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Modeling the Formation of Molybdenum Oxides from Alkoxides: Crystal Structures of $[Mo_4O_4Cl_4(\mu_2\text{-OEt})_4(HOEt)_2(\mu_3\text{-O})_2]$ and $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-O})_2Mo(O)Cl_2]^{2-}$

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The reactions of the binuclear oxomolybdenum(V) complex $[Cl_2(O)Mo(\mu\text{-OEt})_2(\mu\text{-HOEt})Mo(O)Cl_2]$ (**1**) with Me_3Si(allyl) and SbF_3 produce the compounds $[Mo_6O_6Cl_6(\mu_3\text{-O})_2(\mu_2\text{-OEt})_6(\mu_2\text{-Cl})_2]$ (**2**) and $[Mo_8O_8Cl_6(\mu_3\text{-O})_4(OH)_2(\mu_2\text{-OH})_4(\mu_2\text{-OEt})_4(HOEt)_4]$ (**3**), respectively. Treatment of **1** with the Lewis base PMe_3 affords the tetrameric complex $[Mo_4O_4Cl_4(\mu_2\text{-OEt})_4(HOEt)_2(\mu_3\text{-O})_2]$ (**4**), which represents another link in the chain of clusters produced by the reactions of **1** and simulating the build-up of polymeric molybdenum oxides by sol−gel methods. The crystal structure of **4** has been determined [$C_{12}H_{32}Cl_4Mo_4O_{12}$, triclinic, $P\bar{1}$, $a = 7.376(2)$ Å, $b = 8.807(3)$ Å, $c = 11.467(4)$ Å, $\alpha = 109.61(1)°$, $\beta = 92.12(3)°$, $\gamma = 103.75(2)°$, $Z = 1$]. By contrast, reaction of **1** with the nitrogen base NEt_3, followed by treatment with $[PPN]Cl\cdot 2H_2O$ ($[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$), gives the complex $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-O})_2Mo(O)Cl_2]^{2-}$ (**6**) in 90% yield. Its crystal structure [$C_{36}H_{30}Cl_4MoNOP_2$, triclinic, $Pna2_1$, $a = 21.470(6)$ Å, $b = 16.765(2)$ Å, $c = 9.6155(14)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $Z = 16$] includes the anion $[Cl_2(O)Mo(\mu_2\text{-O})_2Mo(O)Cl_2]^{2-}$, which is a charged derivative of the species forming the gels in sol−gel processes starting from chloromolybdenum ethoxides. Furthermore, compound **1** is found to be catalytically active in esterification and dehydration reactions of alcohols.

Introduction

The ultrastructural control of materials through sol−gel processes offers significant promise for the achievement of reliable performance in glasses, glass ceramics, ceramics, and composites.[1] The most versatile way of making oxide gels undoubtedly entails the hydrolysis and condensation of metal alkoxides, since the latter are renowned for their susceptibility to hydrolysis to form the corresponding metal oxides, *e.g.*[2]

$$M(OR)_4 + 2H_2O \rightarrow MO_2 + 4ROH \quad (M = \text{metal}) \quad (1)$$

On the other hand, the mechanism by which the alkoxide—typically an oligomer, $[M(OR)_n]_m$—is converted to the macromolecular $[M_mO_n]_p$ oxide network is relatively obscure. Selective decomposition of an alkoxide to an oxo alkoxide can occur for an oxophilic metal such as tungsten or molybdenum.[3]

Hence it is important to investigate the nature of the metal oxide alkoxides so as to bridge the gap between the oligomeric metal alkoxide, $[M(OR)_n]_m$, and the macromolecular metal oxide.[2] The oxide alkoxides hold significance not only in relation to the reaction mechanisms operating at a molecular level in sol−gel processes but also for their much enhanced solubility in common solvents compared with that of the corresponding parent oxides, the metal oxide core being surrounded by a lipophilic layer of alkoxy groups. The molecular aggregates present in these intermediates can be regarded as small fragments of the extended structures characteristic of the parent oxides; they still mimic some of the important properties of typical inorganic oxides—O_2 activation, for instance—and represent attractive model systems at the frontier between homogeneous and heterogeneous catalysis.[3]

Amorphous films of MoO_3 obtained by vacuum evaporation show both photo- and electrochromism,[4] and the color center phenomenon has been observed in crystalline and amorphous forms of H_xMoO_3 with absorptions appearing at 870 nm.[5] These and other exploitable properties of the molybdenum oxides have already prompted two groups to investigate sol−gel methods of production. In 1967 Anand *et al.* synthesized molybdenum alkoxides from molybdenum oxide tetrachloride ($OMoCl_4$) and the appropriate alcohols.[6] Alkoxide hydrolysis and condensation reactions were shown to occur in the course of sol−gel operations. The results of a spectroscopic analysis led Méndez-Vivar *et al.* to conclude that the final product of the hydrolysis is a dimer (**I**), which, after being calcined at 400 °C, transforms into MoO_3; on heating at 900 °C, this becomes Mo_8O_{23}.[7] The reactions can be written as in Scheme 1.

Greenblatt and Nagano hydrolyzed compounds of the type $MoCl_{5-x}(OEt)_x$ to give colloidal products. These 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.[8]

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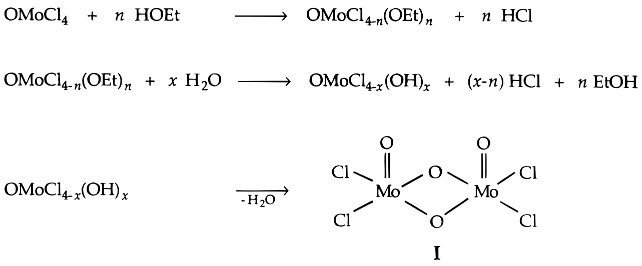
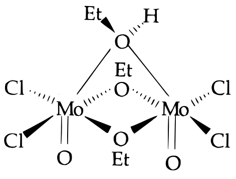
Scheme 1. Production of Oxomolybdenum Chloride Gels from Oxomolybdenum Chloride Ethoxides



The studies described here had as their basis the stepwise preparation, isolation, and characterization of compounds which might emulate intermediates in such sol−gel processes. Hence it was hoped to elucidate the nature of the bonding and polycondensation in the species of interest. The intention was to start from a novel precursor superior to those used in previous studies and then pursue a systematic exploration of its chemistry. This needs ideally to be a simple reagent containing (EtO)-MoCl or (O)Mo(OEt)Cl units and therefore resembling the sort of molecules which have been postulated as intermediates in the sol−gel processes mentioned above. It should also contain a reactive center bearing a good leaving group so that interaction with a simple reagent is likely to release highly reactive fragments capable of rearranging to the most stable complexes or clusters which the conditions will allow. By varying the reagents and the reaction conditions, it should be possible to generate clusters which have different sizes and bonding patterns and which may afford insights into the course of events under the more drastic conditions operating in sol−gel processes.

Results and Discussion

Since the speed of hydrolysis and polycondensation reactions has made it impossible to isolate intermediates under the reaction conditions of the sol−gel synthesis of molybdenum oxides, access to such intermediates has been sought under rigorously anhydrous conditions. A starting material possessing the desiderata outlined above was found in the binuclear oxomolybdenum(V) complex [$Cl_2(O)Mo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)Mo(O)Cl_2$], **1**, whose synthesis and structure have been described previously.[9] One class of intermediates in the sol−gel synthesis of molybdenum oxides, as performed by Méndez-Vivar *et al.* (Scheme 1), was found to consist of compounds with the composition $OMoCl_{4-n}(OEt)_n$. The product with $n = 2$ is then very similar to **1** in relation to the environment of just one of the Mo centers. Intermediates in the Greenblatt and Nagano process starting from $MoCl_5$ are of the type $MoCl_{5-x}(OEt)_x$. Again, with $x = 2$, the product is one which has been mooted as an intermediate during the formation of **1** and which subsequently loses EtCl to form an Mo═O bond.[9] Hence it appears that **1** is of some relevance to these proposed reaction sequences. In addition, **1** provides the first authenticated example of an EtOH bridge between two transition metal atoms, and this feature invites further investigation as a potentially labile leaving group or reaction center.



1

1. Catalytic Properties of 1. The presence of the EtOH bridge, with its potential lability as a leaving group, suggests that **1** may show catalytic activity. The most obvious reactions for which this activity might be tested involve the EtOH molecule itself, viz. esterification, dehydration, and oxidation.

Esterification. A control experiment showed that heating a 1:1 mixture of EtOH and CH_3CO_2H to 80 °C for 1 h in the presence of an excess of $MgSO_4$ failed to bring about any detectable reaction. Introduction of catalytic amounts of **1**, together with an excess of $MgSO_4$, into the 1:1 mixture, followed by heating to 80 °C for 1 h, led to the generation of ethyl acetate in *ca.* 95% yield.

