybdenum in the highest oxidation states V and VI as catalytic intermediates in industrial[2] and biological[3] processes, there have been relatively few reports of model complexes relevant to these systems.[4] Our early reconnaissance revealed also a dearth of useful starting materials from which the compounds might be prepared by metathesis. Starting from simple molybdenum oxide halides such as MoO_2Cl_2 and $MoOCl_3$ is liable to result, as noted elsewhere,[1,5] in reduction of the molybdenum centre, a change which can be avoided only by the attachment of bulky π-donor ligands to the metal.[6]

Most known oxomolybdenum-(V) and -(VI) compounds have in common the feature of being furnished with strong π-donor ligands which serve to stabilise the high oxidation state of the metal. Alkoxide groups form one such class of ligands which are potentially suitable for our longer term objectives. Accordingly, we have been investigating the synthesis of new Mo(O)(OEt)-containing compounds. Ideally these should also carry good leaving groups, although this purpose may be served by the alkoxide groups themselves under appropriate conditions.

Earlier studies[7] showed that dissolution of $MoCl_5$ in ethanol causes a vigorous reaction to take place and an equilibrium to be reached in the solution after 20 min, as shown by electrical conductivity measurements. The mean number of Cl atoms, n, of the $MoCl_5$ which are substituted by OEt groups in the reaction has been calculated from the conductivity data to be $n = 1.2 \pm 0.05$ in a 0.0106 mol dm^{-3} $[MoCl_{5-n}(OEt)_n]$ solution.[8] The compound $[MoCl_3(OEt)_2]$ has also been isolated.[7] The colour of $MoCl_5$ solutions in ethanol varies with concentration from yellow-green to brown owing to the formation of different solvolysis products.[9] On the evidence of mass spectrometric and GC analysis, the vapour over such solutions contains chloroethane.[10] Methanolic solutions of $MoCl_5$ give ESR spectra which have been interpreted in terms of a dimethoxymolybdenum dimer, $[\{MoOCl(OMe)_2\}_2]$, rather than $[\{MoOCl_2(OMe)\}_2]$, as the major solute species.[10] Here we describe the isolation, characterisation and crystal structure of a new binuclear oxomolybdenum(V) ethoxide, incorporating an unusual ethanol bridging unit, derived from the reaction of $MoCl_5$ with ethanol.

Results and Discussion

There has in the past been some confusion about the behaviour of $MoCl_5$ in different solvents,[11] but many of the oxomolybdenum compounds obtained under these conditions arise merely from the use of solvents which have not been rigorously dried and freed from alcoholic or other impurities.[12] Adding a $CHCl_3$–EtOH mixture to solid $MoCl_5$ leads to the formation of the orange complex $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** in quantitative accordance with equation (1). The stoichiometry

$$2MoCl_5 + 5EtOH \xrightarrow{CHCl_3} \underset{\mathbf{1}}{[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]} + 4HCl + 2EtCl \quad (1)$$

of the reaction was verified by isolating the products EtCl (identified by its ^1H NMR and IR spectra) and HCl (identified by its IR spectrum), when the reaction was performed in a sealed vessel. These were the only products to be isolated having an appreciable volatility at 178 K.

Consequently we may suppose that the ethanolysis of the Mo–Cl bonds takes place in steps with successive formation of Mo=O bonds *via* the mechanism shown in equation (2).

$$MoCl_5 + 2EtOH \xrightarrow{-2HCl} Cl_3Mo(OEt)_2 \xrightarrow{-EtCl} Cl_2Mo(O)OEt \xrightarrow{Cl_2Mo(O)OEt\cdot EtOH} \mathbf{1} \quad (2)$$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: 1 Torr = 133 Pa.

The failure to detect any Et_2O enables us to rule out another possible mechanism, suggested previously[10] for the methanolysis of $MoCl_5$, equation (3).

$$Cl_3Mo(OR)_2 \longrightarrow Cl_3Mo{=}O + ROR \qquad (3)$$

Compound **1** has been characterised by elemental analysis and by its IR, UV/VIS and ^1H NMR spectra. The chemistry of oxomolybdenum(v) complexes is dominated by binuclear structures which are diamagnetic as a result of interaction between the two Mo^V centres, directly and/or *via* the bridging atoms, leading to spin pairing of the 4d electrons formally associated with the metal atoms. In this context, it may be noted that **1** shows only a small paramagnetic susceptibility which is virtually independent of temperature, implying an electronic ground state which is diamagnetic.

This observation is consistent with a short Mo–Mo distance of 2.697(3) Å (see below). Nevertheless, it is possible to obtain ESR spectra of analytically pure **1** either in CH_2Cl_2 solution [$g = 1.949$; $a(^{97,95}Mo) \approx 5.2$ mT] or in the solid state [$g = 1.946$ (br)]. Whether this finding is linked to the presence of a paramagnetic component in equilibrium with **1** or to contamination by a small amount of impurity, which cannot be detected by any of the other spectroscopic methods applied, cannot be determined on the evidence of the results presently available. However, the *g* value of the ESR spectrum of **1** in CH_2Cl_2 solution is almost identical with that of one of the signals previously reported for a methanolic solution of $MoCl_5$.[10] The earlier signal was assigned to the presence of $MoOCl_4^-$ or $MoOCl_3$.

