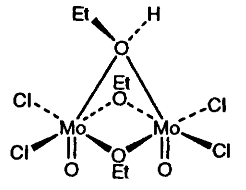
Synthesis and Crystal Structure of an Encapsulated Fragment of MoO_2 in the Unique Mo_8 Oxo-cluster Compound $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ and its Relevance to the Sol–Gel Synthesis of Molybdenum Oxides†

Alexander J. Blake,[a] **Anthony J. Downs,**[b] **Christian Limberg***[,b] **and Simon Parsons***[,a]
[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[b] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*

Reaction of the dimeric oxomolybdenum(V) complex $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** with SbF_3 in toluene followed by overlaying with light petroleum followed an unexpected course to give crystals of the complex $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2** in low yield. The crystal structure of **2** [triclinic, space group $P\bar{1}$, $a = 10.803(5)$, $b = 11.159(6)$, $c = 11.659(6)$ Å, $\alpha = 69.66(3)$, $\beta = 64.06(3)$, $\gamma = 66.258(24)^\circ$, $Z = 1$, $R = 0.058$, $wR_2 = 0.143$] has been determined and reveals a new structural type for an M_8 cluster which is closely related to the distorted rutile structure adopted by MoO_2. Incorporating two Mo_4 layers connected with each other by a layer of four bridging oxygen atoms in a centrosymmetric arrangement, it serves as a model for intermediates in the sol–gel synthesis of molybdenum oxides.

Competitive π-bonding at the metal centre can induce a π-donor ligand to adopt a bridging role in association reactions of mononuclear precursors to produce oligo- or poly-nuclear metal complexes. Owing to the potential of alkoxide ligands to engage in these interactions, metal alkoxides are becoming increasingly important as precursors for oxide preparation, notably *via* the 'sol–gel' process.[1] A sol–gel synthesis was reported as early as the last century;[2] the method makes use of hydrolysis of organometallic compounds (alkoxides) with well-defined properties to bring about polycondensation, first forming a colloidal solution, known as a sol, from which a gel is subsequently obtained. Gels prepared from metal alkoxide solutions are porous with a very large surface area, and so are excellent candidates for metallic catalysts or enzyme carriers, filters, adsorbents or membranes.[3] Examples of gel-derived transition metal oxides with special electrical and/or optical properties are the semiconducting V_2O_5, electrochromic WO_3 (which is used for display devices), thin film photoelectrodes of TiO_2, and monolithic gels of TiO_2, ZrO_2 and Nb_2O_5.[4] It is noteworthy, then, that amorphous films of MoO_3 obtained by vacuum evaporation show both photo- and electro-chromism[5] and, accordingly, the synthesis of molybdenum oxides by sol–gel techniques depending on the hydrolysis of compounds of the type Mo(O)(OR)Cl has already attracted some attention. Nagano and Greenblatt[4] produced compounds of the type $[MoCl_{5-x}(OEt)_x]$ from the reaction of $MoCl_5$ with KOEt; these were not characterised but hydrolysed to give colloidal products. The latter products could be converted to MoO_3 by heating to 300 °C in air, to MoO_2 by heating to 400 °C *in vacuo*, and to a mixture of Mo_4O_{11}, MoO_3 and MoO_2 by heating under a helium atmosphere.

One of the aims of the present research was to produce and isolate intermediates relevant to the sol–gel synthesis of molybdenum oxides starting from molybdenum-containing compounds incorporating ethoxide and chloride ligands. The true intermediates cannot be isolated from what is probably a complex mixture formed during the actual sol–gel process, and are likely in any case to be short-lived under these conditions. It is clearly of interest, however, to explore the nature of metal oxide alkoxides which are likely to form a bridge between the oligomeric metal alkoxides and the macromolecular metal oxides. Relatively few of these compounds have been isolated in crystalline form, so that there is a dearth of definitive structural data.[6]



1

The dimeric oxomolybdenum(V) compound $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1**[7] posseses several reactive centres and therefore seemed to be an ideal starting material for the generation of such species. It is well known that any strong Lewis acid can promote oxide and ether formation from alkoxides[8] and hence it was hoped, by working under suitably anhydrous conditions, that it would be possible to isolate tractable oligomeric species which might emulate intermediates in the sol–gel synthesis of molybdenum oxides. From the wide range of Lewis acids that might react with **1**, antimony(III) fluoride, SbF_3, was chosen because it has moderate strength and, in addition, is able to exchange Cl for F atoms under certain circumstances;[9] this possibility of Cl/F exchange was also significant for the light it might shed on the reactivity of the Cl ligands in **1**.