The same result can be achieved by heating a 1:1 EtOH/CH_3CO_2H mixture saturated with HCl. It is remarkable, nevertheless, that **1** promotes this reaction so efficiently in the absence of a significant concentration of HCl, albeit functioning only as a precatalyst which is modified by the CH_3CO_2H, so that it cannot be recovered. The possibility that the observed catalytic activity is merely a result of protonation of **1** by CH_3CO_2H, thereby delivering HCl as the active agent, is ruled out by the reaction of **1** with an excess of CH_3CO_2H, which yields, after removal of the volatile components, a brown solid. Elemental analysis showed that the brown solid retains molybdenum and chlorine in the proportion 1:2, thereby arguing against the formation of HCl during the reaction and implying that the Mo−Cl bonds in **1** resist protonation. This does not of course prove that HCl is totally absent when **1** is used as the catalyst.

Other molybdenum oxo compounds, like $(NH_4)_2MoO_4$ and MoO_3, show no such catalytic activity. Evidently, therefore, the presence of Mo═O bonds is not sufficient to catalyze esterification. The results of the present experiments suggest that **1** might be useful as a catalyst in esterification reactions where one of the substrates is susceptible to acid attack.

Dehydration and Oxidation. Experiments trying to employ **1** as a catalyst for the dehydration of alcohols gave the corresponding alkenes in low yields, while **1** appeared to be completely inactive in promoting the oxidation of alcohols.

2. Hydrolysis of 1. To test the potential of **1** as a starting material for the synthesis of molybdenum oxide gels by sol−gel methods, its hydrolysis was investigated. For this purpose, a solution of **1** in CH_2Cl_2 was allowed to stand for 1 week in air at ambient temperatures and with continuous stirring.

Dissolution of **1** in dry CH_2Cl_2 gave at first an orange-brown solution. Subsequently, within 5 days under the action of the moist air, a fine blue powder precipitated. The blue color suggests the formation of mixed-valent compounds (Mo^{V}/Mo^{VI}). After drying overnight *in vacuo*, the powder had the composition $Mo_{6.5}O_{31.2}(OEt)Cl_{4.6}H_{18.3}$ on the basis of elemental analysis. Our experiments gave no sign of a clear sol-to-gel transition.

The production of a powder rather than a gel under these conditions is not unduly surprising since the sol−gel process is highly mutable, and fine control of the hydrolysis parameters and/or the drying procedures is liable to lead to quite different products. For instance, fast hydrolysis yields reactive powders which, on sintering, give ceramics, whereas slow hydrolysis can lead to transparent films and whiskers.[3] Accordingly, the hydrolysis of **1** was also performed slowly by using a valve to control the access of air to a CH_2Cl_2 solution of **1**. Within about

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8 weeks, a blue oil was observed to separate and collect at the bottom of the container, where it became relatively hard over an additional period of about 2 weeks. This product, being transparent in thin layers, corresponded to a gel in the general sense. The solid products obtained by slow and fast hydrolysis probably consist of different molybdenum oxides and hydrates resulting from variations in the extent of hydrolysis and polymerization.

Our results are in excellent agreement with those of Nagano and Greenblatt, who hydrolyzed Mo(OEt)Cl compounds of unknown composition. It appears, then, that **1** is indeed a possible source of molybdenum oxides by way of sol−gel methods.

3. Generation of Ethoxomolybdenum Oxide Clusters. Alkoxides of metals or metalloids other than silicon are subject to hydrolysis and condensation reactions which are so fast as to make it difficult to gain microstructural control over the resulting gel.[11] In an attempt to achieve better control over microstructural evolution of the metal oxide, attention has been drawn to alternative, nonhydrolytic routes to these materials.[12] The highly reactive compound **1** could be an ideal precursor for such investigations, since it can be expected to respond differently to various types of reagent through one functional group or another. Thus, Fuchs was able to produce new types of tungstate by performing the hydrolysis and condensation reactions of alkoxides in the presence of soluble bases in an organic solvent, rather than in water.[13] By totally excluding water from the aggregation stages, it should be possible to isolate derivatives of the polyanions which still contain alkoxide functions.

(a) Reaction with an Organic Nucleophile. First, the reactivity of the Cl atoms of **1** was studied in experiments focusing on possible exchange pathways involving organic and inorganic nucleophiles. Because of its π-donating alkoxy ligands, **1** constitutes a potentially useful starting material for the synthesis of organomolybdenum oxides. Treatment with allyltrimethylsilane, $Me_3Si(allyl)$, at room temperature, with the aim of making the corresponding allylmolybdenum compound *via* metathesis, resulted in the evolution of 1 mol of propene/mol of **1** taken. Hence, it appears that the first step in the reaction of **1** with $Me_3Si(allyl)$ involves the EtOH bridge:

$$\mathrm{EtOH} + \mathrm{Me_3Si(allyl)} \rightarrow \mathrm{EtOSiMe_3} + \mathrm{CH_3CH{=}CH_2} \qquad (2)$$

That the allyl group is indeed protonated by the EtOH molecule has been confirmed by the reaction of the C_2H_5OD version of **1** with $Me_3Si(allyl)$, which yields $CH_2DCH{=}CH_2$.

After removal of the volatile components of the reaction mixture, an oily red residue remained. From this a bright orange microcrystalline material with the composition $[MoO_3C_4H_{9.25}Cl_2]_n$ could be obtained by extraction with petroleum ether (40:60). Once the properties of this solid made it clear that the reaction of **1** with $Me_3Si(allyl)$ at room temperature does not cleave the Mo−Cl bonds, attempts were made to force their replacement by heating the mixture overnight at 75 °C. This caused the precipitation of red crystals of the compound $[Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}EtO)_6(\mu_2\text{-}Cl)_2]$, which, as described previously, consists of a cyclic array of six (Cl−Mo═O) units in a unique chair configuration (see Figure 1).[14] The same structure survives in solution, as shown by the ^1H NMR spectrum of a CD_2Cl_2 solution; distinct sets of signals were observed for the three different types of EtO groups present in **2**. Corresponding to the three different Me groups, three triplets occur at δ_H 1.56 [$^3J(HH) = 6.8$ Hz], 1.73 [$^3J(HH) = 6.8$ Hz], and 2.08 [$^3J(HH) = 7.0$ Hz]. Instead of the three quartets expected for the CH_2 groups, there appear (at 300 MHz) three signals of higher order at δ_H 4.86, 5.57, and 5.95. Since NMR properties of this sort are unprecedented for EtOMo compounds, several decoupling experiments were undertaken in an attempt to seek an explanation for the additional coupling, and it appears that, if **2** has a rigid structure, the CH_2 protons are diastereotopic, showing different ^1H resonances and being coupled to each other. Every chemically distinct $O{-}CH_2$ group should show a set of two doublets which are subject to additional coupling with the neighboring CH_3 group, giving rise to higher order signals. The spectrum is complicated because the three multiplets arise from the protons of different EtO groups and overlap one another. In every case, the coupling constant between the two diastereotopic methylene protons amounts to 11.7 Hz and the three sets of two protons absorb at δ_H 5.64 and 6.01, 4.87 and 5.71, and 5.62 and 6.02. It is not possible, however, to determine which of the three different sets of signals belongs to which of the EtO groups in **2**.

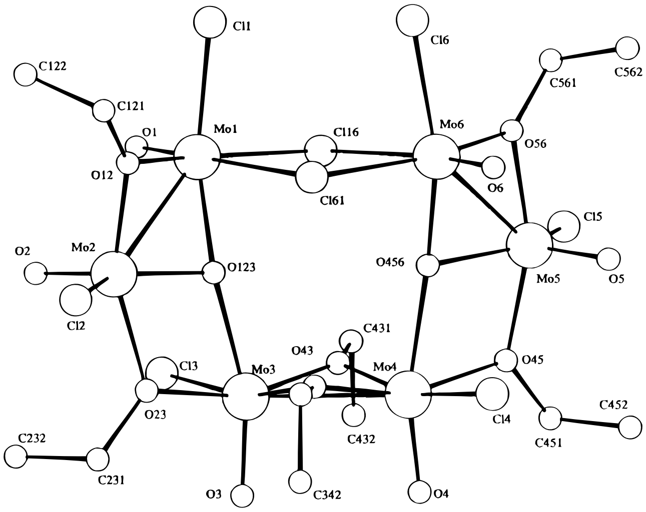

Figure 1. Molecular structure of $Mo_6O_6Cl_6(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_6(\mu_2\text{-}Cl)_2]$, **2**. Hydrogen atoms have been omitted for clarity.

The initial reaction of $Me_3Si(allyl)$ with the EtOH bridge to form propene probably produces an intermediate from which the reactive fragments composed of O═MoCl(OEt) units are generated by decomposition. These fragments then react with one another and with other species present in solution to yield the most stable cluster *via* Mo−Mo bond formation, in this case the six-membered metallacycle **2**.