The ^1H NMR spectrum of a solution of **1** in toluene shows reasonably sharp signals for the EtO groups but quite broad signals for the EtOH bridge; the resonance for the OH hydrogen could not be detected. Cooling the sample to −40 °C leaves the resonances due to the EtO groups unchanged, while the signals due to the EtOH molecule become progressively sharper. At temperatures below −40 °C the linewidths of the EtO signals increase because of viscosity effects, leading to loss of their fine structure, while the EtOH signals continue to sharpen until at −80 °C all the signals have the same linewidths. Heating the sample to 80 °C causes a progressive decrease in the linewidths of the EtOH signals and an increase in the linewidths of the EtO signals. Changes in temperature also result in slight shifts (< 0.4 ppm) of all the signals. These results indicate that the ethanol bridge is involved in a fluxional process which may be associated with a shift of the ethanol molecule between the two molybdenum atoms.

Complex **1** is extremely sensitive to moisture, in the presence of which it first turns into a blue solid; later this gives way to a brown oil; finally the oil changes into a brown solid. Under anaerobic conditions, the complex undergoes thermal decomposition at 343–363 K. If it is heated *in vacuo* to 363 K, a yellow oil together with EtCl condenses on a finger cooled to 77 K, leaving behind a dark brown solid the IR spectrum of which shows a strong band at 748 cm^{-1} diagnostic of the presence of Mo–O–Mo units.[5d,6] On warming, the yellow oil turns dark brown and the resulting product can no longer be vaporised at temperatures below 353 K.

The Crystal Structures of **1** *and* $\mathbf{1}\cdot0.45CH_2Cl_2$.—During the course of this study two crystalline habits of **1** were structurally characterised by X-ray crystallography. Slow removal of the volatile material from the reaction mixture in chloroform leads to an unsolvated orthorhombic phase containing four molecules per unit cell and exhibiting one molecule of **1** per asymmetric unit. In the monoclinic phase, obtained by recrystallisation of **1** from methylene chloride, the asymmetric unit contains two crystallographically distinct molecules of **1** and a partially occupied, disordered CH_2Cl_2 molecule. The unit cell contains four of these units, and therefore has slightly more than twice the volume of the orthorhombic cell. A CAMERON[13] plot of one of these molecules is shown in Fig. 1, and selected bond distances and angles observed in the monoclinic phase are listed in Tables 1 and 2.

The packing arrangements in the two crystal structures are closely related with, for example, the group of four molecules clustered around the inversion centres of the monoclinic cell [shown in Fig. 2(*a*)] being reminiscent of the group of four molecules about the 2_1 axes along the *b* direction of the orthorhombic cell [marked on Fig. 2(*b*)]. Nevertheless, incorporation of solvent of crystallisation into the lattice lowers the dimensionality of the symmetry creating channels in which the solvent molecules reside. In the solid state, then, **1** consists of two $O{=}MoCl_2$ units bridged by two ethoxy groups and one ethanol molecule; the $Mo(\mu\text{-}OEt)_2Mo$ moiety contains a planar Mo_2O_2 heterocycle. Each Mo atom is therefore placed in a distorted octahedral environment conforming to the commonly occurring co-ordination type MoX_6L_2.[14] While the metal atoms are formally in the +5 oxidation state (d^1), the

Table 1 Bond distances (Å) in the monoclinic phase of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]\cdot0.45CH_2Cl_2$ *

Mo(1)–Mo(2)	2.683(1)	Mo(4)–Cl(42)	2.356(3)
Mo(1)–Cl(11)	2.336(3)	Mo(4)–O(4)	1.638(8)
Mo(1)–Cl(12)	2.329(3)	Mo(4)–O(341)	2.470(6)
Mo(1)–O(1)	1.649(7)	Mo(4)–O(342)	1.990(6)
Mo(1)–O(121)	2.495(6)	Mo(4)–O(343)	2.006(6)
Mo(1)–O(122)	2.001(7)	O(121)–C(121)	1.48(1)
Mo(1)–O(123)	1.992(7)	O(122)–C(122)	1.48(1)
Mo(2)–Cl(21)	2.351(3)	O(123)–C(123)	1.47(1)
Mo(2)–Cl(22)	2.341(3)	O(341)–C(341)	1.48(1)
Mo(2)–O(2)	1.650(8)	O(342)–C(342)	1.48(1)
Mo(2)–O(121)	2.484(6)	O(343)–C(343)	1.46(1)
Mo(2)–O(122)	1.993(7)	C(121)–C(124)	1.51(1)
Mo(2)–O(123)	2.006(6)	C(122)–C(125)	1.51(1)
Mo(3)–Mo(4)	2.695(1)	C(123)–C(126)	1.50(1)
Mo(3)–Cl(31)	2.329(3)	C(341)–C(344)	1.49(1)
Mo(3)–Cl(32)	2.329(4)	C(342)–C(345)	1.50(1)
Mo(3)–O(3)	1.659(8)	C(343)–C(346)	1.51(1)
Mo(3)–O(341)	2.481(7)	Cl(1)–C(1)	1.66(2)
Mo(3)–O(342)	1.987(6)	Cl(2)–C(1)	1.73(2)
Mo(3)–O(343)	2.002(7)	Cl(3)–C(2)	1.76(2)
Mo(4)–Cl(41)	2.334(3)	Cl(4)–C(2)	1.73(2)