The reaction of **1** with SbF_3 produced a novel crystalline molybdenum ethoxide oxide $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**, derived from **1**. The structure of **2**, as determined by X-ray crystallography, is remarkable for having as its core an unprecedented $Mo_8(\mu_3\text{-}O)_4(\mu\text{-}O)_8$ unit which is closely related to the structure of the binary oxide MoO_2.[10] The results are discussed in relation to the likely mechanism of formation of **2** and to its potential significance

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

as a model for intermediates in the sol–gel synthesis of molybdenum oxides.

Experimental

All manipulations were carried out with a high vacuum line, in a glove-box, or by means of Schlenk-type techniques under a dry nitrogen atmosphere. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien GMBH, Gummersbach, Germany. Infrared spectra were recorded with a Mattson 'Galaxy' FTIR spectrometer. The SbF_3 (BDH) was purified by sublimation in high vacuum.

Synthesis of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**.—Freshly sublimed SbF_3 (0.08 g, 4.5 mmol) and $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1** (0.46 g, 0.9 mmol), prepared by the method described previously,[7] were mixed under an inert atmosphere in a flame-dried Schlenk tube, and toluene (30 cm^3) was added *via* a cannula. After stirring for 15 h, the suspension was filtered, and the volatile components were evaporated from the filtrate to leave a brown solid. This residue was redissolved in toluene (30 cm^3) and the solution layered with light petroleum (b.p. 40–60 °C, 150 cm^3). After 3 months, brown-red, well-formed crystals of **2** precipitated (0.019 g, 0.012 mmol, 5% yield based on **1** (Found: C, 12.60; H, 2.90; Mo, 45.30. $C_{16}H_{50}Cl_6Mo_8O_{26}$ requires C, 11.75; H, 3.10; Mo, 46.85%). We ascribe the deviations of the values found from those calculated to the presence of small amounts of a brown amorphous by-product, from which individual crystals of **2** could be seperated only by hand. IR: $\tilde{\nu}$/cm^{-1} (KBr disc): 3425m [ν(OH)], 3139m [ν(OH)], 2978m, 2933m, 2870m, 1632w [δ(OH)], 1440m, 1429m, 1383m, 1087m, 1001vs [ν(C–O) + ν(Mo=O)], 908m, 868m, 719s [ν(Mo–O–Mo)], 536m(br) [ν(Mo–O)]. Compound **2** was found to be soluble only in very polar solvents like dimethylformamide and dimethyl sulfoxide, and it is likely that these cause decomposition of the compound. Accordingly, no useful NMR measurements aimed at characterising **2** in solution could be made. The compound was reasonably stable in air and decomposed visibly only when heated to temperatures above 210 °C.

Crystal Structure of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$, **2**.—Crystals of **2** were loaded into carefully dried 0.3 or 0.5 mm Lindemann capillaries under dry nitrogen and the capillaries quickly sealed off.

Crystal data. $C_{16}H_{50}Cl_6Mo_8O_{26}$, $M = 1638.78$, triclinic, $P\bar{1}$, $a = 10.803(5)$, $b = 11.159(6)$, $c = 11.659(6)$ Å, $\alpha = 69.66(3)$, $\beta = 64.06(3)$, $\gamma = 66.258(24)°$, $U = 1131.6(10)$ Å^3, $Z = 1$, $D_c = 2.405$ g cm^{-3}, crystal size 0.43 × 0.31 × 0.12 mm, $\lambda = 0.710\,73$ Å, $T = 298$ K, μ(Mo-Kα) = 2.57 mm^{-1}, $F(000) = 792$.

Data collection and processing. Measurements were made on a Stöe Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation, 3852 reflections measured ($\theta_{max} = 22.5°$; $-10 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 12$), 2941 unique; $R_{int} = 0.0748$.

Structure analysis and refinement. Following data reduction and application of an absorption correction (ψ-scans, $T_{max} = 0.714$, $T_{min} = 0.615$), the crystal structure of **2** was solved by Patterson methods (DIRDIF[11]) to reveal the positions of all non-hydrogen atoms except four carbon and four oxygen atoms, which were located in a subsequent F_o synthesis. The positions of most hydrogen atoms could be calculated from the carbon atom coordinates, while the locations of hydrogen atoms attached to oxygen were derived either from difference maps [O(10) and O(23)] or [in the cases of O(13) and O(40)] by inference based on the environment of the oxygen atom in question. During subsequent refinement, each hydrogen atom was assigned an isotropic thermal parameter equal to 1.2 times the equivalent isotropic thermal parameter of the atom to which it is attached, and on which it was allowed to ride. The model, which is completely consistent with both analytical and spectroscopic evidence, was refined (against F^2, SHELXL-93[12]) with anisotropic thermal parameters on all non-hydrogen atoms to give a final 'conventional' R of 0.058 [based on F and 1585 data with $F > 4\sigma(F)$] and $wR_2 = 0.143$ (based on F^2 and all 2929 data) for 255 least-squares parameters $\{w^{-1} = [\sigma^2(F_o^2) + (0.0567P)^2]$ where $P = \frac{1}{3}[(F_o^2, 0)_{max} + 2F_c^2]\}$. The final difference synthesis maximum and minimum were 1.19 and -0.85 e Å^{-3}, respectively. Fractional atomic coordinates of all non-hydrogen atoms are listed in Table 1.

