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Organometallic Oxides: Preparation and Properties of the Clusters $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$

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Abstract: Reaction of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ with $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ plus O_2 gave $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. This cluster contains $(\eta\text{-}C_5Me_5)Mo(O)_2$ attached to a $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2$ unit by a bridging oxygen atom. The $[Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo$ structure is favored over the alternative adamantane-like $[M_4(\mu\text{-}O)_6]$ structure because of the π-bonding of the terminal oxygen atoms attached to the apical Mo atom. The $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2$ unit contains four cluster electrons which are associated with the three basal molybdenum atoms. The magnetic moment of $(\eta\text{-}C_5Me_5)_4Mo_4O_{11}$ was 3.16 μ_B at 291 K, indicating that the cluster core has two unpaired electrons. Crystal data: $C_{40}H_{60}Mo_5O_{11}$, triclinic, $P\bar{1}$, a = 10.851(2) Å, b = 12.450(4) Å, c = 18.153(3) Å, α = 91.07(2)°, β = 102.04(1)°, γ = 109.27(2)°, Z = 2, R = 0.063 for 4575 observed reflections and 505 parameters. Reduction of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ with zinc in HCl/$CHCl_3$ gave $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$, which was characterized by elemental analysis, mass spectrometry, and IR, NMR, and EPR spectroscopies. A partial crystal structure analysis showed that the trinuclear cluster had oxygen or hydroxo ligands bridging the edges of a molybdenum triangle. The magnetic moment (1.13 μ_B at 4 K) and NMR and EPR spectra suggested that the cluster with n = 5 (six cluster electrons, diamagnetic) was in a redox equilibrium with clusters with n = 4 (five cluster electrons, one unpaired electron) and n = 6 (seven cluster electrons, one unpaired electron). This is the first example of a redox equilibrium in a cluster of this type. The cation $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ is compared to related $\{[(\eta\text{-}C_5R_5)M]_3(\mu\text{-}A)_n(\mu\text{-}O)_{6-n}\}^{q+}$ clusters. Crystal data: $C_{44}H_{66}Cl_2Mo_3O_6$, monoclinic, $C2/c$, a = 27.97(4) Å, b = 11.260(6) Å, c = 16.865(15) Å, β = 117.93(8)°, Z = 4, R = 0.147 for 921 observed reflections and 61 parameters.

Introduction

Mono- and dinuclear (cyclopentadienyl)molybdenum oxo complexes were among the earliest[1–3] and the most investigated[4–6] of all organometallic oxo compounds. There have been few attempts at synthesizing higher nuclearity (cyclopentadienyl)molybdenum oxides[7–9] (except for polyoxometallate derivatives[10]), although some trinuclear species have been obtained serendipitously.[3,5,11–13] Oxidative aggregation is an excellent route to (cyclopentadienyl)metal oxides of vanadium and chromium.[14–16] Oxidation of the only readily available low-valent (cyclopentadienyl)molybdenum complex, $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$, gave $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$,[9] but in general only mono- or dinuclear oxo complexes were formed.[2,4,7] We therefore turned to reductive aggregation to prepare polynuclear (cyclopentadienyl)molybdenum oxides. In an earlier paper we described convenient preparations of the starting materials $(\eta\text{-}C_5Me_5)MoCl(O)_2$ and $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$.[17] We describe here the reaction of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ with $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ to form $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and the reduction of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ with zinc to form $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$.

Results and Discussion

Preparation of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. Reduction of a (cyclopentadienyl)metal oxo complex normally requires the presence of a ligand such as chloride to serve as a leaving group. However, Curtis and Williams showed that $[(\eta\text{-}C_5R_5)Mo(CO)_2]_2$ could function as a reducing agent without such a ligand. They prepared $(\eta\text{-}C_5R_5)_2(\eta\text{-}C_5R'_5)_2Mo_4(\mu_3\text{-}S)_4$ from $[(\eta\text{-}C_5R_5)Mo(\mu\text{-}\eta^2\text{-}SC_3H_6S)]_2$ and $[(\eta\text{-}C_5R'_5)Mo(CO)_2]_2$.[18] We therefore reacted $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ with $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ in refluxing toluene and obtained a 68% yield of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ (Figure 1), accompanied by $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ in 14% yield. However, there was no reaction unless O_2 was present. The relative mole ratios of the products suggest that the equation for the reaction is 1. When large quantities of O_2 were present, the yield of $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ increased at the expense of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. The mass spectrum of the crude reaction mixture showed no peaks assignable to $(C_5Me_5)_4Mo_4O_6$, which, as $[(\eta\text{-}C_5Me_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$, would be the parent cluster of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. There was also no evidence for (η-C$_5$-