* The numbering in both molecules contained in the asymmetric unit follows the scheme shown in Fig. 1.

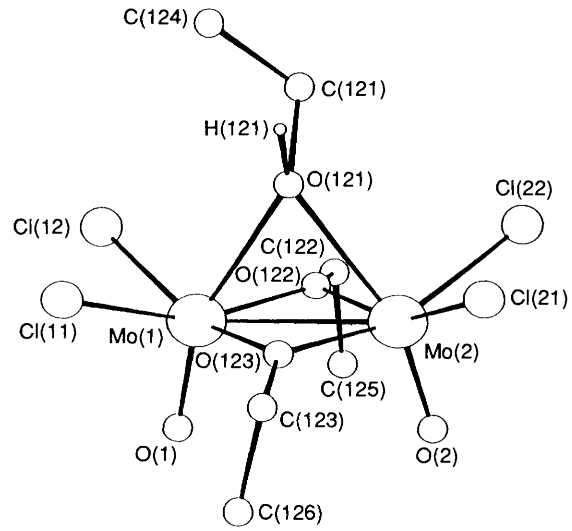

Fig. 1 The structure of one of the crystallographically independent $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]$ molecules in the monoclinic phase of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]\cdot0.45CH_2Cl_2$. The second molecule contained in the asymmetric unit of this phase and the molecule contained in the orthorhombic phase have the same structure

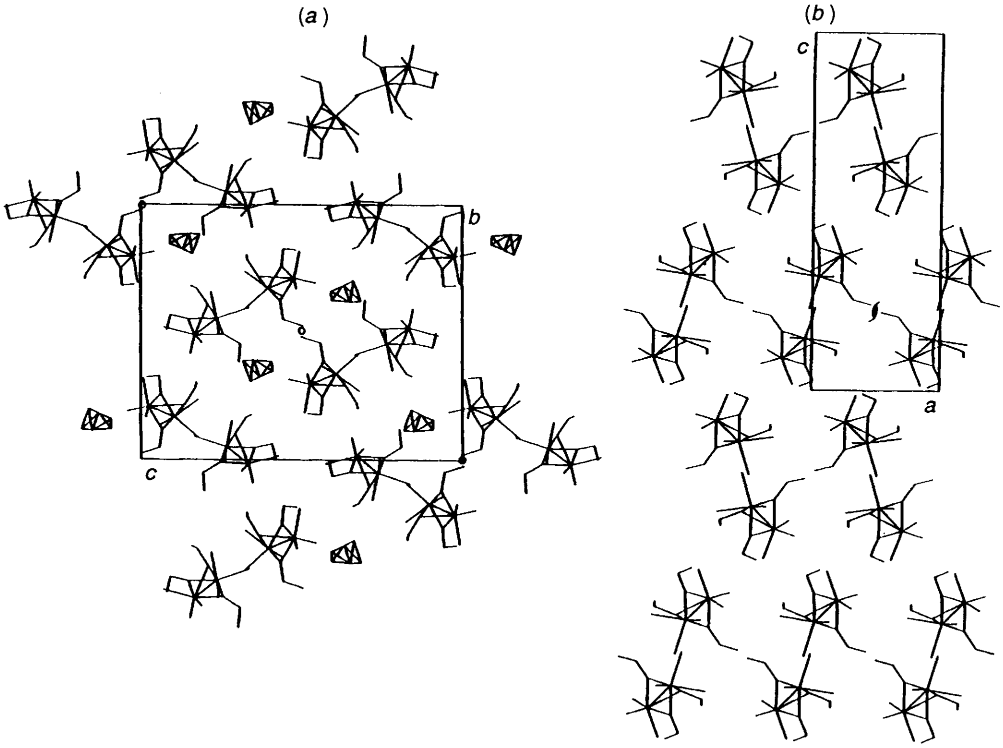

Fig. 2 (*a*) Projection of the monoclinic unit cell of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]\cdot 0.45CH_2Cl_2$ along the *a* axis. (*b*) Projection of the orthorhombic unit cell of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]$ viewed along the *b* axis. Symmetry elements referred to in the text are shown with their usual symbols; both unit cells contain more symmetry elements than are shown here

diamagnetism of the complex implies that the two d electrons form a single Mo–Mo bond. Of the three crystallographically distinct complexes to have been characterised in this study, two have essentially the same Mo–Mo bond length of 2.697(3) Å (in **1**) and 2.695(1) Å (in $\mathbf{1}\cdot 0.45CH_2Cl_2$), whereas one exhibits a significantly shorter Mo–Mo bond length of 2.683(1) Å. Such a difference should be reflected in the other bond lengths in the molecule, but the relatively poorer precision with which these have been determined precludes a detailed analysis, and there are no significant differences between the lengths of the other chemically equivalent bonds in the three structures (*i.e.* none differs from the average by more than three estimated standard deviations).[15]