(b) Reaction with SbF_3. The inherent Lewis basicity of an alkoxy ligand bonded to molybdenum has prompted us also to examine the response of **1** to electrophilic attack, having as a target the initiation of fragmentation and cluster formation by opening the ethoxy bridges. The reaction of **1** with SbF_3 in toluene, followed by overlayering with petroleum ether, has been found to lead (after 3 months) to the formation of the Mo_8 complex $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu_2\text{-}OH)_4(\mu_2\text{-}OC_2H_5)_4(HOC_2H_5)_4]$, **3**.[15] The crystal structure of **3** reveals a unique, centrosymmetric $Mo_8(\mu_3\text{-}O)_4(\mu_2\text{-}O)_8$ core encapsulated

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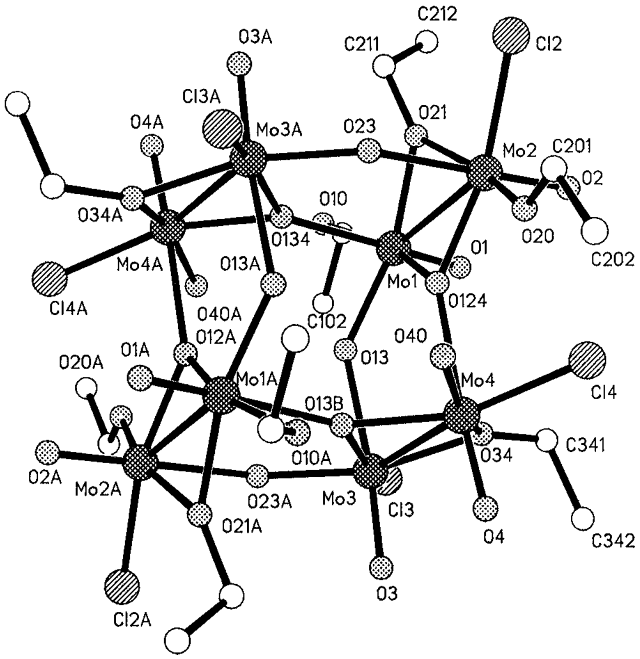

Figure 2. Molecular structure of $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu_2\text{-}OH)_4(\mu_2\text{-}OEt)_4(HOEt)_4]$, **3**. Hydrogen atoms have been omitted for clarity.

by terminal oxo, ethoxy, hydroxy, chloro, and ethanol ligands (see Figure 2). The framework is strongly reminiscent of the distorted rutile structure of MoO_2,[15] providing a clear indication of the preassembly of a fragment of molybdenum dioxide, as may occur during the synthesis of molybdenum oxides by the sol−gel methods described, for example, by Nagano and Greenblatt. Accordingly, **3** may well be representative of key intermediates formed on the microscopic scale during other sol−gel processes.

(c) Reactions with Lewis Bases. (i) PMe_3. It was natural also to explore the response of **1** to a Lewis base. An additional stimulus to such a study came from the possibilities (i) of hydrogen abstraction from the EtOH bridge and (ii) of coordination of the base at one Mo, thereby confining the EtOH to the second Mo center. The reaction of **1** with 1 equiv of PMe_3 in toluene led, after workup, to the formation of a red solid, **4**. A single crystal of **4** obtained by cooling a CH_2Cl_2 solution was shown by X-ray crystallography to be $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$ (Figure 3). Tables 1 and 2 list the principal bond lengths and angles. The structure consists of a tetrameric arrangement of 4 O=Mo−Cl units. Each O=Mo−Cl unit is linked by an Mo−Mo bond [2.6647(10) Å] and a μ_2-OEt bridge to a second unit to form two dimers in the first place. Additionally, each Mo−Mo bond is spanned by a μ_3-O ligand; this links one dimer by its vacant coordination site to one Mo atom of the second dimer, whose other Mo atom is in turn linked *via* a μ_2-OEt bridge to one of the Mo atoms of the first dimer. Hence, the average oxidation state of molybdenum in the complex is +5, and the four Mo atoms yield a total of four electrons for metal−metal bonding. These are evidently used to form two localized metal−metal single bonds (i) between Mo(1) and Mo(2) and (ii) between Mo(1′) and Mo(2′), so that **4** is diamagnetic.

In general terms, this array is very similar to the molecular structure of **2** in terms of bonding modes, bond lengths, and bond angles. The bridging μ_2-OEt units are, as in **2** and **3**, almost planar in the immediate environment of the O atom. The geometry around the triply bridging oxygen atoms is distorted with three different O(121)−Mo(1,2,1′) bond lengths [viz. 1.983(3), 1.986(3), and 2.237(3) Å] and three different Mo−O−Mo angles [viz. 105.27(13), 108.58(14), and 84.21(12)° about O(121)]. The $Mo_3(\mu_3\text{-}O)$ interactions contrast therefore with the $Mo_3(\mu_3\text{-}O)$ interactions in **2** and **3** in that they afford a nonplanar OMo_3 moiety. As in **2** and **3**, however, the smallest angles and shortest bridges are associated with singly bonded Mo−Mo interactions, while the longest bridging bonds [O(121)−Mo(1′) and O(121′)−Mo(2)] are formed *trans* to terminal Mo=O bonds, in a manner consistent with the *trans* influence of such bonds. The unit formed by the atoms Mo(1), Mo(2), O(12), and O(121) is a folded bridge. Each Mo atom is bonded to a terminal O atom [O(1) and O(2)] at 1.660(3) and 1.667(3) Å, the bond lengths being almost identical with those found previously in **1**−**3**. These oxygen atoms are, like O(3) and O(4) in **2**, in eclipsed positions and the fold in the bridge decreases the contact between them. The Mo−O distances of the bridge are 1.983(3), 2.010(3), 1.986(3), and 1.995(3) Å, the Mo−O−Mo angles are 84.21(12) and 83.39(13)°, and the O−Mo−O angles are 93.46(13) and 93.97(13)°. It appears, then, that the bridge is remarkably symmetrical, despite the fact that O(12) belongs to an ethoxy ligand, whereas O(121) is an oxide ligand.

Whereas, according to Green's terminology,[16] **2** consists of an assembly of 2 MoX_6L and 4 MoX_6L_2 units, **4** is composed of 4 MoX_6L_2 units which are very common and particularly stable in molybdenum chemistry. The building blocks are most aptly described as distorted octahedra since the Mo−Mo bond

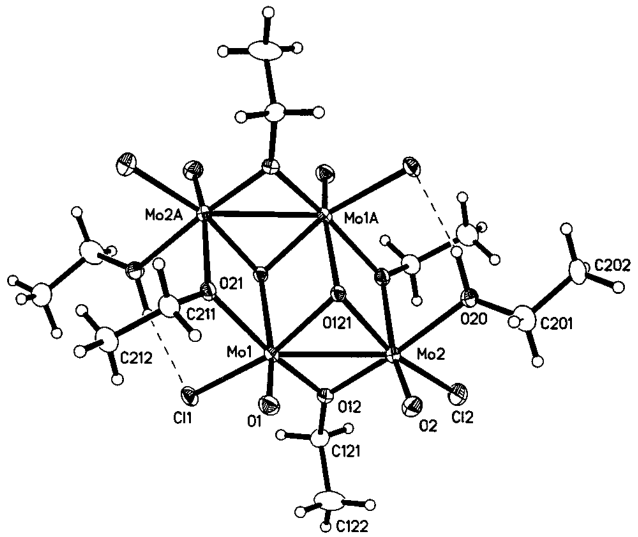

Figure 3. Molecular structure of $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, **4**. The diagram shows 50% probability ellipsoids.

Table 1. Selected Bond Lengths (Å) for $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, **4**[a]

Mo(1)−O(1)	1.660(3)	Mo(2)−O(21)^i	2.190(3)
Mo(1)−O(121)	1.983(3)	Mo(2)−Cl(2)	2.372(2)
Mo(1)−O(12)	2.010(3)	O(20)−C(201)	1.438(6)
Mo(1)−O(21)	2.068(3)	C(201)−C(202)	1.499(8)
Mo(1)−O(121)^i	2.237(3)	O(121)−Mo(1)^i	2.237(3)
Mo(1)−Cl(1)	2.406(2)	O(12)−C(121)	1.463(6)
Mo(1)−Mo(2)	2.6647(10)	C(121)−C(122)	1.488(7)
Mo(2)−O(2)	1.667(3)	O(21)−C(211)	1.463(6)
Mo(2)−O(121)	1.986(3)	O(21)−Mo(2)^i	2.190(3)
Mo(2)−O(12)	1.995(3)	C(211)−C(212)	1.497(7)
Mo(2)−O(20)	2.144(4)		

[a] Symmetry transformation used to generate equivalent atoms: (i) $-x, -y + 2, -z + 1$.