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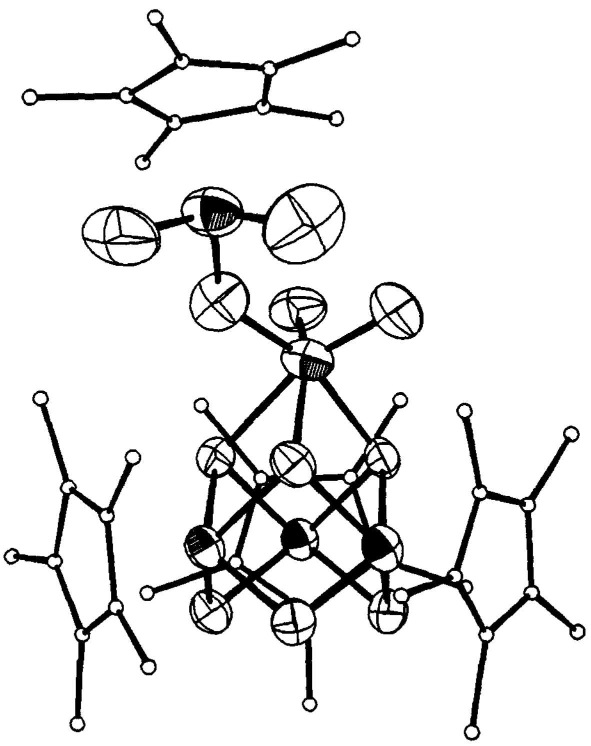

Figure 1. Molecular structure of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$.

$$6[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2 + 6[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2 + 15O_2 \rightarrow 4(\eta\text{-}C_5Me_5)_4Mo_5O_{11} + 2[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O) + 2(C_5Me_5)_2 + 24CO \quad (1)$$

$Me_5)_6Mo_8O_{16}$, which is closely related to $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and was obtained by oxidizing $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ with $[MeAsO]_4$.[9] It is not clear whether traces of O_2 play a role in the oxidation with $[MeAsO]_4$ also, but it is significant that $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ was produced.[19]

Molecular and Electronic Structure of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. The molecular structure of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ is shown in Figure 1, and important distances and angles are listed in Table 1. It is seen that the cluster is composed of a $(\eta\text{-}C_5Me_5)Mo(O)_2$ moiety linked by a bridging oxygen atom to a $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2$ unit. The $(\eta\text{-}C_5Me_5)Mo(O)_2(\mu\text{-}O)$ group has dimensions similar to those found in $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$.[19-21] The molybdenum oxide core of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ is shown in Figure 2. It contains a distorted tetrahedron of molybdenum atoms, of which the basal three (Mo(1)–Mo(3) in Figure 2, designated Mo^b hereafter) carry a $\eta\text{-}C_5Me_5$ ligand and the apical (Mo(4) in Figure 2, designated Mo^a) carries two terminal oxygen atoms and the μ-O link to $(\eta\text{-}C_5Me_5)Mo(O)_2$. The basal molybdenum atoms are connected by two-coordinate oxygen atoms (designated O^2). The base is connected to the apex by three-coordinate oxygen atoms (designated O^3). Thus the core is held together by oxygen atoms, and it is the molybdenum–oxygen bridges which determine its dimensions. The average Mo^b–Mo^b distance is 2.730(13,2) Å,[22] whereas the Mo^b–Mo^a distances average 3.313(49,1) Å. The short basal distances are due to the formation of π-bonds between the two coordinate oxygen atoms and the molybdenum and, to a small extent, the occupation of the $1a_1$ orbital (see below) by two electrons. This orbital is bonding with respect to the basal molybdenum atoms.[23] The Mo^b–Mo^a distances are long because these atoms are connected by three-coordinate oxygen atoms which cannot take part in π-bonding. These distances are also very asymmetric, because of the *trans* influence of the terminal oxygen atoms O(4A) and O(4B). The Mo^a–O^3 distances *trans* to O(4A) and O(4B) are 2.194(7) and 2.251(8) Å, respectively. *Trans* to the bridging oxygen (O(45) in Figure 2), the Mo^a–O^3 distance is 2.060(7) Å. The long Mo^a–O^3 distances connect Mo(4) to Mo(3), whereas Mo(4) is connected to Mo(1) and Mo(2) by one long and one short Mo^a–O^3 distance. As a result, the Mo(4)–Mo(3) distance is 3.399(1) Å, whereas Mo(4)–Mo(1) is 3.264(2) Å and Mo(4)–Mo(2) is 3.277(2) Å. Such influences were discussed previously for $[(\eta\text{-}C_5H_5)TiMo_5O_{18}]^{3-}$,[24] $[(\eta\text{-}C_5Me_5)Mo_6O_{18}]^{-}$,[7] and $[(Mo_5O_{18})Mo(NC_6H_4Me)]^{2-}$.[25]