The structure of **1** is remarkable not only because of the relative rarity of complexes in which two Mo^V centres are bridged by three oxygen atoms, but also because it contains an unusual bridging alcohol unit.[16,17] The average Mo–O(μ-HOEt) bond length [2.48(2) Å] is 0.48 Å longer than the average Mo–O(μ-OEt) length [2.00(2) Å], while being similar to that reported for the Mo–O bond to the bridging alcohol function in the anion $[Mo_2O_5(HL)]^-$ (H_4L = butane-1,2,3,4-tetraol) [2.52(2) Å].[16] This is consistent with the much reduced basicity of EtOH compared with EtO^- as a bridging function, together with the *trans* influence of the terminal oxo ligands. Similar features are observed in $[Mo_2O_2(S_2CNEt_2)_2(\mu\text{-}O)(\mu\text{-}SPh)_2]$ where there are two μ-SPh bridging regimes with Mo–S(μ-SPh) bond lengths differing by 0.2 Å as a result of the *trans* influence exerted by the terminal oxygen atoms.[18]

With molybdenum in the +5 oxidation state stabilised by bridging ethoxy groups, and with four chloride anions as leaving groups, compound **1** is also well adapted to act as a starting material for the synthesis of organooxomolybdenum compounds. In addition, the bridging ethanol molecule invites further investigations as a potentially functional and highly labile leaving group. Such studies are now under way, with results to be reported shortly.

Experimental

All manipulations were carried out on a vacuum line, or in a glove box or by means of Schlenk-type techniques under a nitrogen atmosphere. Solvents were dried according to standard procedures; $[^2H_8]$toluene was dried and transferred from activated 4 Å molecular sieves. The $MoCl_5$ was used as received (Aldrich). Microanalyses were performed by the Analytische Laboratorien GMBH, Gummersbach, Germany. The ^1H NMR spectra were measured for $[^2H_8]$toluene solutions using a Bruker AM 300 spectrometer, IR spectra were recorded with a Mattson 'Galaxy' FTIR spectrometer, and ESR spectra with a Varian E-Line 'Century' Series spectrometer (microwave frequency 9.251 GHz). Measurements of UV/VIS spectra were made with a Perkin-Elmer Hitachi model 330 spectrophotometer. Magnetic susceptibilities were determined in the temperature range $6 < T < 300$ K using a Cryogenics Consultants SCU500 Squid magnetometer in conjunction with a Lakeshore DRC-91C temperature controller, operating at a field of 0.05 T.

Synthesis of $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$.—Under nitrogen a dry $CHCl_3$–EtOH (166 g : 1.9 g) mixture (60 g) was added in portions *via* a cannula to $MoCl_5$ (1.56 g, 5.7 mmol) in a Schlenk tube. After each addition of the solvent mixture, the suspension turned green and was stirred until the brown colour was restored before the next portion was added. Finally a green solution was obtained; this was stirred for another hour to ensure completion of the reaction. The volatile materials were then evaporated *in vacuo* leaving a bright orange, highly air-sensitive solid. After washing with light petroleum (b.p. 40–60 °C), pure compound **1** (1.39 g, 2.8 mmol) was obtained; yield 97%, based on equation (1) and the quantity of $MoCl_5$ used. The product was found to be soluble in solvents such as chloroform, CH_2Cl_2, Et_2O and toluene but quite insoluble in light petroleum. It dissolved in thf (tetrahydrofuran) but only with decomposition. Decomposition of the solid also occurred when it was heated to 70–90 °C (Found: C, 14.55; H, 3.20; Cl,

Table 2 Bond angles (°) in the monoclinic phase of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]\cdot 0.45CH_2Cl_2$