Table 1 Atomic coordinates (× 10^4) for $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	244(2)	7864(1)	4652(1)
Mo(2)	2768(2)	7665(2)	2750(2)
Mo(3)	60(2)	8731(2)	7702(1)
Mo(4)	2648(2)	8607(2)	5878(2)
Cl(2)	3708(7)	7664(6)	522(6)
Cl(3)	−1198(7)	7177(6)	9017(5)
Cl(4)	4510(8)	6958(8)	5030(7)
O(1)	561(12)	6280(10)	5396(10)
O(2)	3520(12)	6049(11)	3257(12)
O(3)	449(14)	8969(12)	8840(11)
O(4)	3325(13)	8825(11)	6791(12)
O(10)	−1934(12)	7853(11)	5049(10)
O(13)	−664(9)	8556(8)	6269(8)
O(20)	4408(15)	8380(16)	2448(12)
O(21)	905(12)	7662(11)	2818(11)
O(23)	1810(10)	9831(9)	2041(9)
O(34)	1768(12)	7185(9)	7090(10)
O(40)	3464(9)	9833(9)	4260(9)
O(124)	1892(11)	8302(10)	4414(10)
O(134)	−801(10)	9930(10)	3827(10)
C(101)	−2534(21)	6780(16)	5784(16)
C(102)	−3293(20)	6822(19)	7195(17)
C(201)	5546(22)	8783(29)	1398(20)
C(202)	6569(23)	8979(25)	1784(22)
C(211)	204(19)	7764(15)	1964(16)
C(212)	178(20)	6449(15)	1991(17)
C(341)	2252(22)	5757(14)	7575(18)
C(342)	2865(22)	5486(18)	8603(17)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Intermediates in the Nagano and Greenblatt process are of the type $[MoCl_{5-x}(OEt)_x]$.[4] In the case where $x = 2$, a dimeric molecule is formed, which has been isolated previously.[13] The monomer, it has been suggested, is an intermediate formed *en route* to the complex $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)MoOCl_2]$ **1**;[7] it appears subsequently to lose EtCl during this reaction with the creation of an Mo=O bond. Analogously, the oxide chloride derivative **1** may play an important role in sol–gel processes, a feature we have been exploring through our studies of its hydrolysis and other reactions.[14]

In its reaction with $SiMe_3(CH_2CH{=}CH_2)$,[15] **1** suffers destruction of its dimeric framework. This is initiated by the reaction of $SiMe_3(CH_2CH{=}CH_2)$ with the EtOH bridge affording propene, and the immediate molybdenum-containing products decompose generating reactive fragments containing O=MoCl(OEt) units. The fragments arrange themselves, in combination with other species present in solution, to generate the most stable cluster *via* Mo–Mo bond formation; for reactions brought about by $SiMe_3(CH_2CH{=}CH_2)$, this leads to the six-membered metallacycle $[Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu\text{-}OEt)_6(\mu\text{-}Cl)_2]$, **3**.[15] Encouraged by the intriguing way in which the fragments of **1** rearrange following the reaction with $SiMe_3(CH_2CH{=}CH_2)$, and bearing in mind the Lewis basicity of the alkoxide ligands in these circumstances, we have been exploring the response of **1** to Lewis acids, having as a target the initiation of fragmentation by opening the ethoxide bridges to initiate cluster formation. In the event, **1** reacts with SbF_3 in a dry toluene medium at ambient temperatures, not to yield any isolable molybdenum fluoride, but with the formation of red-brown crystals of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**, albeit in relatively low yields (*ca.* 5%). The brown crystals are insoluble in most common organic solvents like toluene, light petroleum, diethyl ether and dichloromethane. They dissolve in polar solvents like dimethylformamide and dimethyl sulfoxide, but probably react in doing so; similar complexes certainly react with co-ordinating solvents such as these.[7,15] Complex **2** is thermally relatively stable, showing no visible signs of decomposition at temperatures below 210 °C. Although long-term storage requires it to be kept under an inert atmosphere, it can be handled in air for short periods. The IR spectrum of the solid includes two distinct ν(OH) absorptions (at 3425 and 3139 cm^{-1}), implying the presence of two different kinds of OH group. A very intense band at 1001 cm^{-1} is attributable to the superposition of features originating in ν(C–O) and ν(Mo=O) vibrations, whereas a prominent band at 719 cm^{-1} is suggestive of the presence of Mo–O–Mo units.[17]