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Table 2. Selected Bond Angles (deg) in $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, **4**^{a}

O(1)−Mo(1)−O(121)	102.3(2)	O(121)−Mo(2)−O(21)$^{\mathrm{i}}$	73.21(12)
O(1)−Mo(1)−O(12)	104.2(2)	O(12)−Mo(2)−O(21)$^{\mathrm{i}}$	90.45(13)
O(121)−Mo(1)−O(12)	93.46(13)	O(20)−Mo(2)−O(21)$^{\mathrm{i}}$	79.73(12)
O(1)−Mo(1)−O(21)	93.4(2)	O(2)−Mo(2)−Cl(2)	96.88(13)
O(121)−Mo(1)−O(21)	85.99(13)	O(121)−Mo(2)−Cl(2)	160.05(10)
O(12)−Mo(1)−O(21)	162.07(13)	O(12)−Mo(2)−Cl(2)	89.03(10)
O(1)−Mo(1)−O(121)$^{\mathrm{i}}$	163.9(2)	O(20)−Mo(2)−Cl(2)	87.76(11)
O(121)−Mo(1)−O(121)$^{\mathrm{i}}$	74.73(13)	O(21)$^{\mathrm{i}}$−Mo(2)−Cl(2)	87.06(10)
O(12)−Mo(1)−O(121)$^{\mathrm{i}}$	91.82(13)	O(2)−Mo(2)−Mo(1)	95.34(12)
O(21)−Mo(1)−O(121)$^{\mathrm{i}}$	70.72(12)	O(121)−Mo(2)−Mo(1)	47.92(9)
O(1)−Mo(1)−Cl(1)	97.86(12)	O(12)−Mo(2)−Mo(1)	48.54(10)
O(121)−Mo(1)−Cl(1)	159.39(9)	O(20)−Mo(2)−Mo(1)	133.38(10)
O(12)−Mo(1)−Cl(1)	85.79(10)	O(21)$^{\mathrm{i}}$−Mo(2)−Mo(1)	90.26(9)
O(21)−Mo(1)−Cl(1)	88.48(10)	Cl(2)−Mo(2)−Mo(1)	137.49(4)
O(121)$^{\mathrm{i}}$−Mo(1)−Cl(1)	84.70(9)	C(201)−O(20)−Mo(2)	125.7(3)
O(1)−Mo(1)−Mo(2)	97.14(12)	O(20)−C(201)−C(202)	110.2(5)
O(121)−Mo(1)−Mo(2)	47.87(9)	Mo(2)−O(121)−Mo(1)	84.21(12)
O(12)−Mo(1)−Mo(2)	48.06(9)	Mo(2)−O(121)−Mo(1)$^{\mathrm{i}}$	108.58(14)
O(21)−Mo(1)−Mo(2)	133.85(9)	Mo(1)−O(121)−Mo(1)$^{\mathrm{i}}$	105.27(13)
O(121)$^{\mathrm{i}}$−Mo(1)−Mo(2)	92.35(8)	C(121)−O(12)−Mo(2)	136.7(3)
Cl(1)−Mo(1)−Mo(2)	133.71(4)	C(121)−O(12)−Mo(1)	139.4(3)
O(2)−Mo(2)−O(121)	101.7(2)	Mo(2)−O(12)−Mo(1)	83.39(13)
O(2)−Mo(2)−O(12)	102.4(2)	O(12)−C(121)−C(122)	110.2(4)
O(121)−Mo(2)−O(12)	93.97(13)	C(211)−O(21)−Mo(1)	121.2(3)
O(2)−Mo(2)−O(20)	87.6(2)	C(211)−O(21)−Mo(2)$^{\mathrm{i}}$	131.1(3)
O(121)−Mo(2)−O(20)	85.85(13)	Mo(1)−O(21)−Mo(2)$^{\mathrm{i}}$	107.41(14)
O(12)−Mo(2)−O(20)	169.81(13)	O(21)−C(211)−C(212)	112.5(4)
O(2)−Mo(2)−O(21)$^{\mathrm{i}}$	166.6(2)		

^{a} Symmetry transformation used to generate equivalent atoms: (i) $-x, -y, -z + 1$.

has little effect on the geometries of the individual coordination polyhedra. The four octahedra are linked together through edges in a manner similar to that found in $Ti_4(OEt)_{16}$,[17] the structure of which, determined in 1963, afforded the first experimental evidence in support of Bradley's theory regarding metal alkoxides (based on the desire of metal atoms to achieve their preferred coordination environments by the minimum degree of oligomerization).[18]

Overall, the complex possesses an inversion center. A compound very similar to **4** is $[Mo_4O_4Cl_4(\mu_3\text{-}O)_2(\mu_2\text{-}O^nPr)_4(O^nPr)_2]$, which has been reported previously.[19] **4** can be conceived as deriving from this compound by exchanging the ^{n}Pr groups for Et groups and protonating the two terminal O^{n}Pr groups. On the other hand, the second change makes a considerable difference since it causes two Mo atoms in the ^{n}PrO-based complex to adopt the oxidation state +6 rather than +5 as in **4**. It was claimed that this leads to Mo−Mo bonds which are slightly longer than usual with the withdrawal of 2 d electrons from a bonding role. However, the bond length of 2.669(2) Å which is found is almost exactly the length of the Mo−Mo bond in **4** [2.6647(10) Å]. All the other bond lengths and angles in the two complexes are quite similar, giving us grounds to wonder whether the earlier crystallographic study simply failed to locate two hydrogen atoms, the presence of which should have been signaled by the IR and NMR spectra; unfortunately no such spectra were reported.

Another complex similar to **4** is $[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_2(py)_4]$,[17] which was produced by Chisholm *et al.* by the reaction of $[Mo_2(O^iPr)_6]$ with molecular oxygen. This cluster is constructed formally by replacement of the Cl atoms of **4** by pyridine (py) ligands, two of the μ_2-OEt by μ_2-O bridges, and the terminal HOEt by terminal O^{i}Pr ligands. The resulting arrangement possesses Mo atoms in the oxidation state +5, leading to Mo−Mo bonding. However, because of the quite different ligation afforded, for instance, by the neutral py ligands, bond lengths and angles differ significantly from those in **4**, although the general appearance of the structure is the same.

The ^{1}H NMR spectrum of **4** in CD_2Cl_2 solution revealed three distinct triplets of equal intensity at δ_H 1.70, 1.57, and 1.26, corresponding to the CH_3 groups of two different bridging OEt and the terminal HOEt ligands. The two resonances of higher order at δ_H 4.6 and 4.8 as well as the quartet at δ_H 6.0 are assigned to the CH_2 fragments of the three different Et groups. The triplet at 7.98 is attributed to the OH groups of the EtOH ligands. As in the case of **2**, decoupling experiments again offered a basis for the interpretation of the higher order signals. Of the two sets of CH_2 signals, one couples with the OH proton and must therefore be assigned to the terminal EtOH ligands. Which of the two kinds of bridging EtO group is more likely to be responsible for the second higher order signal is not obvious from the structure. However, the individual chemical shifts of the two sets of diastereotopic protons are δ 4.65 and 4.69 [$^2J(HH) = 11.7$ Hz] and 4.82 and 4.90 [$^2J(HH) = 10.7$ Hz, CH_3CH_2OH].

In an attempt to elucidate how **4** comes to be formed in the reaction of **1** with PMe_3, we examined the byproducts of the reaction, with due recognition of the fact that the conversion of **1** to **4** is relatively inefficient (yield typically ca. 17%). First, we investigated the yellow solid which precipitates after prolonged stirring of the reaction mixture. This proved to be insoluble in most organic solvents, but the ^{1}H NMR spectrum of a D_2O solution showed just one resonance, viz. a doublet at δ_H 1.69 [$^2J(PH) = 15.8$ Hz], which can be associated with a P−Me unit. Elemental analysis pointed to the composition $MoP_2C_6H_{20}Cl_4O_3$, and the IR spectrum of the solid showed, apart from the bands attributable to PMe_3 groups, only absorptions in the region characteristic of ν(Mo═O) vibrations. It has not yet been possible to identify all the volatile products, but analysis of the IR and ^{1}H NMR spectra established that Et_2O is one of these products. The identification of Et_2O we regard as significant in offering an explanation for the presence of μ_3-O groups in **4**, since one possible route involves elimination of Et_2O from two EtO ligands of **1**. Such a process must be responsible for the production of **4** since the presence of traces of water not only failed to improve the yield but even inhibited the formation of **4**. Only in a few cases reported to date has it been proved that single oxo ligands formed unexpectedly in metal oxo alkoxides have their origin in C−O bond cleavage and not in hydrolysis due to traces of moisture.[20] There are precedents, however, for the elimination of Et_2O from molybdenum ethoxides.[21]

(ii) NEt_3. The relatively soft base PMe_3 evidently fails to abstract a proton from the ethanol bridge in **1** and so produces a dimolybdenum anion with three ethoxy bridges, **II** (see Scheme 2). Nevertheless, it would be highly desirable to produce and characterize such an anion, which may well be formed in the first step of many reactions of **1** and may be expected also to provide further clues to the mechanism of formation of the clusters **2**−**4**. Accordingly, attempts have been made to generate the anion **II** from **1** by the action of the harder

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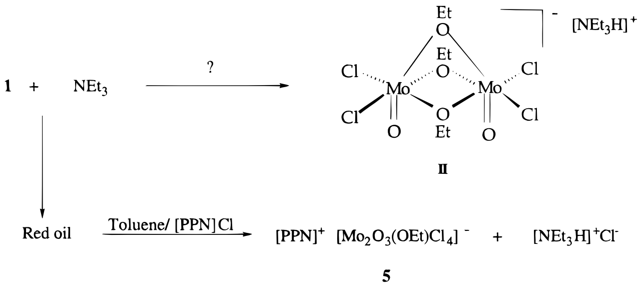
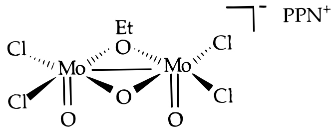
Scheme 2. Reaction of **1** with Triethylamine



base triethylamine. The reaction taking place in CH_2Cl_2 solution at ambient temperatures led, after workup, to an involatile, air-sensitive red oil whose IR and ^1H NMR spectra showed that an N−H bond had indeed been formed. However, the other features in the ^1H NMR spectrum were not wholly consistent with the spectrum to be expected for the relatively simple species **II**. The IR spectrum included bands implying the presence of Mo═O and MoOEt units but otherwise gave no further hints about the composition of the oil. Cooling caused the oil to freeze to a glass, and the product has so far defied all attempts at crystallization.