Cl(11)–Mo(1)–Cl(12)	86.2(1)
Cl(11)–Mo(1)–O(1)	104.1(3)
Cl(12)–Mo(1)–O(1)	102.8(3)
Mo(2)–Mo(1)–O(121)	57.2(2)
Cl(11)–Mo(1)–O(121)	90.4(2)
Cl(12)–Mo(1)–O(121)	92.8(2)
O(1)–Mo(1)–O(121)	159.2(3)
Cl(11)–Mo(1)–O(122)	157.0(2)
Cl(12)–Mo(1)–O(122)	85.0(2)
O(1)–Mo(1)–O(122)	98.6(3)
O(121)–Mo(1)–O(122)	68.9(2)
Mo(2)–Mo(1)–O(123)	48.1(2)
Cl(11)–Mo(1)–O(123)	84.7(2)
Cl(12)–Mo(1)–O(123)	158.1(2)
O(1)–Mo(1)–O(123)	98.8(3)
O(121)–Mo(1)–O(123)	67.4(2)
O(122)–Mo(1)–O(123)	95.8(3)
Cl(21)–Mo(2)–Cl(22)	85.3(1)
Cl(21)–Mo(2)–O(2)	104.3(3)
Cl(22)–Mo(2)–O(2)	104.2(3)
Mo(1)–Mo(2)–O(121)	57.6(2)
Cl(21)–Mo(2)–O(121)	89.2(2)
Cl(22)–Mo(2)–O(121)	90.8(2)
O(2)–Mo(2)–O(121)	160.4(3)
Cl(21)–Mo(2)–O(122)	156.0(2)
Cl(22)–Mo(2)–O(122)	84.6(2)
O(2)–Mo(2)–O(122)	99.3(3)
O(121)–Mo(2)–O(122)	69.2(3)
Cl(21)–Mo(2)–O(123)	85.2(2)
Cl(22)–Mo(2)–O(123)	156.3(2)
O(2)–Mo(2)–O(123)	99.2(4)
O(121)–Mo(2)–O(123)	67.4(2)
O(122)–Mo(2)–O(123)	95.5(3)
Cl(31)–Mo(3)–Cl(32)	85.6(1)
Cl(31)–Mo(3)–O(3)	105.0(3)
Cl(32)–Mo(3)–O(3)	102.4(3)
Mo(4)–Mo(3)–O(341)	56.8(2)
Cl(31)–Mo(3)–O(341)	88.4(2)
Cl(32)–Mo(3)–O(341)	92.7(2)
O(3)–Mo(3)–O(341)	160.4(4)
Cl(31)–Mo(3)–O(342)	155.6(2)
Cl(32)–Mo(3)–O(342)	85.9(2)
O(3)–Mo(3)–O(342)	99.2(4)
O(341)–Mo(3)–O(342)	69.2(3)
Cl(31)–Mo(3)–O(343)	84.3(2)
Cl(32)–Mo(3)–O(343)	157.7(2)
O(3)–Mo(3)–O(343)	99.4(4)
O(341)–Mo(3)–O(343)	67.2(2)
O(342)–Mo(3)–O(343)	95.2(3)
Cl(41)–Mo(4)–Cl(42)	85.5(1)
Cl(41)–Mo(4)–O(4)	104.5(3)
Cl(42)–Mo(4)–O(4)	103.6(3)
Mo(3)–Mo(4)–O(341)	57.2(2)
Cl(41)–Mo(4)–O(341)	90.2(2)
Cl(42)–Mo(4)–O(341)	89.5(2)
O(4)–Mo(4)–O(341)	160.8(4)
Cl(41)–Mo(4)–O(342)	85.4(2)
Cl(42)–Mo(4)–O(342)	156.9(2)
O(4)–Mo(4)–O(342)	99.2(4)
O(341)–Mo(4)–O(342)	69.4(2)
Cl(41)–Mo(4)–O(343)	155.7(2)
Cl(42)–Mo(4)–O(343)	84.9(2)
O(4)–Mo(4)–O(343)	99.5(4)
O(341)–Mo(4)–O(343)	67.4(2)
O(342)–Mo(4)–O(343)	95.0(3)
Mo(1)–O(121)–Mo(2)	65.2(2)
Mo(1)–O(121)–C(121)	126.3(6)
Mo(2)–O(121)–C(121)	124.8(6)
Mo(1)–O(122)–Mo(2)	84.4(2)
Mo(1)–O(123)–Mo(2)	84.3(2)
Mo(3)–O(341)–Mo(4)	65.9(2)
Mo(3)–O(341)–C(341)	124.8(6)
Mo(4)–O(341)–C(341)	123.8(5)
Mo(3)–O(342)–Mo(4)	85.3(2)
Mo(3)–O(343)–Mo(4)	84.5(2)
Cl(1)–C(1)–Cl(2)	104.4(9)
Cl(3)–C(2)–Cl(4)	105.2(9)

28.00; Mo, 38.00; O, 16.00. $C_6H_{16}Cl_4Mo_2O_5$ requires C, 14.35; H, 3.20; Cl, 28.25; Mo, 38.25; O, 15.95%); $\tilde{\nu}$/cm^{-1}: 3347m (br) [ν(OH)], 2972w [ν(CH)], 1450m, 1392m, 1383m, 1085w, 1001vs [ν(CO)], 987s [ν(Mo=O)], 899s, 854m [δ(CH out of plane)], 542w and 513w [ν(Mo–O)] (KBr); ^{1}H NMR: δ_H(300 MHz, [$^2H_8$]toluene, standard $SiMe_4$) 0.3 (3 H, br, $HOCH_2CH_3$), 1.2 [6 H, t, *J*(HH) 6.5, OCH_2CH_3], 2.5 (2 H, br, $HOCH_2CH_3$), 5.6 [4 H, q, *J*(HH) 6.5 Hz, OCH_2CH_3]; λ_{max}(0.019 mol dm^{-3} in CH_2Cl_2): 220 (ε 4981), 320 (4756), 685 nm (6 dm^3 mol^{-1} cm^{-1}).