Crystal Structure of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**.—The crystal structure of **2** reveals a unique, centrosymmetric $Mo_8(\mu_3\text{-}O)_4(\mu\text{-}O)_8$ core encapsulated by terminal oxo, ethoxide, hydroxo, chloro and ethanol ligands, as shown in Fig. 1; selected bond lengths and angles are listed in Tables 2 and 3. The oxidation state of the molybdenum is +5 (d^1), and eight electrons are used in the formation of four Mo–Mo single bonds [Mo(1)–Mo(2) 2.639(3), Mo(3)–Mo(4) 2.655(3) Å]. The other Mo···Mo distances exceed the commonly accepted minimum for two non-bonding Mo atoms bridged by alkoxide ligands (3.3 Å).[18] Although there is no significant difference between the chemically distinct Mo–Mo bonds in **2**, they are slightly shorter [by 0.022(4) Å] than those in the related complex $[Mo_6O_6Cl_6(\mu\text{-}OEt)_6(\mu_3\text{-}O)_2(\mu\text{-}Cl)_2]$ **3**.[15] In common with **3**, **2** exhibits two chemically distinct, essentially planar $(\mu_3\text{-}O)Mo_3$ moieties centred on O(124) and O(134), and each incorporating a bridging interaction across a Mo–Mo single bond. The lengths of the μ_3-O–Mo bonds are determined mainly by the ligands *trans* to the oxygen atoms. Thus, the shortest such bond [Mo(1)–O(124) 1.913(10) Å] is formed *trans* to a terminal ethanol ligand; Mo(3)–O(134), Mo(4)–O(134) and Mo(2)–O(124), with lengths in the range 1.979(10)–1.994(10) Å, are formed *trans* to terminal Mo–Cl bonds; and the longest bonds [Mo(4)–O(124) 2.355(10) Å and Mo(1)–O(134) 2.197(10) Å] are located *trans* to Mo=O bonds. The trend is consistent with the well known *trans* influence of strongly-bound ligands.[19] The bond angles at the μ_3-O atoms in **2** (85–143°) do not vary as widely as those in **3** (85–174°), but the smallest angle is consistently formed across the Mo–Mo bond in both complexes.

In addition to the μ_3-O functions, there are four μ-OH and four μ-OEt ligands. By contrast with the symmetrical Mo(μ-OEt)Mo bridges, the Mo(μ-OH)Mo bridges are highly unsymmetrical [Mo(1)–O(13) 1.974(8), Mo(3)–O(13) 2.222(8), Mo(3)–O(23) 1.986(9), Mo(2)–O(23) 2.223(9) Å], although, as with the distribution of μ_3-O–Mo bond lengths, this feature appears once again to reflect the influence of ligands *trans* to the bonds in question (μ_2-OEt and Mo=O for the shorter and longer bonds, respectively). As in **3**, the methylene carbon and two metal substituents are coplanar with the μ-O atom of the ethoxide bridge.

In terms of Green's MLX notation (X = one-electron ligand; L = two-electron ligand),[20] the co-ordination about each metal centre in **2** can be described as MoX_6L_2. This particularly stable co-ordination motif is achieved in **2** by four sets of two edge-sharing octahedra linked by corner-sharing interactions at the four μ_3-oxo atoms. As shown in Fig. 2, the structure is strongly reminiscent of the distorted rutile structure of MoO_2.[10] There are, naturally, some differences between the two structures arising from variations in oxidation state and ligation. This is exemplified by the difference in Mo–Mo bond lengths [2.647(3) Å (av.) in **2** and 2.5106(5) Å in MoO_2] and by the more symmetrical distribution of bond lengths about the μ_3-oxygen atoms of MoO_2 [1.972(3)–2.073(3) Å]. Nevertheless, the core of **2** is a clear indication of the pre-assembly of a fragment of molybdenum dioxide, such as may occur during the synthesis of molybdenum oxides by the sol–gel methods described, for example, by Nagano and Greenblatt.[4] Accordingly, **2** may well be representative of key intermediates formed on the microscopic scale during this and other sol–gel processes.