The cluster $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ is similar to $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$, prepared by Harper and Rheingold,[9] which contains two $[(\eta\text{-}C_5Me_5)Mo(\mu_2\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)$ units linked by two bridging oxygen atoms and a molybdenum–molybdenum bond. The clusters $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ are unusual, firstly for showing such a wide variety of environments for oxygen and secondly for containing the $[Mo(\mu_2\text{-}O)]_3(\mu_3\text{-}O)_3Mo$ core. It would be expected that the core would have the well-known adamantane-like $M_4(\mu_2\text{-}O)_6$ structure, as occurs in $[(\eta\text{-}C_5Me_5)M]_4(\mu\text{-}O)_6$ (M = Ti,[26] V[27]). We have shown elsewhere that the reasons for the change in cluster geometry is the π-bonding of the terminal oxygen atoms to the apical molybdenum.[23]

The ^1H NMR spectrum of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ (benzene solution) showed two resonances: a sharp singlet at 1.78 ppm and a broad signal at 11.72 ppm. The effective magnetic moment in $^2H_1$ $CHCl_3$ solution at 291 K, as measured by the Evans method,[29] was 3.16 ± 0.25 μ_B. The value is higher than the spin-only moment for two unpaired electrons (2.83 μ_B) but is subject to uncertainty because samples of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ contained varying amounts (0–0.5 molecules) of toluene for each molecule of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. A measurement of the magnetic moment in the solid state was not attempted because the toluene solvate could not be completely removed even under vacuum for several days.

The cluster $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ formally contains Mo_5^{XXVI} and therefore four cluster electrons. The ^1H NMR signal at 1.78 ppm is assigned to the protons of the $\eta\text{-}C_5Me_5$ ligand in the $(\eta\text{-}C_5Me_5)Mo(O)_2(\mu\text{-}O)$ appendage and the broad signal at 11.72 ppm to the $\eta\text{-}C_5Me_5$ ligands in the $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ core. The chemical shift suggests that there is little d-electron density on the Mo atom in the $(\eta\text{-}C_5Me_5)Mo(O)_2(\mu\text{-}O)$ appendage (compare the value of 1.79 ppm for $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$[28]). Therefore, the four cluster electrons are associated with the $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ core. Assuming C_{3v} symmetry (i.e., disregarding the *trans* influence of the terminal oxygen atoms), the nine cluster orbitals of the core have the energy levels shown in Figure 3. The predicted ground state of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ is therefore $1a_1^2$ $1e^2$. The magnetic moment is in agreement with there being two unpaired electrons in the core of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. The cluster

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[28] The ^1H NMR spectra of these compounds were very solvent dependent. We found that in $[^2H_6]C_6H_6$ solution, $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ showed a signal at 1.79 ppm, but in $^2H_1$ $CHCl_3$, the signal was at 2.01 ppm. The literature reports 1.62 ppm in toluene[20] and 2.01 in $^2H_1$ $CHCl_3$.[4]

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Table 1. Important Distances (Å) and Angles (deg) in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$