Recrystallisation from CH_2Cl_2 between room temperature and −80 °C resulted in orange needles, which proved to contain 0.45 CH_2Cl_2 molecules per molecule of **1**. $\tilde{\nu}$/cm^{-1}: 3296m (br), 2972w, 1447m, 1394m, 1381m, 1266w [ρ(CH_2)], 1082w, 1001vs, 897s, 851m, 742m [ν(C–Cl)], 538w, 509w, 464w (KBr); ^{1}H NMR: δ_H(300 MHz, [$^2H_8$]toluene, standard $SiMe_4$) 0.3 (3 H, br, $HOCH_2CH_3$), 1.2 [6 H, t, *J*(HH) 6.5, OCH_2CH_3], 2.5 (2 H, br, $HOCH_2CH_3$), 4.3 (1 H, s, CH_2Cl_2), 5.6 [4 H, q, *J*(HH) 6.5 Hz, OCH_2CH_3].

Crystal Structure of $[Mo_2O_2Cl_4(\mu\text{-}OHEt)(\mu\text{-}OEt)_2]$.—Crystals of $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** were loaded into carefully dried 0.3 or 0.5 mm Lindemann capillaries under dry nitrogen and the capillaries quickly sealed off. It was important to avoid the use of grease in this procedure since earlier attempts to mount the crystals were frustrated by their decomposition under the action of either silicone or fluorocarbon greases. Oscillation and Weissenberg photographs of over a dozen crystals (from several batches) revealed a marked tendency to form clumps or twins, and all were characterised by significant background scattering, possibly implying the presence of some amorphous phase. Eventually a strongly diffracting single crystal was obtained, although photographs showed that it too exhibited strong background scattering, while the appearance of satellite spots suggested that it may also have been cracked or damaged in some way.

Crystal data. $C_6H_{16}Cl_4Mo_2O_5$, *M* = 501.9, orthorhombic, $P2_12_12_1$, *a* = 8.186(2), *b* = 8.319(2), *c* = 24.114(4) Å, *U* = 1642.1(7) Å^3 (by least-squares refinement of the diffractometer setting angles for 24 centred reflections with $11.3 \leqslant \theta \leqslant 12.1°$, λ = 0.710 69 Å), *Z* = 4, D_c = 2.03 g cm^{-3}, *F*(000) = 976; orange blocks, dimensions 0.19 × 0.28 × 0.34 mm; μ(Mo-Kα) = 21.54 cm^{-1}.

Data collection and processing. CAD-4 diffractometer, ω mode with ω-scan width (1 + 0.35 tanθ)°, ω scan speed 2.0–6.7° min^{-1}, graphite-monochromated Mo-Kα radiation, 2094 reflections measured (θ_{max} = 24°; $-1 \leqslant h \leqslant 9$, $-1 \leqslant k \leqslant 9$, $-1 \leqslant l \leqslant 27$), 1522 unique, 1167 observed with $I > 3\sigma(I)$. R_{int} = 0.113. Variation of three intensity standards, measured every 3600 s of X-ray exposure time, was no greater than 1.2%.

Structure analysis and refinement. The data were reduced to a standard scale and a Lorentz polarization correction was applied; although a psi-scan absorption profile was measured, it possessed rather irregular features and more than two maxima between 0 and 360° (probably reflecting the quality of the crystal), and so an absorption correction was not applied at this stage. The structure was solved by direct methods (SIR92)[19] to reveal the positions of all non-hydrogen atoms with the exception of O(2) (see Fig. 1), which was located in a subsequent Fourier synthesis.[20] Following several cycles of isotropic least-squares refinement, hydrogen atoms were placed geometrically on the carbon atoms. Chemical analysis indicated the presence of one more hydrogen atom in addition to those of the three ethoxy groups, and the IR spectrum of the solid included a strong absorption at 3347 cm^{-1} suggestive of the presence of an O–H bond. Consistent with these findings was a bond valence analysis of the type described by Brown, which showed that the atomic valence of O(3) was conspicuously low (0.94).[21] Accordingly, an additional hydrogen was placed on this atom.