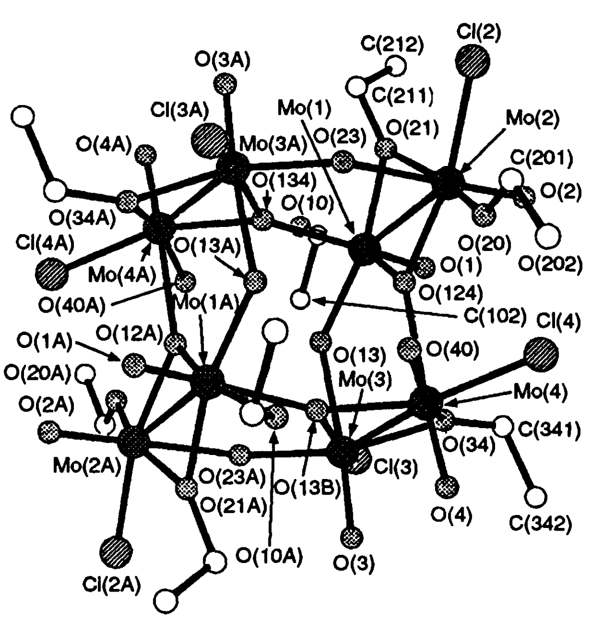


Fig. 1 Molecular structure[16] of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**. For clarity all hydrogen atoms have been omitted. Apart from hydrogens bonded to carbon atoms, hydrogen atoms are located at the oxygen atoms O(10), O(13), O(20), O(23), O(10A), O(13A), O(20A) and O(23A)

Table 2 Bond distances (Å) for $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2***

Mo(1)–O(1)	1.643(10)	Mo(3)–Cl(3)	2.331(6)
Mo(1)–O(124)	1.913(10)	Mo(3)–Mo(4)	2.655(3)
Mo(1)–O(13)	1.974(8)	Mo(4)–O(4)	1.654(10)
Mo(1)–O(21)	2.001(11)	Mo(4)–O(34)	1.975(11)
Mo(1)–O(10)	2.195(11)	Mo(4)–O(40)	1.982(9)
Mo(1)–O(134)	2.197(10)	Mo(4)–O(134A)	1.982(10)
Mo(1)–Mo(2)	2.639(3)	Mo(4)–Cl(4)	2.226(8)
Mo(2)–O(2)	1.661(11)	Mo(4)–O(124)	2.355(10)
Mo(2)–O(21)	1.980(11)	O(10)–C(101)	1.42(2)
Mo(2)–O(124)	1.994(10)	O(20)–C(201)	1.40(2)
Mo(2)–O(20)	2.074(13)	O(21)–C(211)	1.445(14)
Mo(2)–O(23)	2.223(9)	O(23)–Mo(3A)	1.986(9)
Mo(2)–Cl(2)	2.339(6)	O(34)–C(341)	1.447(14)
Mo(3)–O(3)	1.682(11)	O(134)–Mo(3A)	1.979(10)
Mo(3)–O(134A)	1.979(10)	O(134)–Mo(4A)	1.982(10)
Mo(3)–O(23A)	1.986(9)	C(101)–C(102)	1.49(2)
Mo(3)–O(34)	2.007(10)	C(201)–C(202)	1.47(2)
Mo(3)–O(13)	2.222(8)	C(211)–C(212)	1.468(14)
		C(341)–C(342)	1.50(2)

* Symmetry operation used to generate equivalent atoms: A $-x, -y + 2, -z + 1$.

Table 3 Bond angles (°) in $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**