Experiments were therefore carried out with the aim of converting the oil into a solid by exchanging the cation $[NEt_3H]^+$ for $[PPN]^+$ ($[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$). The oil was found to react with [PPN]Cl in toluene, yielding $[NEt_3H]Cl$ and a solid orange product **5** with the composition $[PPN]^+[Mo_2Cl_4O_4C_2H_5]^-$ (Scheme 2). However, the failure to grow crystals and so determine the crystal structure still made it impossible to reach any definite conclusions about the nature of **5**. One option consistent with the observed properties would be an oligomer of the fragment **III** formed by elimination of diethyl ether from **II**,



III

following the precedents already set by the formation of **4**. The fragment would then need to aggregate in such a way as to create three different kinds of ethoxy groups to be consistent with the ^1H NMR spectrum of **5**. Beyond this requirement, however, the structure of **5** remains a matter for speculation.

During some of the crystallization attempts with mixtures of **5** and $[NEt_3H]Cl$, it was noticed that traces of moisture caused the formation of small amounts of red crystals which, according to their IR spectra, were not identical with the starting material. In particular, the absorptions associated with the EtOMo units in **5** were absent from the spectrum of the red crystals. This finding prompted us to study the hydrolysis of **5** in the presence of $[NEt_3H]Cl$. Solutions containing **5** and $[NEt_3H]Cl$ reacted rapidly with moist air; this led not to an increase in the yield of the red crystals but to the formation of green crystals suggestive of a monomeric species, probably formed by exhaustive hydrolysis of **5**. The green crystals were therefore of less interest than the red crystals with respect to the characterization of **5**. In order to produce the red crystals in larger quantities, the hydrolysis had to be performed in a more controlled way. This was achieved by avoiding the isolation of **5** and causing the initial red oil, from which **5** was formed, to react with a sample having the composition $[PPN]Cl{\cdot}2H_2O$. Following the procedure leading to the synthesis of **5**, but with $[PPN]Cl{\cdot}2H_2O$ in place of the anhydrous salt, resulted in the precipitation of a red-brown solid **6** in near-quantitative yield (reaction 3).

$$\mathbf{1} + NEt_3 \rightarrow \text{red oil} \xrightarrow[\text{[PPN]Cl}\cdot 2H_2O]{\text{toluene}} [PPN]^+[NEt_3H]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-} \quad (3)$$

$$\mathbf{6}\ (90\%)$$

Single crystals of **6** obtained by recrystallization from a CH_2Cl_2/toluene mixture have been characterized by X-ray diffraction. The results disclose two crystallographically independent sets of $[PPN]^+[NEt_3H]^+[Mo_2O_4Cl_4]^{2-}$ assemblies in the unit cell (see Figure 4). The bond lengths and angles found for the constituent ions are listed in Tables 3 and 4.

Each $[Mo_2O_4Cl_4]^{2-}$ anion conforms roughly to C_{2v} symmetry, being composed of two approximately square-pyramidal MoO_3Cl_2 units linked by two oxygen bridges; two chlorine and two oxygen atoms form the basal plane, and a terminal oxygen atom (O_t) completes the apex of the pyramid. As in all known cases of bis(μ-oxo) species, the Mo(μ-O)$_2$Mo bridge of **6** has a nonplanar arrangement, with the Mo−O_t groups on the same side of the bridge (i.e. *cis* to each other).[22] The complex is diamagnetic as a result of spin-pairing of the two d^1 electrons at the Mo centers, with the formation of a strong Mo−Mo bond [2.609(2) Å]. A terminal Mo═O group has the ability to weaken the bond *trans* to it, and in the extreme, as represented by **6**, the *trans* ligand is absent. The Mo═O bond, the Mo−Mo bonding, and repulsion between the two O_t atoms are then the primary influences determining the overall geometry of the $[Mo_2O_4Cl_4]^{2-}$ anion.

The structure of such an anion was reported previously. Analysis of the disordered crystals of the trihydrated pyridinium salt[23] (prepared by heating a solution of $[C_5H_6N]_2[OMoCl_5]$ in 96% ethanol and subsequent addition of dioxane) discloses pseudo-six-coordinate Mo atoms created by the short Mo═O··· Mo interactions between the anions stacked along the short *c* axis of the orthorhombic unit cell. A more precise determination has been performed on the same anion in the form of a solvated tetraphenylarsonium salt[24] (synthesized by the reaction of $OMoCl_3{\cdot}SMe_2$ with $[Ph_4As]Cl$ in wet CH_2Cl_2). The dimensions of the anion in **6** do not differ significantly from those in the tetraphenylarsonium salt. In both cases, the bulky cation precludes any significant Mo═O···Mo interactions between the anions, and consequently the Mo atoms are truly pentacoordinated. There is known only one other bis(μ-oxo) molybdenum complex, which (discounting any Mo−Mo bonding as part of the coordination sphere) incorporates pentacoordinated molybdenum atoms. This is $[Mo_2O_4(O\text{−}Etcys)_2]$ [*O*-Etcys = L-cysteinato ethyl ester, $SCH_2CH(CO_2Et)NH_2$];[25] although the geometry about each Mo center is clearly distorted, it has been described as being derived not from a square pyramid but from a trigonal bipyramid.

For the structural arrangement of the $[Mo_2O_4Cl_4]^{2-}$ anion in **6**, each Mo center has an electron count of 16, if it is assumed that the O_t atom supplies 4 electrons, thereby forming Mo−O triple bonds. Molybdenum normally exhibits a marked tendency to obey the 18-electron rule, and moreover, the size of the Mo atom is such that 6-fold coordination is commonly adopted. Lower coordination numbers are most likely to arise as a response either to the requirements of the 18-electron rule or to the presence of bulky ligands. Neither of these factors seems to apply to $[Mo_2O_4Cl_4]^{2-}$. It is possible, however, that the two

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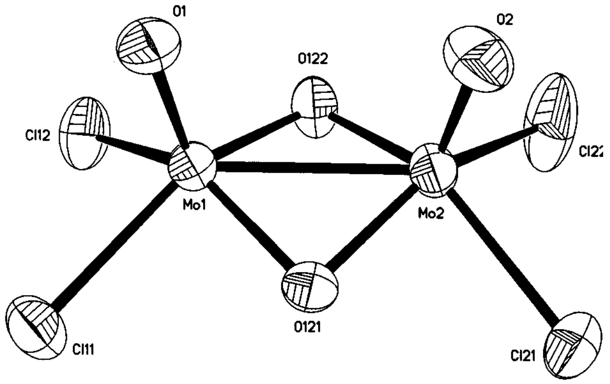

Figure 4. Molecular structure of one of the crystallographically independent $[Mo_2O_4Cl_4]^{2-}$ anions in $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, **6**. The second anion contained in the unit cell has the same structure. The diagram shows 30% ellipsoids.

Table 3. Selected Bond Lengths (in Å) for the Anions in $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, **6**

Mo(1)−O(1)	1.667(7)	Mo(3)−O(3)	1.701(9)
Mo(1)−O(121)	1.911(6)	Mo(3)−O(342)	1.887(7)
Mo(1)−O(122)	1.919(6)	Mo(3)−O(341)	1.940(7)
Mo(1)−Cl(12)	2.382(3)	Mo(3)−Cl(32)	2.352(4)
Mo(1)−Cl(11)	2.391(3)	Mo(3)−Cl(31)	2.375(4)
Mo(1)−Mo(2)	2.6091(12)	Mo(3)−Mo(4)	2.590(2)
Mo(2)−O(2)	1.678(8)	Mo(4)−O(4)	1.661(8)
Mo(2)−O(121)	1.925(6)	Mo(4)−O(342)	1.910(8)
Mo(2)−O(122)	1.920(6)	Mo(4)−O(341)	1.910(7)
Mo(2)−Cl(21)	2.366(3)	Mo(4)−Cl(41)	2.385(4)
Mo(2)−Cl(22)	2.382(4)		

bridging oxo ligands contribute to each Mo center more than the three electrons originally assumed. For this, it must be said, there is no definitive experimental criterion.[16] On the other hand, some support for increased electron donation from the bridging oxo ligands comes from the finding that the analogous dihydrated dianion $[Mo_2O_4Cl_4(OH_2)_2]^{2-}$,[26] in which each hexacoordinated Mo atom acquires additional electron density by coordination of H_2O, has bridging Mo−O bond lengths of 1.943(4) Å, that is, about 0.025 Å longer than the average of the corresponding distances in **6** [1.916(17) Å] and in $[AsPh_4]_2[Mo_2O_4Cl_4]$ [1.92(1) Å].