Anisotropic refinement of all the non-hydrogen atoms produced some thermal parameters with negative principal components. The structure was returned to an isotropic model and re-refined to convergence. An empirical absorption correction using DIFABS[22] showed minimum and maximum corrections in the ratio 1:2 (1.471 and 0.705, respectively), which is at odds with both the φ-scan estimate and the theoretical ratio of the maximum:minimum correction (1:1.2) based on the absorption coefficient and the crystal dimensions. This is likely to be another symptom of the low quality of the crystal which was manifested in broad, overlapping diffraction peaks, even though the data were collected in ω mode. Even with the 'absorption' correction, further anisotropic refinement led to physically implausible thermal parameters for O(1), O(4), C(1) and C(3), indicating that not all the problems had been resolved. These atoms were then given thermal parameters appropriate to the overall motion of the $Cl_2OMo(\mu\text{-}O)_3\text{-}MoOCl_2$ unit when treated as a rigid body. Even under these conditions, however, F_{calc} for the (232) reflection was in poor agreement with F_{obs}, and so it was omitted from subsequent refinements. The thermal parameters of the chlorine and oxygen atoms were then restrained to be similar to those of the metal atoms to which they were bonded. After optimisation of the weighting scheme (Chebychev two-term polynomial),[23] the solution was refined anisotropically to *R* = 0.0809 [$R' = \Sigma(|F_o| - |F_c|)w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}} = 0.0784$] for 154 parameters and 1167 reflections. The final difference synthesis maximum and minimum were 1.7 and −1.4 e Å^{-3}, respectively. Final atomic positional parameters and calculated positions of non-hydrogen atoms are given in Table 3.

Crystal Structure of [$Mo_2O_2Cl_4$(μ-OHEt)(μ-OEt)$_2$]·0.45CH_2Cl_2.—*Crystal data.* $C_{12}H_{32}Cl_8Mo_4O_{10}$·0.45$CH_2Cl_2$, M = 1033.9, monoclinic, $P2_1/c$, a = 8.449(1), b = 22.127(2), c = 19.526(2), β = 96.06(1)°, U = 3630.2(7) Å^3 (by least-squares refinement of the diffractometer setting angles for 24 centred reflections with $10.5 \leqslant \theta \leqslant 12.2°$, λ = 0.710 69 Å), Z = 4, D_c = 1.89 g cm^{-3}, $F(000)$ = 1988; brown elongated block, dimensions 0.19 × 0.09 × 0.40 mm, mounted in a 0.3 mm Lindemann capillary; μ(Mo-Kα) = 20.17 cm^{-1}.

Data collection and processing. CAD-4 diffractometer, ω–2θ mode with ω-scan width (0.80 + 0.35tanθ)°, ω scan speed 1.3–6.7° min^{-1}, graphite-monochromated Mo-Kα radiation, 4188 reflections measured (θ_{max} = 20°; $-8 \leqslant h \leqslant 8$, $-1 \leqslant k \leqslant 21$, $-1 \leqslant l \leqslant 18$), 3383 unique, 2307 observed with $I > 3\sigma(I)$. R_{int} = 0.025. Correction for absorption was effected with φ scan, maximum and minimum corrections 1.16 and 1.26, respectively. Variation of three intensity standards, measured every 3600 s of X-ray exposure time, was no greater than 1.3%.

Structure analysis and refinement. Following correction for Lorentz, polarisation and absorption effects, the positions of the molybdenum, oxygen, chlorine and all but two carbon atoms of two crystallographically independent [$Mo_2O_2Cl_4$(μ-OHEt)(μ-OEt)$_2$] complexes were located by direct methods (SIR92);[19] the remaining carbon atoms were located in a F_o synthesis (CRYSTALS).[20] Difference maps calculated with the phasing based on this model exhibited a collection of peaks (maximum height 5 e Å^{-3}) located in channels created by the packing of the [$Mo_2O_2Cl_4$(μ-OHEt)(μ-OEt)$_2$] molecules, while IR and ^{1}H NMR spectra contained peaks assignable to CH_2Cl_2, the solvent from which the crystals had been grown. The residual electron density was therefore modelled with two CH_2Cl_2 molecules both with occupancies set initially at 0.2 and subsequently refined to 0.22 and 0.23.

A difference map led to the location of hydrogen atoms on atom O(121) and on the carbon atoms of the OEt groups, and they were therefore placed in calculated positions on these atoms with isotropic thermal parameters equal to those of the atom to which they were attached. A hydrogen atom was similarly placed on O(341) based on reasons analogous to those given in the previous section.

The model was refined against F by full-matrix least-squares analysis (CRYSTALS) with isotropic thermal parameters for all non-hydrogen atoms. In a free refinement the C–C bond lengths of the OEt units converged to unusually short values (1.45–1.48 Å), but there was no significant change in the minimisation function on restraining them to accepted values [C–C 1.52(2), C–O 1.48(2) Å, O–C–C 109(2)°]. Restraints were similarly placed on the geometry of the CH_2Cl_2 of crystallisation [C–Cl 1.70(3) Å, Cl–C–Cl 105(1)°]. After optimisation of the weighting scheme (Chebychev five-term polynomial),[23] the refinement converged to R = 0.0427, R' = 0.0452 for 361 parameters and 2307 reflections. The final difference synthesis maximum and minimum were +1.3 and −0.6 e Å^{-3}, respectively, the latter being in the region of the disordered CH_2Cl_2 molecules. Fractional atomic coordinates of all non-hydrogen atoms are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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Table 3 Fractional atomic coordinates for the orthorhombic phase of [$Mo_2O_2Cl_4$(μ-OHEt)(μ-OEt)$_2$]