O(1)–Mo(1)–O(124)	103.6(5)
O(1)–Mo(1)–O(13)	94.8(4)
O(124)–Mo(1)–O(13)	85.4(4)
O(1)–Mo(1)–O(21)	99.7(5)
O(124)–Mo(1)–O(21)	95.4(4)
O(13)–Mo(1)–O(21)	164.7(4)
O(1)–Mo(1)–O(10)	87.2(5)
O(124)–Mo(1)–O(10)	165.7(4)
O(13)–Mo(1)–O(10)	84.4(4)
O(21)–Mo(1)–O(10)	91.8(4)
O(1)–Mo(1)–O(134)	163.5(4)
O(124)–Mo(1)–O(134)	92.5(4)
O(13)–Mo(1)–O(134)	82.8(4)
O(21)–Mo(1)–O(134)	82.0(4)
O(10)–Mo(1)–O(134)	76.3(4)
O(1)–Mo(1)–Mo(2)	97.6(4)
O(124)–Mo(1)–Mo(2)	48.8(3)
O(13)–Mo(1)–Mo(2)	134.2(3)
O(21)–Mo(1)–Mo(2)	48.1(3)
O(10)–Mo(1)–Mo(2)	139.9(3)
O(134)–Mo(1)–Mo(2)	95.8(3)
O(2)–Mo(2)–O(21)	101.7(5)
O(2)–Mo(2)–O(124)	100.6(5)
O(21)–Mo(2)–O(124)	93.5(4)
O(2)–Mo(2)–O(20)	98.6(6)
O(21)–Mo(2)–O(20)	159.7(6)
O(124)–Mo(2)–O(20)	82.9(5)
O(3)–Mo(3)–Cl(3)	98.8(4)
O(134A)–Mo(3)–Cl(3)	159.6(3)
O(23A)–Mo(3)–Cl(3)	88.8(3)
O(34)–Mo(3)–Cl(3)	87.4(3)
O(13)–Mo(3)–Cl(3)	80.4(3)
O(3)–Mo(3)–Mo(4)	95.6(4)
O(134A)–Mo(3)–Mo(4)	48.0(3)
O(23A)–Mo(3)–Mo(4)	132.2(3)
O(34)–Mo(3)–Mo(4)	47.7(3)
O(13)–Mo(3)–Mo(4)	88.8(2)
Cl(3)–Mo(3)–Mo(4)	134.7(2)
O(4)–Mo(4)–O(34)	100.5(5)
O(4)–Mo(4)–O(40)	96.8(5)
O(34)–Mo(4)–O(40)	161.9(4)
O(4)–Mo(4)–O(134A)	100.5(5)
O(34)–Mo(4)–O(134A)	94.7(4)
O(40)–Mo(4)–O(134A)	87.4(4)
O(4)–Mo(4)–Cl(4)	98.1(4)
O(34)–Mo(4)–Cl(4)	85.7(4)
O(40)–Mo(4)–Cl(4)	86.5(3)
O(134A)–Mo(4)–Cl(4)	161.0(3)
O(4)–Mo(4)–O(124)	174.6(5)
O(34)–Mo(4)–O(124)	83.4(4)
O(40)–Mo(4)–O(124)	79.0(4)
O(134A)–Mo(4)–O(124)	82.9(4)
Cl(4)–Mo(4)–O(124)	78.3(3)
O(2)–Mo(2)–O(23)	178.7(5)
O(21)–Mo(2)–O(23)	79.4(4)
O(124)–Mo(2)–O(23)	80.0(4)
O(20)–Mo(2)–O(23)	80.3(5)
O(2)–Mo(2)–Cl(2)	97.1(5)
O(21)–Mo(2)–Cl(2)	89.1(4)
O(124)–Mo(2)–Cl(2)	161.2(3)
O(20)–Mo(2)–Cl(2)	88.2(4)
O(23)–Mo(2)–Cl(2)	82.2(3)
O(2)–Mo(2)–Mo(1)	96.7(4)
O(21)–Mo(2)–Mo(1)	48.8(3)
O(124)–Mo(2)–Mo(1)	46.2(3)
O(20)–Mo(2)–Mo(1)	128.7(4)
O(23)–Mo(2)–Mo(1)	84.5(2)
Cl(2)–Mo(2)–Mo(1)	137.6(2)
O(3)–Mo(3)–O(134A)	100.9(5)
O(3)–Mo(3)–O(23A)	95.5(5)
O(134A)–Mo(3)–O(23A)	84.3(4)
O(3)–Mo(3)–O(34)	101.0(5)
O(134A)–Mo(3)–O(34)	93.8(4)
O(23A)–Mo(3)–O(34)	163.4(4)
O(3)–Mo(3)–O(13)	174.4(5)
O(134A)–Mo(3)–O(13)	79.4(3)
O(23A)–Mo(3)–O(13)	79.0(4)
O(34)–Mo(3)–O(13)	84.5(4)
O(4)–Mo(4)–Mo(3)	94.8(5)
O(34)–Mo(4)–Mo(3)	48.7(3)
O(40)–Mo(4)–Mo(3)	135.2(3)
O(134A)–Mo(4)–Mo(3)	47.8(3)
Cl(4)–Mo(4)–Mo(3)	134.2(2)
O(124)–Mo(4)–Mo(3)	90.6(3)
C(101)–O(10)–Mo(1)	126.8(11)
Mo(1)–O(13)–Mo(3)	136.9(5)
C(201)–O(20)–Mo(2)	137.9(12)
C(211)–O(21)–Mo(2)	140.5(11)
C(211)–O(21)–Mo(1)	135.3(11)
Mo(2)–O(21)–Mo(1)	83.1(4)
Mo(3A)–O(23)–Mo(2)	141.9(5)
C(341)–O(34)–Mo(4)	137.3(11)
C(341)–O(34)–Mo(3)	136.7(11)
Mo(4)–O(34)–Mo(3)	83.6(4)
Mo(1)–O(124)–Mo(2)	85.0(4)
Mo(1)–O(124)–Mo(4)	132.4(5)
Mo(2)–O(124)–Mo(4)	138.6(5)
Mo(3A)–O(134)–Mo(4A)	84.2(4)
Mo(3A)–O(134)–Mo(1)	132.5(5)
Mo(4A)–O(134)–Mo(1)	143.2(5)
O(10)–C(101)–C(102)	112.9(13)
O(20)–C(201)–C(202)	114(2)
O(21)–C(211)–C(212)	111.6(12)
O(34)–C(341)–C(342)	109.7(12)