Mo(1)–Mo(2)[a]	2.745(1)[b]	Mo(2)–Cp(2)	2.04(1)	Mo(4)–O(134)	2.194(7)
Mo(1)–Mo(3)	2.730(2)	Mo(3)–O(13)	1.947(7)	Mo(4)–O(234)	2.251(8)
Mo(2)–Mo(3)	2.717(2)	Mo(3)–O(23)	1.929(7)	Mo(4)–O(4A)	1.719(8)
Mo(1)–Mo(4)	3.264(2)	Mo(3)–Cp(3)	2.04(1)	Mo(4)–O(4B)	1.71(1)
Mo(2)–Mo(4)	3.277(2)	Mo(1)–O(124)	2.045(6)	Mo(4)–O(45)	1.91(1)
Mo(3)–Mo(4)	3.399(1)	Mo(1)–O(134)	2.025(7)	Mo(5)–O(45)	1.865(9)
Mo(1)–O(12)	1.942(7)	Mo(2)–O(124)	2.032(7)	Mo(5)–O(5A)	1.72(1)
Mo(1)–O(13)	1.906(9)	Mo(2)–O(234)	2.031(7)	Mo(5)–O(5B)	1.73(1)
Mo(1)–Cp(1)[c]	2.04(1)	Mo(3)–O(134)	2.033(8)	Mo(5)–Cp(5)	2.12(1)
Mo(2)–O(12)	1.939(6)	Mo(3)–O(234)	2.014(6)		
Mo(2)–O(23)	1.916(8)	Mo(4)–O(124)	2.060(7)		

Mo(1)–O(12)–Mo(2)	90.0(3)	Mo(1)–O(134)–Mo(4)	101.3(4)
Mo(1)–O(13)–Mo(3)	90.2(3)	Mo(2)–O(124)–Mo(4)	106.5(4)
Mo(2)–O(23)–Mo(3)	89.9(3)	Mo(2)–O(234)–Mo(4)	99.7(3)
O(12)–Mo(1)–O(13)	92.2(3)	Mo(3)–O(134)–Mo(4)	107.0(3)
O(12)–Mo(2)–O(23)	91.3(3)	Mo(3)–O(234)–Mo(4)	105.5(3)
O(13)–Mo(3)–O(23)	91.6(3)	Mo(4)–O(45)–Mo(5)	136.8(6)
Mo(1)–O(124)–Mo(4)	105.3(3)		

[a] For the numbering scheme, see Figure 2. [b] Estimated standard deviations in parentheses. [c] Cp is the centroid of the $\eta\text{-}C_5Me_5$ ring.

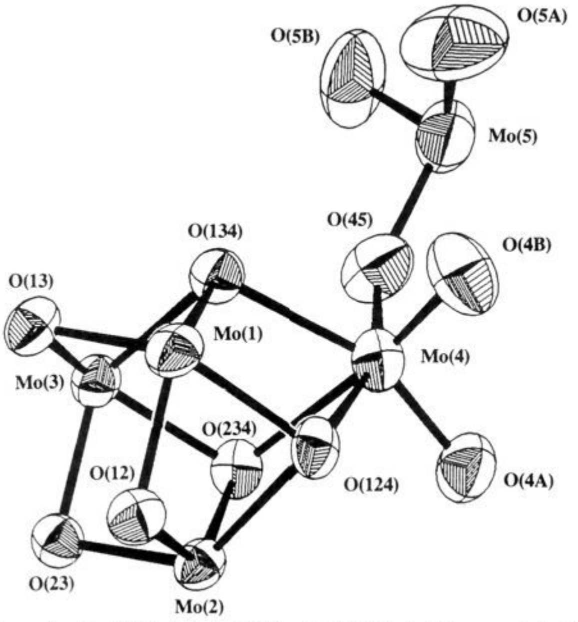


Figure 2. $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ core of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$, showing the numbering scheme.

$(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$,[9] with two $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2$ cores and a molybdenum–molybdenum bond, is predicted to have a magnetic moment appropriate for four unpaired electrons. The moment does not appear to have been measured.

Formation of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$. Reduction of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ with zinc in hydrochloric acid/$CHCl_3$ gave a mixture of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ (10%) and the turquoise salt $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ (37%). The reaction occurred readily and was very reproducible. A higher yield was obtained by *in situ* reduction of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ prepared from $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$. There was no evidence of $[Zn_nCl_{(2n+2)}]^{2-}$ as a counterion to the $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ cation. Neither was there evidence for any cation except that with a dipositive charge. The cluster was moderately sensitive to O_2 but was thermally and hydrolytically stable for reasonable periods of time. In polar solvents, some decomposition was evident after 2 weeks at room temperature.