Atom	*x*	*y*	*z*
Mo(1)	0.731 6(2)	0.155 9(3)	0.597 01(8)
Mo(2)	0.551 9(3)	−0.046 3(2)	0.659 61(8)
Cl(1)	0.647(1)	0.288 0(9)	0.516 2(2)
Cl(2)	0.844(1)	0.404 2(9)	0.621 8(3)
Cl(3)	0.473(1)	−0.016 5(8)	0.753 4(2)
Cl(4)	0.283 3(9)	−0.130 9(8)	0.644 4(3)
O(1)	0.892(2)	0.053(2)	0.579 4(6)
O(2)	0.669(2)	−0.212(2)	0.658 1(8)
O(3)	0.473(2)	0.233(2)	0.644 9(6)
O(4)	0.731(2)	0.105(2)	0.678 8(6)
O(5)	0.549(2)	0.004(2)	0.578 2(6)
C(1)	0.308(4)	0.284(3)	0.622(1)
C(2)	0.312(4)	0.454(4)	0.606(1)
C(3)	0.824(3)	0.161(4)	0.726 4(9)
C(4)	0.964(6)	0.059(6)	0.739(2)
C(5)	0.489(4)	−0.072(3)	0.528(1)
C(6)	0.595(5)	−0.214(4)	0.512(1)

Table 4 Fractional atomic coordinates for the monoclinic phase of [$Mo_2O_2Cl_4$(μ-OHEt)(μ-OEt)$_2$]·0.45CH_2Cl_2

Atom	*x*	*y*	*z*
Mo(1)	1.290 6(1)	0.333 32(4)	1.015 00(4)
Mo(2)	1.061 1(1)	0.263 76(4)	0.950 48(5)
Mo(3)	0.751 2(1)	0.024 22(4)	0.793 67(5)
Mo(4)	0.539 1(1)	0.104 67(4)	0.833 09(5)
Cl(11)	1.558 7(3)	0.310 3(2)	1.045 0(2)
Cl(12)	1.378 7(4)	0.428 2(1)	0.984 0(2)
Cl(21)	1.081 8(4)	0.164 8(1)	0.908 4(2)
Cl(22)	0.904 3(4)	0.282 6(2)	0.846 5(2)
Cl(31)	1.019 9(4)	0.016 5(2)	0.833 8(2)
Cl(32)	0.832 9(5)	0.008 0(2)	0.684 9(2)
Cl(41)	0.397 4(4)	0.177 9(1)	0.765 8(2)
Cl(42)	0.580 7(4)	0.181 4(1)	0.916 7(2)
O(1)	1.221 1(9)	0.346 6(4)	1.089 4(4)
O(2)	0.931 5(9)	0.258 3(4)	1.007 7(4)
O(3)	0.673(1)	−0.042 1(4)	0.811 3(5)
O(4)	0.401 6(9)	0.062 2(4)	0.861 8(4)
O(121)	1.305 7(8)	0.291 2(3)	0.897 3(3)
O(122)	1.094 2(8)	0.353 0(3)	0.952 5(3)
O(123)	1.260 7(8)	0.244 0(3)	1.011 4(3)
O(341)	0.786 9(8)	0.135 2(3)	0.785 8(3)
O(342)	0.559 4(8)	0.062 7(3)	0.744 3(3)
O(343)	0.733 2(8)	0.066 4(3)	0.883 2(3)
C(121)	1.308(1)	0.326 3(5)	0.833 1(5)
C(122)	0.995(1)	0.407 2(5)	0.937 1(6)
C(123)	1.325(2)	0.191 0(5)	1.050 9(6)
C(124)	1.478(2)	0.343 8(7)	0.823 6(7)
C(125)	0.893(2)	0.418 7(6)	0.994 8(8)
C(126)	1.280(2)	0.196 8(7)	1.122 8(7)
C(341)	0.791(1)	0.169 2(6)	0.720 9(5)
C(342)	0.464(1)	0.057 5(6)	0.676 6(5)
C(343)	0.797(2)	0.056 9(6)	0.954 5(5)
C(344)	0.955(2)	0.172 8(7)	0.700 4(7)
C(345)	0.321(2)	0.017 9(8)	0.681 2(8)
C(346)	0.740(2)	−0.003 6(7)	0.978 1(7)
Cl(1)[a]	0.636(2)	0.089 7(8)	0.157(1)
Cl(2)[a]	0.802(2)	0.184 4(6)	0.116 4(8)
Cl(3)[b]	0.868(2)	0.160 0(8)	0.197 2(9)
Cl(4)[b]	0.639(2)	0.091 8(9)	0.120 3(9)
C(1)[a]	0.800(4)	0.129(2)	0.179(2)
C(2)[b]	0.772(6)	0.150(2)	0.114(1)

[a] Occupancy 0.2310. [b] Occupancy 0.2239.

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