Interestingly the dianion is a charged derivative of species **I** which forms the xerogels following the sol−gel process performed by Méndez-Vivar *et al.*[7] The structure and other properties of the dianion are therefore of some significance.

Conclusions

Table 4. Selected Bond Angles (deg) for the Anions in $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, **6**

O(1)−Mo(1)−O(121)	112.3(4)	O(2)−Mo(2)−O(121)	110.8(4)
O(1)−Mo(1)−O(122)	108.1(4)	O(2)−Mo(2)−O(122)	108.8(4)
O(121)−Mo(1)−O(122)	90.0(3)	O(121)−Mo(2)−O(122)	89.5(3)
O(1)−Mo(1)−Cl(12)	105.7(4)	O(2)−Mo(2)−Cl(21)	104.7(3)
O(121)−Mo(1)−Cl(12)	141.7(2)	O(121)−Mo(2)−Cl(21)	83.2(2)
O(122)−Mo(1)−Cl(12)	81.8(2)	O(122)−Mo(2)−Cl(21)	144.2(3)
O(1)−Mo(1)−Cl(11)	102.0(3)	O(2)−Mo(2)−Cl(22)	102.7(4)
O(121)−Mo(1)−Cl(11)	84.0(2)	O(121)−Mo(2)−Cl(22)	148.2(3)
O(122)−Mo(1)−Cl(11)	149.3(3)	O(122)−Mo(2)−Cl(22)	82.6(2)
Cl(12)−Mo(1)−Cl(11)	84.45(13)	Cl(21)−Mo(2)−Cl(22)	85.4(2)
O(1)−Mo(1)−Mo(2)	102.8(3)	O(2)−Mo(2)−Mo(1)	102.2(3)
O(121)−Mo(1)−Mo(2)	47.2(2)	O(121)−Mo(2)−Mo(1)	46.9(2)
O(122)−Mo(1)−Mo(2)	47.3(2)	O(122)−Mo(2)−Mo(1)	47.2(2)
Cl(12)−Mo(1)−Mo(2)	127.39(9)	Cl(21)−Mo(2)−Mo(1)	128.79(10)
Cl(11)−Mo(1)−Mo(2)	130.73(9)	Cl(22)−Mo(2)−Mo(1)	129.20(11)

The initial aim of the present research was the production of cluster compounds which might simulate the formation of the binary molybdenum oxides in sol−gel processes known to start from ClMo(OEt) precursors. As a specific precursor, the novel compound $[Cl_2(O)Mo(\mu\text{-}OEt)_2(\mu\text{-}HOEt)Mo(O)Cl_2]$, **1**, was selected, and this too appears to model possible intermediates in the sol−gel process. Reactions of this binuclear species with different reagents under varying conditions have led to the synthesis of tetranuclear (**4**), hexanuclear (**2**), and octanuclear (**3**) products (see Figure 5). These are notable for providing the first clues to the manner of formation of molybdenum oxide clusters and, ultimately, of polymeric, homoleptic molybdenum oxides, viz. the final products of the sol−gel process. The cluster compounds characterized to date may well display the structural and bonding features of essential intermediates formed during the actual sol−gel process (but which cannot be isolated from what is liable to be a complex mixture, being in all probability short-lived under these conditions); the compounds also provide some insight into the polycondensation reactions giving access to them. The proposed exemplary character of the new compounds acquires considerable weight from the finding of an encapsulated, preformed fragment of MoO_2 in the cluster compound $[Mo_8O_8Cl_6(\mu_3\text{-}O)_4(OH)_2(\mu_2\text{-}OH)_4(\mu_2\text{-}OEt)_4(HOEt)_4]$, **3**. Furthermore, the product **6** derived from the reaction of **1** with NEt_3, followed by treatment with wet [PPN]Cl, contains the anion $[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, which is a charged derivative of the species reported to form the gels in some sol−gel processes (see Figure 5).

The first step in many reactions of the binuclear oxomolybdenum(V) complex **1** is likely to be the deprotonation of the EtOH bridge. The anion formed by this reaction is noteworthy for its relevance to the decomposition of **1**, but attempts to isolate and characterize this species have as yet been to no avail. In the reactions affording the compounds **2**−**4**, the stable arrangment of **1** is destroyed, with the formation of fragments which undergo elimination reactions. Furthermore, the fragments then react with smooth C−O bond cleavage under remarkably mild conditions. The achievement of the favorable MoX_xL_l environments[16] for the Mo centers is probably responsible for the production, conformation, and stable existence of each of the clusters **2**−**4**.

Experimental Details

All manipulations were carried out with a vacuum line (at a background pressure $<10^{-4}$ mmHg) or else in a glovebox or by means of Schlenk-type techniques involving the use of a dry nitrogen atmosphere. Solvents were dried according to standard procedures; microanalyses were performed by the Analytische Laboratorien GMBH, Gummersbach, Germany. IR spectra were recorded with a Mattson Galaxy FTIR spectrometer. ^1H NMR spectra of solutions were recorded using a Bruker FT Model AM 300 instrument operating at 300 MHz. X-ray diffraction measurements were made on single crystals at various temperatures either on a Stöe Stadi-4 four-circle diffractometer with graphite-monochromated Mo Kα radiation or on an Enraf-Nonius CAD-4 diffractometer, also with graphite-monochromated Mo Kα radiation.

Synthesis of $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, 4. A glovebox was used to load 1.01 g (2 mmol) of **1**[9] into a flamed-out Schlenk tube. A solution of this in 50 cm^3 of toluene, frozen initially with 0.15 g (2 mmol) of PMe_3 at −196 °C, was allowed gradually to anneal, the reaction vessel including a stirrer bar and being mounted above a magnetic stirrer. As soon as the outer coating of the frozen toluene block melted, the block started to rotate in the vessel under the action of the stirrer, thereby mixing the PMe_3 into the liquid phase. At first, a brown oil appeared and the solution also turned deep brown. After the mixture had warmed to room temperature, it was stirred for 15 h, yielding a deep red solution and a yellow solid precipitate (ca. 300 mg). The solution was filtered, and the volatile components were evaporated *in vacuo*. The resulting red oil/solid mixture was redissolved in CH_2Cl_2, and cooling the solution to −80 °C resulted in the

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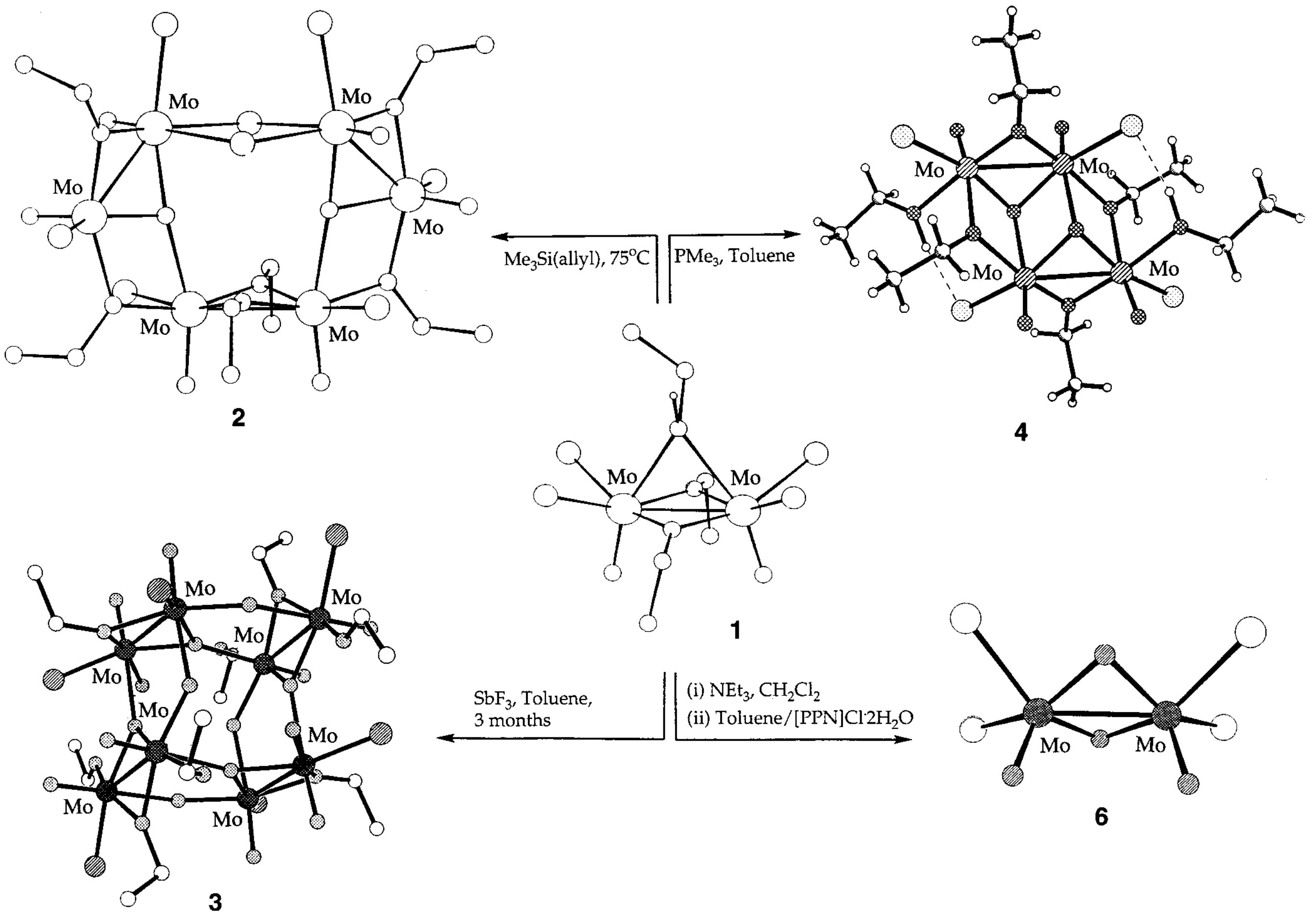

Figure 5. Reactions of **1** yielding the cluster compounds **2**−**4** and **6**.