Physical and Chemical Properties of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$. Microanalysis (C, H, Cl, and Mo), mass spectrometry, and infrared, EPR, and NMR spectroscopies established that the product obtained by reducing $(\eta\text{-}C_5Me_5)MoCl(O)_2$ with zinc had the formula $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$. The value of *n* is not trivial, since it determines the number of cluster electrons and therefore the magnetic properties of the cluster. A partial X-ray structure determination showed the $[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}O)_6$ framework of the cluster (see Figure 4, Table 2, and the Experimental Section). In addition to chloride anions, the crystal contained ill-defined solvent molecules which appeared to be toluene. All physical measurements were made on unsolvated material which had been subjected to microanalysis.

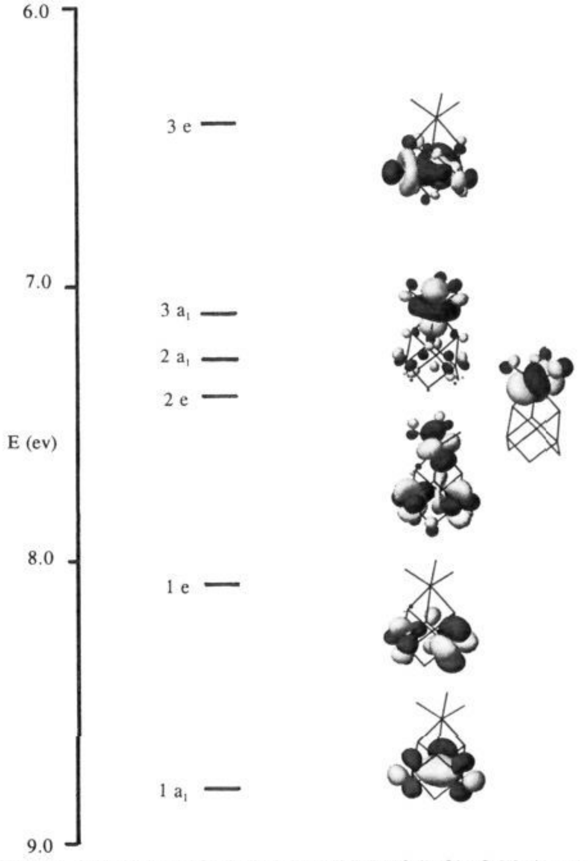
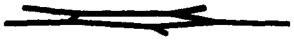


Figure 3. Energy levels for the cluster orbitals of the $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ core of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$.

The mass spectra of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ were both significant and unusual. Although the cluster was a dication, consistent spectra of monocations were readily obtained by the FAB technique in both glycerol ($C_3H_8O_3$) and 3-nitrobenzyl alcohol ($C_7H_7NO_3$) matrices. The monocations can be derived only from the parent dication and its fragments by loss of protons and/or addition of OH^-. The spectrum in glycerol is shown in Figure 5. The peak of highest mass was best simulated by the



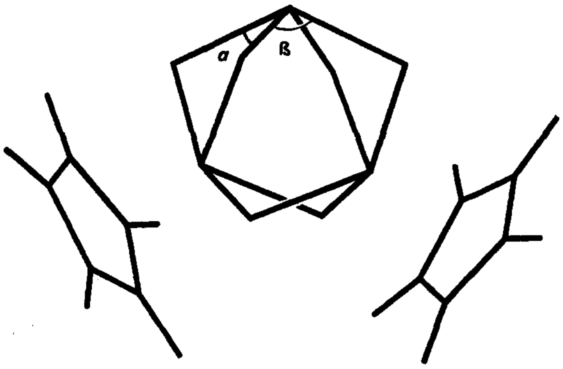


Figure 4. Molecular structure of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$. α and β are the two O–Mo–O angles in Table 2.