Mechanism of Formation of **2**.—While the structural details are relatively clearcut, the mechanism leading to the formation of **2** is far from clear. The fact that the compound is only sparingly soluble in toluene suggests that it is not a significant component of the original toluene-soluble mixture which was overlayered with light petroleum. A ^1H NMR spectrum of this mixture had shown that it consisted of quite a number of molybdenum ethoxides, whose signals overlapped to yield two broad features between δ_H 1.0–2.0 and 5.0–6.0. In a ^{19}F NMR experiment no signal could be detected, but this is not necessarily a sign for the absence of any metal fluorides, since flourine bonded to a paramagnetic molybdenum centre would give rise to a broad feature which, combined with a low concentration of the corresponding species, could become difficult to identify. However, after the formation of **2**, SiF_4 was identified as a gaseous product by its IR spectrum.[21] This implies that the brown solid obtained initially after evaporating the volatile material from the filtrate contains a metal fluoride other than SbF_3 which is virtually insoluble in toluene. This fluoride must then react slowly either with the solvent or with other organic ligands, or it may simply decompose, with the elimination of HF. The HF reacts in the next step with the walls of the glass container, thereby accounting for the SiF_4 formed. The water co-produced with the SiF_4 may cause slow hydrolysis of one of the compounds in the original mixture, and so give rise to the bridging OH groups occurring in **2**.

If this explanation is correct, addition of HF should speed up the formation of **2**. The experiment was therefore repeated, but without removing the volatile material before overlaying, the solution then being saturated with HF generated by reaction (1), which inevitably occurred during the long period of

$$SbF_3 + EtOH \longrightarrow SbF_2(OEt) + HF \qquad (1)$$

interaction (15 h). In these circumstances, crystal growth of **2** started within two weeks instead of two months, although the

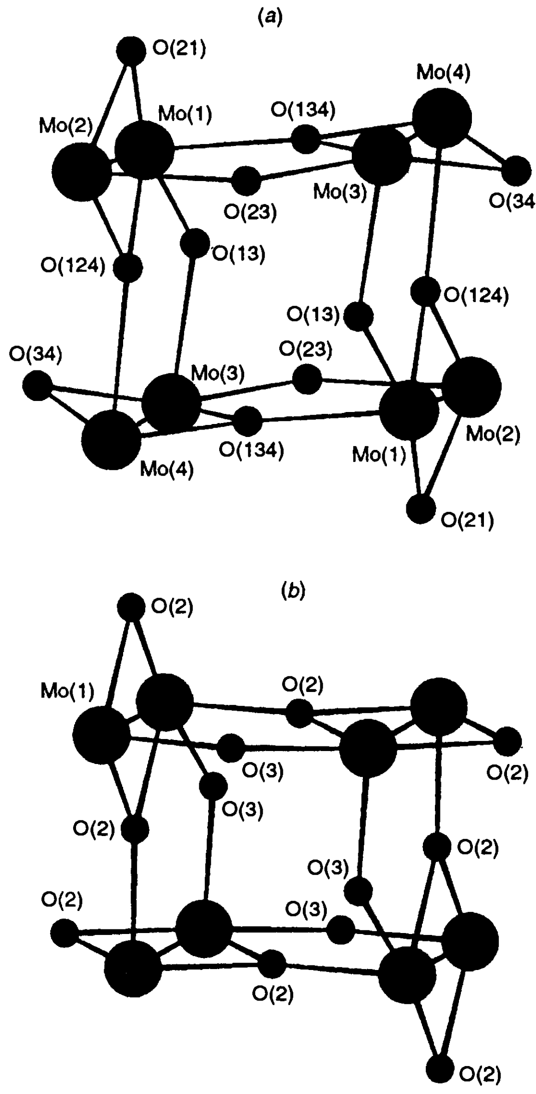


Fig. 2 Comparison of the $Mo_8(\mu_3\text{-}O)_4(\mu\text{-}O)_8$ core of 2(*a*) with a similar fragment of the crystal structure of molybdenum dioxide (*b*). The numbering scheme in (*b*) is taken from Ref. 10

quality of the crystals was inferior to those grown by the original method over an interval of three months.

Another control experiment was undertaken using glassware which had not been pre-conditioned by 'flaming out'. In this case, a brown powder precipitated on the walls of the reaction vessel, and this was shown by elemental analysis and by its IR spectrum to be the compound **2**. There can be little doubt therefore that protonation reactions play an important role in the formation of **2**.

Conclusion

The reactions of **1** with different reagents, leading for instance to the cluster compounds **2** and **3**, seem to have some features in common, which call for comment. In all the reactions, the primary step probably involves attack of the reagent at the highly reactive EtOH bridging ligand of **1**. For the reaction with $SiMe_3(CH_2CH{=}CH_2)$, this step was demonstrated to lead to the formation of propene and presumably $SiMe_3(OEt)$ as well. If SbF_3 is chosen as the reagent, HF and probably $SbF_2(OEt)$ is formed.