Table 5. Selected Crystallographic Data for **4** and **6**

	4	6
empirical formula	$C_{12}H_{32}Cl_4Mo_4O_{12}$	$C_{42}H_{46}Cl_4Mo_2N_2O_4P_2$
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
a/Å	7.376(2)	15.096(2)
b/Å	8.807(3)	16.2885(8)
c/Å	11.467(4)	37.234(3)
α, deg	109.61(1)	90
β, deg	92.12(3)	90
γ, deg	103.75(2)	90
V/Å^3	676.0(4)	9156(2)
Z	1	16
fw	893.94	1038.43
T/°C	−120.0(2)	25(2)
λ/Å	0.710 73	0.710 73
R_1[a]	0.0254	0.0388
wR_2[b]	0.0577	0.0938

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ based on $I > 2\sigma(I)$. [b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{0.5}$, where w = weighting factor.

precipitation of orange-red crystals of $[Mo_4O_{12}Cl_4C_{12}H_{32}]$, **4**. These were filtered off under N_2 and amounted to 0.150 g (0.17 mmol), representing 17% conversion of **1** to **4**. The outcome of the attempted synthesis was found to be extremely sensitive to any deviation from this procedure. Thus, annealing and mixing too quickly or not stirring resulted in the formation of different products. Anal. Calcd for $C_{12}H_{32}Cl_4Mo_4O_{12}$ (Mr = 893.94): C, 16.12; H, 3.61; Cl, 15.86; Mo, 42.93%. Found: C, 16.53; H, 3.32; Cl, 16.74; Mo, 44.55%. The compound was found to decompose when heated to 150−160 °C.

The IR spectrum of **4** shows bands at 3210 (m) [ν(O−H)], 1469 (m), 1442 (m), 1396 (m), 1379 (m), 1084 (s) [δ(C−H)], 1016 (vs) [ν(C−O)], 982 (vs) [ν(Mo═O)], 667 (vs) [ν(Mo−O−Mo)], and 511 (m) cm^{-1}. The solubility properties of **4** are very similar to those of **2**. Thus, it is sparingly soluble without decomposition in CH_2Cl_2 and toluene, but $CHCl_3$ solutions undergo slow decomposition. Solid **4** is reasonably stable in air, under which it can be handled for short periods.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, **4**

atom	x/a	y/b	z/c	U(equiv)[a]
Mo(1)	1372(1)	1908(1)	5190(1)	12(1)
Mo(2)	825(1)	−131(1)	2814(1)	14(1)
Cl(1)	4059(2)	3144(2)	6772(1)	18(1)
Cl(2)	2639(2)	−1477(2)	1340(1)	28(1)
O(1)	1261(5)	3624(4)	4922(3)	19(1)
O(2)	674(5)	1328(5)	2219(3)	22(1)
O(20)	−1639(5)	−1728(4)	1554(3)	20(1)
C(201)	−2325(9)	−1534(7)	437(5)	36(2)
C(202)	−3664(9)	−3136(8)	−402(5)	37(2)
O(121)	−894(4)	227(4)	4115(3)	12(1)
O(12)	3153(5)	988(4)	4040(3)	16(1)
C(121)	5176(7)	1182(6)	4016(5)	19(1)
C(122)	5991(8)	2508(7)	3508(6)	35(2)
O(21)	−335(5)	2299(4)	6594(3)	15(1)
C(211)	−857(7)	3875(6)	7096(5)	20(1)
C(212)	532(8)	5145(6)	8163(5)	26(1)

[a] U(equiv) is defined as one-third of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-Ray Crystallography of $[Mo_4O_4Cl_4(\mu_2\text{-}OEt)_4(HOEt)_2(\mu_3\text{-}O)_2]$, 4. Crystals obtained by cooling a CH_2Cl_2 solution of **4** were sealed in a matrix of an inert oil, and one of them was loaded on top of a fiber. Crystal data collection and refinement parameters are collected in Table 5.

The crystal structure was solved by direct methods (SHELXS-86)[27] and refined against F^2 by full-matrix least-squares analysis (SHELXL-

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(27) Sheldrick, G. M. SHELXS-86: Program for Crystal Structure Solution. *Acta Crystallogr., Sect. A* **1990**, 46, 467.