Table 2. Important Average Distances (Å) and Angles (deg) in the $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ Dication

Mo–Mo	2.78(3,1)[a]	Mo–O–Mo	86.9(25,17)
Mo–O	2.02(5,4)	α[b]	74.1(16,18)
Mo–Cp	2.04(7)	β[b]	87.9(6,18)

[a] The first digit given in parentheses is the maximum deviation from the mean, the second the e.s.d. [b] α and β are defined in Figure 4.

formula with $m/e = \{(C_5Me_5)_3Mo_3(OH)O_5\}^+$, but the major components of the envelopes between 750–800 and 600–660 amu required different numbers of protons for the best simulation. Thus, in Figure 5, only the simulated patterns with no protons are shown. The mass spectrum shows the $[(C_5Me_5)Mo]_3(\mu\text{-}O)_6$ framework of the cluster conclusively. There was no evidence for chlorine in any of the parent ion or fragment peaks.

The infrared spectrum showed a very broad, intense absorption band between 3400 and 2400 cm^{-1}, assignable to ν(OH) vibrations. Superimposed on this was a spike at 2950 cm^{-1}, assigned to the ν(CH) vibration of the η-C_5Me_5 ligand. The intensity of the ν(OH) band suggested the presence of more than one OH ligand, and the broadness indicated that the OH ligands were strongly hydrogen bonded. There was no absorption band in the infrared spectrum in the region in which a ν(Mo═O) vibration would be observed (900–980 cm^{-1}).

The NMR spectrum in $[^2H_6]$benzene solution at 295 K over the range +250 to −250 ppm showed two signals: one relatively broad at 0.29 ppm and one relatively sharp at 1.59 ppm. In toluene the signals appeared at 0.28 and 1.62 ppm and in CH_2Cl_2 at 0.07 and 2.08 ppm. The signal at higher field was assigned to the methyl protons of η-C_5Me_5 attached to paramagnetic molybdenum and the signal at lower field to the methyl protons of η-C_5Me_5 attached to diamagnetic molybdenum. No signals assignable to OH protons were observed. The $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)_2]_3$ framework of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ has D_{3h} symmetry, and the three molybdenum atoms are electronically equivalent. Thus the two signals in the NMR spectrum must arise from different species, some of which are diamagnetic and some paramagnetic.

The magnetic moment of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ over the temperature range 4–85 K is shown in Figure 6. The relatively large uncertainties in the data, particularly at higher temperatures, are due to the low spin density in the compound. Below 50 K the magnetic moment is essentially constant at 1.13 ± 0.02 μ_B, with a slight increase to 1.28 ± 0.07 μ_B at 85 K. The value of 1.13 μ_B is considerably lower than the spin-only value for a single electron, 1.73 μ_B. Spin–orbit coupling may introduce a small orbital contribution to the susceptibility, resulting in a reduction in the moment below the spin-only value.[30] The species observed in the EPR experiment described below has a g value of 1.962, which is less than the free-ion value because of such spin–orbit coupling. The effective moment of this species would be 1.70 μ_B ($\mu_{eff} = g(S(S+1))^{1/2}$). Therefore, the low value of 1.13 μ_B exhibited by the bulk sample cannot be accounted for by spin–orbit coupling alone and occurs because the sample is a mixture of diamagnetic and paramagnetic $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ species.

The EPR spectrum of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ in liquid toluene at 293 K is shown in Figure 7. It is clear that the species responsible for this spectrum, which was centered at $g = 1.962$, had a single unpaired electron ($S = {}^1/_2$) with hyperfine interactions to more than one molybdenum nucleus (^{95}Mo, $I = {}^5/_2$, 15.9%; ^{97}Mo, $I = {}^5/_2$, 9.6%). The intensities of the ^{95,97}Mo satellites relative to the nuclear-spin-free central resonance, together with spectral simulation (Figure 7), indicated that the species contained three equivalent molybdenum nuclei.

Formula of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$. Hofmann, Rösch, and Schmidt developed an energy level diagram for clusters of the type $\{[(\eta\text{-}C_nR_n)M(\mu\text{-}A)_2]_3\}^{n+}$, such as $\{[(\eta\text{-}C_5Me_5)Re(\mu\text{-}O)_2]_3\}^{2+}$ and $\{[(\eta\text{-}C_6Me_6)Nb(\mu\text{-}Cl)_2]_3\}^{m+}$ (m = 1, 2).[31] We extended this model to $\{[(\eta\text{-}C_5R_5)M]_3(\mu\text{-}A)_n(\mu\text{-}B)_{6-n}\}^{n+}$.[32] The diagram for $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)_2]_3$, with an effective symmetry of D_{3h}, is shown in Figure 8. Applying this diagram to $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ for the possible values of n gives the electron configurations and magnetic properties listed in Table 3.