During the formation of both complexes **2** and **3**, the stable arrangement of **1** is destroyed and the intermediates initially formed decompose [in the case of the reaction with $SiMe_3(CH_2CH{=}CH_2)$, heating is required, whereas the formation of **2** requires the intervention of H_2O]. This decomposition seems to generate reactive fragments containing O=MoCl(OEt) units, which are common to the two products. The subsequent aggregation processes have the common feature of proceeding with C–O bond cleavage, which occurs under extremely mild conditions and leads to the creation of μ_3-O or μ-OH bridging ligands. These oxo or hydroxo groups hold together the cluster framework and are probably responsible for the special structural features brought to light for the first time in the complexes **2** and **3**. The Mo centres of **2** and **3** typically show the extremely stable MoX_6L_2 co-ordination mode (although the mode MoX_5L_2 also occurs in **2**), a feature undoubtedly contributing to the stability of the complexes, and one which may well be the driving force for their formation.

At the outset of the present research, the aim was to produce and isolate intermediates relevant to the sol–gel synthesis of molybdenum oxides starting from molybdenum compounds incorporating ethoxide and chloride ligands. By the interaction with different reagents under varying conditions, it has proved possible to convert the dinuclear species **1** into hexanuclear (**3**) and octanuclear (**2**) products. By degrees, therefore, there is emerging a picture of the formation of molybdenum oxide clusters, a process which may be expected to terminate in the polymeric, homoleptic molybdenum oxides, *viz.* the ultimate products of the sol–gel process. The connection between the intermediate and final products is highlighted by the finding of an encapsulated, preformed fragment of MoO_2 in the cluster compound $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu\text{-}OH)_4(\mu\text{-}OEt)_4(HOEt)_4]$ **2**.

Further research will be aimed at directing the cluster size, with reagents and reaction conditions optimised to provide a more systematic basis for the investigation of such intermediates. With respect to the reaction of **1** with SbF_3 to form **2** further experiments will be undertaken in order to shed some more light on its formation. These will include the treatment of **1** with for instance $SbCl_3$, HF and other Lewis acids.

Nevertheless, the results of the present research give some illuminating insights into the nature of the bonding in potential intermediates and into the polycondensation reactions which give rise to them.

Acknowledgements

We thank the Studienstiftung des Deutschen Volkes and the BASF AG for a post-doctoral scholarship (to C. L.) and the EPSRC for provision of a diffractometer (at Edinburgh), as well as other equipment (at Oxford) and for post-doctoral funding (to S. P.).

References

1 J. J. Ebelmen, *Ann. Chem.*, 1846, **57**, 319.
2 C. J. Brinker and G. W. Scherer, *Sol–Gel Science: the Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990; R. C. Mehrotra, *Struct. Bonding (Berlin)*, 1992, **77**, 1.
3 L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1987, **11**, 663.
4 M. Nagano and M. Greenblatt, *J. Non-Cryst. Solids*, 1988, **101**, 255.
5 R. J. Colton, A. M. Guzman and J. W. Rabalais, *Acc. Chem. Res.*, 1978, **11**, 170.
6 D. C. Bradley, *Chem. Rev.*, 1989, **89**, 1317.
7 C. Limberg, S. Parsons, A. J. Downs and D. J. Watkin, *J. Chem. Soc., Dalton Trans.*, 1994, 1169.
8 K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.*, 1990, **90**, 969.
9 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., Syst. No. 18, Gmelin-Verlag, Clausthal-Zellerfeld, 1949, p. 396.
10 B. G. Brandt and A. C. Skapski, *Acta Chem. Scand.*, 1967, **21**, 661.
11 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

12 G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, 1993.
13 D. C. Bradley, R. K. Multani and W. Wardlaw, *J. Chem. Soc.*, 1958, 4647.
14 C. Limberg, D. Phil. Thesis, University of Oxford, 1995.
15 C. Limberg, S. Parsons and A. J. Downs, *J. Chem. Soc., Chem. Commun.*, 1994, 497.
16 L. J. Pearce and D. J. Watkin, CAMERON, Chemical Crystallography Laboratory, University of Oxford, 1993.
17 E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 45.
18 M. H. Chisholm, J. C. Huffman, C. C. Kirkpatrick, J. Leonelli and K. Folting, *J. Am. Chem. Soc.*, 1981, **103**, 6093 and refs. therein.
19 A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1707.
20 M. L. H. Green, in *Molybdenum: An Outline of its Chemistry and Uses*, ed. E. Braithwaite, Elsevier, Amsterdam, 1994; E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984, p. 20.
21 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

Received 26th April 1995; *Paper* 5/02676H