Table 7. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, **6**

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(equiv)[a]	atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(equiv)[a]
Mo(1)	2436(1)	1317(1)	6644(1)	52(1)	C(29)	4973(6)	−2062(7)	7117(3)	113(7)
Mo(2)	2788(1)	−247(1)	6592(1)	61(1)	C(30)	5682(7)	−1532(7)	7064(2)	81(5)
Mo(3)	−7066(1)	−1058(1)	−1026(1)	67(1)	C(31)	6845(5)	75(4)	6980(2)	47(3)
Mo(4)	−7034(1)	451(1)	−808(1)	62(1)	C(32)	5986(5)	376(6)	7008(2)	68(4)
Cl(11)	1760(3)	2084(2)	7118(1)	81(1)	C(33)	5711(5)	1020(6)	6790(3)	97(5)
Cl(12)	1502(3)	2114(2)	6263(1)	85(1)	C(34)	6295(8)	1363(5)	6543(3)	93(5)
Cl(21)	2400(4)	−1325(2)	6988(1)	108(2)	C(35)	7153(7)	1062(6)	6515(2)	90(5)
Cl(22)	2413(5)	−1185(2)	6125(1)	127(2)	C(36)	7428(5)	418(5)	6733(2)	67(4)
Cl(31)	−8174(3)	−1781(3)	−1348(1)	99(1)	C(37)	6103(5)	1061(5)	4739(2)	55(3)
Cl(32)	−7004(6)	−2274(3)	−685(2)	151(2)	C(38)	6073(6)	1622(5)	5020(2)	63(3)
Cl(41)	−6762(3)	1057(3)	−235(1)	94(1)	C(39)	5426(7)	2229(5)	5025(2)	78(4)
Cl(42)	−8216(3)	1424(2)	−846(1)	96(1)	C(40)	4808(6)	2274(5)	4749(3)	86(5)
O(1)	3432(6)	1747(6)	6617(3)	71(2)	C(41)	4838(6)	1713(7)	4468(2)	84(5)
O(2)	3902(6)	−256(7)	6583(3)	95(3)	C(42)	5485(6)	1106(6)	4463(2)	72(4)
O(3)	−6178(7)	−1101(9)	−1306(3)	116(4)	C(43)	6511(5)	−585(4)	4520(2)	50(3)
O(4)	−6177(7)	838(8)	−1031(3)	102(4)	C(44)	5742(5)	−892(6)	4676(2)	71(4)
O(121)	2400(6)	435(5)	6982(2)	60(2)	C(45)	5393(5)	−1635(6)	4560(3)	88(5)
O(122)	2319(7)	545(5)	6258(2)	65(2)	C(46)	5812(7)	−2073(5)	4288(3)	81(4)
O(341)	−6733(7)	−558(6)	−572(2)	80(3)	C(47)	6581(6)	−1766(5)	4132(2)	71(4)
O(342)	−7775(6)	−133(6)	−1135(2)	74(3)	C(48)	6930(5)	−1022(5)	4248(2)	63(3)
P(1)	7815(2)	389(2)	7869(1)	42(1)	C(49)	7817(5)	712(5)	4414(2)	49(3)
P(2)	7204(2)	−706(2)	7286(1)	47(1)	C(50)	8699(5)	720(6)	4521(2)	75(4)
P(3)	6983(2)	320(2)	4714(1)	48(1)	C(51)	9344(4)	1030(7)	4291(3)	89(5)
P(4)	7728(2)	−540(2)	5339(1)	49(1)	C(52)	9107(6)	1332(6)	3956(2)	79(4)
N(1)	7500(6)	−405(6)	7675(2)	51(2)	C(53)	8224(7)	1324(6)	3849(2)	80(4)
N(2)	7384(7)	204(6)	5105(2)	53(2)	C(54)	7579(5)	1014(6)	4079(2)	74(4)
N(3)	2568(7)	428(9)	7743(3)	87(4)	C(55)	6851(5)	−939(5)	5618(2)	54(3)
N(4)	2716(7)	941(8)	5525(3)	93(4)	C(56)	6851(5)	−1737(4)	5750(2)	61(3)
C(1)	6957(4)	816(4)	8148(2)	49(3)	C(57)	6178(6)	−1996(4)	5978(2)	74(4)
C(2)	7055(4)	1581(4)	8309(2)	56(3)	C(58)	5505(5)	−1457(6)	6074(2)	79(5)
C(3)	6434(5)	1851(4)	8558(2)	60(3)	C(59)	5505(5)	−658(6)	5942(2)	79(4)
C(4)	5715(5)	1357(5)	8646(2)	68(4)	C(60)	6178(6)	−400(4)	5714(2)	70(4)
C(5)	5618(4)	593(5)	8485(2)	71(4)	C(61)	8239(5)	−1352(4)	5086(2)	54(3)
C(6)	6239(5)	322(4)	8236(2)	56(3)	C(62)	9114(5)	−1263(5)	4975(3)	74(4)
C(7)	8697(4)	114(4)	8170(2)	44(3)	C(63)	9489(5)	−1837(6)	4745(3)	94(5)
C(8)	8890(5)	−705(4)	8241(2)	54(3)	C(64)	8990(7)	−2500(5)	4625(2)	87(5)
C(9)	9594(5)	−906(4)	8465(2)	68(4)	C(65)	8116(7)	−2589(4)	4736(2)	81(5)
C(10)	10104(4)	−288(6)	8619(2)	68(4)	C(66)	7741(4)	−2015(5)	4966(2)	58(3)
C(11)	9911(5)	530(5)	8548(2)	65(4)	C(67)	8537(5)	−130(5)	5648(2)	58(3)
C(12)	9207(5)	731(4)	8324(2)	57(3)	C(68)	8584(6)	711(5)	5709(2)	68(4)
C(13)	8236(5)	1160(5)	7578(2)	47(3)	C(69)	9160(7)	1019(5)	5967(3)	94(5)
C(14)	7718(5)	1810(5)	7459(2)	66(4)	C(70)	9690(6)	487(8)	6164(2)	106(6)
C(15)	8051(7)	2356(5)	7206(3)	89(5)	C(71)	9644(6)	−354(8)	6103(3)	105(6)
C(16)	8903(8)	2252(6)	7072(2)	97(6)	C(72)	9068(7)	−662(5)	5845(3)	84(5)
C(17)	9422(5)	1602(7)	7191(3)	99(6)	C(73)	2929(15)	1257(11)	7827(4)	120(7)
C(18)	9088(5)	1056(6)	7444(3)	89(5)	C(74)	3176(17)	1379(13)	8208(4)	141(9)
C(19)	8092(5)	−1253(5)	7073(2)	52(3)	C(75)	3168(13)	−259(12)	7834(6)	129(8)
C(20)	8912(6)	−1318(6)	7240(2)	70(4)	C(76)	4047(11)	−188(16)	7646(6)	155(11)
C(21)	9591(5)	−1757(7)	7077(3)	97(6)	C(77)	1678(11)	368(14)	7902(5)	125(7)
C(22)	9450(7)	−2131(7)	6746(3)	115(7)	C(78)	1102(10)	−260(13)	7713(5)	114(7)
C(23)	8630(8)	−2066(6)	6579(2)	95(5)	C(79)	3359(12)	1650(10)	5560(5)	101(6)
C(24)	7951(6)	−1627(6)	6742(2)	79(4)	C(80)	4189(10)	1376(14)	5779(5)	122(7)
C(25)	6285(5)	−1393(5)	7339(2)	53(3)	C(81)	3087(12)	157(9)	5392(5)	96(5)
C(26)	6179(6)	−1784(6)	7668(2)	66(4)	C(82)	3606(14)	250(14)	5051(6)	154(10)
C(27)	5470(7)	−2315(7)	7721(3)	105(6)	C(83)	1933(13)	1235(13)	5320(5)	144(9)
C(28)	4867(6)	−2454(7)	7446(4)	122(8)	C(84)	1154(11)	642(13)	5366(5)	125(8)

[a] *U*(equiv) is defined as one-third of the orthogonalized $\mathbf{U}_{ij}$ tensor.

93).[28] Hydrogen atoms were placed in calculated positions on the carbon atoms and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. A further hydrogen atom was allowed to ride on O(20) with $U_{iso}(H) = 1.2U_{eq}(O)$. During the final cycles of least-squares analysis, all nonhydrogen atoms were refined with anisotropic displacement parameters.

Fractional atomic coordinates of all nonhydrogen atoms are listed in Table 6.

Synthesis of $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, 6. A 2 g (4.0 mmol) sample of **1** was loaded, together with a stirrer bar, into a flamed-out Schlenk tube under an inert atmosphere. Co-condensation of 0.4 g (4 mmol) of NEt_3 with a solution of this in 20 cm^3 of CH_2Cl_2 held initially at −196 °C gave a mixture which was allowed to warm with constant agitation. Once the resulting dark red solution had reached room temperature, it was stirred overnight. Evaporation of the volatile material *in vacuo* yielded 2.3 g of a red oil that froze at −80 °C to a glass.

To the oil obtained *via* this procedure was added 2.4 g (4.0 mmol) of $[PPN]Cl\cdot2H_2O$ (on the assumption that all of the NEt_3 initially taken had been transformed into $[NEt_3H]^+$, to be exchanged for the $[PPN]^+$ cation). To this vigorously stirred mixture was added 300 cm^3 of toluene, causing immediate conversion of the toluene-soluble oil into a finely powdered orange solid. The resulting suspension was stirred for 12 h to complete the reaction. After the yellow supernatant solution had been filtered off, the red-brown solid residue (4.2 g) was dried *in*

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(28) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement. University of Göttingen, 1993.

vacuo and proved to be crude $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, **6** (3.7 g, 90% yield).

After the solid had been dried *in vacuo*, it was dissolved in CD_2Cl_2 to give a solution whose ^{1}H NMR spectrum showed signals corresponding to the $[NEt_3H]^+$ cation {δ 1.27 [9H, t, $^3J(HH) = 7.2$ Hz, NCH_2CH_3], 3.42 (6H, m, NCH_2CH_3), 9.40 (1H, s, br, N*H)*]} and the $[PPN]^+$ cation [δ 7.48−7.88 (30H, m, Ph)] in the proportion 1:1. No impurities could be detected. Anal. Calcd for $C_{42}H_{46}Cl_4Mo_2N_2O_4P_2$ (Mr = 1038.43): C, 48.46; H, 4.46; Cl, 13.45; Mo, 18.83; N, 2.69%. Found: C, 47.79; H, 4.35; Cl, 13.86; Mo, 18.18; N, 2.65%. Mp: 171 °C.

The IR spectrum of solid **6** was complicated by the presence of absorptions due to the two cations $[PPN]^+$ and $[NEt_3H]^+$.[29] The only band which could be clearly identified with the dianion of **6** was one appearing at 980 cm^{-1}; this is presumed to originate in a ν(Mo═O) vibration. One would additionally expect a band between 700 and 750 cm^{-1} characterizing the antisymmetric ν(Mo−O−Mo) mode. In the event, this region was obscured by the absorptions due to the cation $[PPN]^+$. However, comparison with the spectrum of [PPN]Cl showed that the band at 723 cm^{-1} was more intense than expected, probably because of intensity borrowing from an absorption associated with the antisymmetric ν(Mo−O−Mo) fundamental.

The compound could be recrystallized by overlayering a CH_2Cl_2 solution with toluene to give a product which showed the same NMR and IR spectra as did the crude material. Although **6** was found to be soluble in CH_2Cl_2, solutions in $CHCl_3$ decomposed slowly at ambient temperature. **6** reacted also with THF, while being insoluble in toluene, Et_2O, and petroleum ether.

X-ray Crystallography of $[PPN]^+[Et_3NH]^+[Cl_2(O)Mo(\mu_2\text{-}O)_2Mo(O)Cl_2]^{2-}$, 6. Crystals obtained by overlayering a CH_2Cl_2 solution of **6** with toluene were loaded into carefully dried 0.3 or 0.5 mm Lindemann capillaries under dry nitrogen and the capillaries quickly sealed off. Crystal data collection and refinement parameters are collected in Table 5.

Following data reduction and the application of an absorption correction (ψ scans, $T_{max} = 0.100$, $T_{min} = 0.080$), the crystal structure was solved by Patterson methods (DIRDIF)[30] to locate all non-H atoms with the exception of the four terminal O atoms, which were located by difference synthesis. The positions of all non-H atoms were refined with anisotropic thermal parameters. During refinement, the Flack enantiopole parameter adopted a value of 0.5(2), and so subsequent cycles assumed inversion twinning. H atoms were placed in calculated positions. There are two crystallographically independent sets of assemblies of **6** in the unit cell.

Fractional atomic coordinates of all nonhydrogen atoms are listed in Table 7.

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Supporting Information Available: Listings of anisotropic thermal parameters, calculated hydrogen positions and isotropic thermal parameters, full crystallographic data, and nonessential bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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