The lack of a chlorine ligand means that the primary reduction product must contain at least one electron per molybdenum atom, i.e., $n \geq 2$. The EPR spectrum (Figure 7) was due to a species having one unpaired electron, but the magnetic moment (Figure 6) was lower than the spin-only value for a single electron. Thus neither the cluster with $n = 3$ (two unpaired electrons) nor that with $n = 5$ (no unpaired electrons) can be the sole product. The clusters with $n = 2$ and $n = 4$ have one and three electrons in an e′ orbital, respectively, and therefore both have an orbitally degenerate ground state. The EPR spectra of such clusters would be broadened beyond detection.[33] We conclude that the EPR spectrum can be due only to the cluster with $n = 6$, which has a $^2A_1{}'$ ground state.

The magnetic moment of 1.13 μ_B in the solid state was low compared to the expected value of 1.73 μ_B for $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_6\}Cl_2$. The NMR, EPR, and IR spectra all indicated the presence of more than one species in solution and in the solid state. The physical and chemical properties of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ were consistently reproducible from one sample to another. We therefore suggest that an equilibrium existed in solution, which gave an equilibrium mixture of clusters in the solid state. This equilibrium is the redox disproportionation of the diamagnetic cluster with $n = 5$ into the paramagnetic (μ_{eff} = 1.73 μ_B) cluster with $n = 4$ and the paramagnetic (μ_{eff} = 1.73 μ_B) cluster with $n = 6$ (eq 2). The observed moment of 1.13 μ_B

$$2\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_5(\mu\text{-}O)\}^{2+} \rightleftharpoons \{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_6\}^{2+} + \{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_4(\mu\text{-}O)_2\}^{2+} \quad (2)$$

suggested that the diamagnetic portion of the equilibrium mixture (i.e., the cluster with $n = 5$) was approximately 35% of the total.

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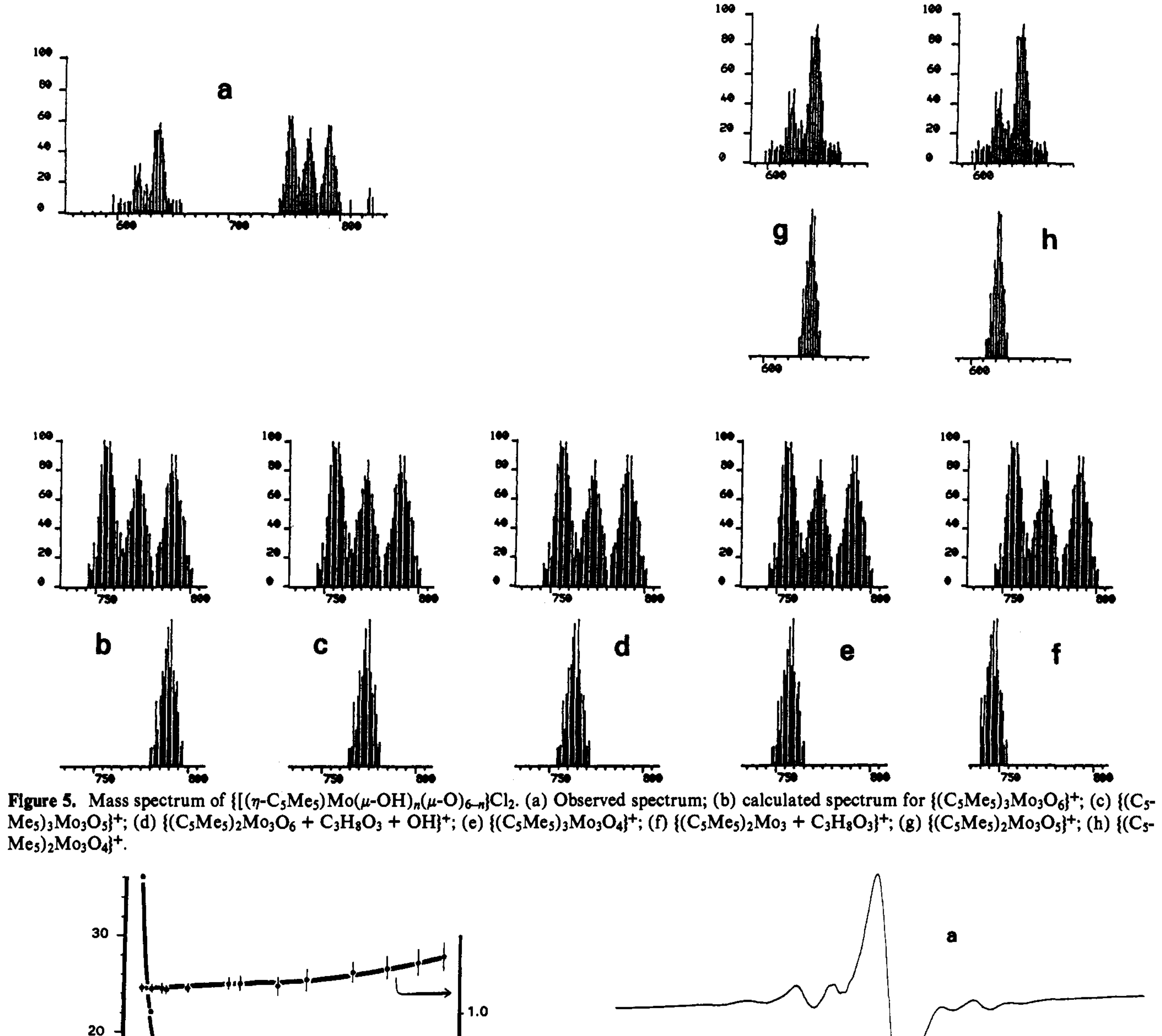

Figure 5. Mass spectrum of $\{[(\eta\text{-C}_5\text{Me}_5)\text{Mo}(\mu\text{-OH})_n(\mu\text{-O})_{6-n}\}\text{Cl}_2$. (a) Observed spectrum; (b) calculated spectrum for $\{(\text{C}_5\text{Me}_5)_3\text{Mo}_3\text{O}_6\}^+$; (c) $\{(\text{C}_5\text{Me}_5)_3\text{Mo}_3\text{O}_5\}^+$; (d) $\{(\text{C}_5\text{Me}_5)_2\text{Mo}_3\text{O}_6 + \text{C}_3\text{H}_8\text{O}_3 + \text{OH}\}^+$; (e) $\{(\text{C}_5\text{Me}_5)_3\text{Mo}_3\text{O}_4\}^+$; (f) $\{(\text{C}_5\text{Me}_5)_2\text{Mo}_3 + \text{C}_3\text{H}_8\text{O}_3\}^+$; (g) $\{(\text{C}_5\text{Me}_5)_2\text{Mo}_3\text{O}_5\}^+$; (h) $\{(\text{C}_5\text{Me}_5)_2\text{Mo}_3\text{O}_4\}^+$.

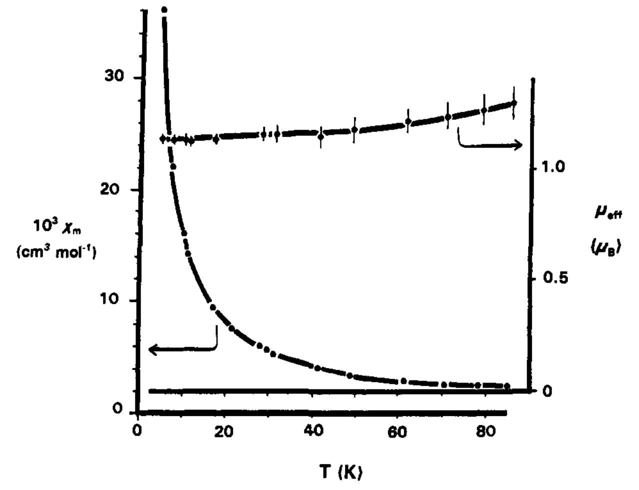

Figure 6. Magnetic moment of $\{[(\eta\text{-C}_5\text{Me}_5)\text{Mo}]_3(\mu\text{-OH})_n(\mu\text{-O})_{6-n}\}\text{Cl}_2$ as a function of temperature.

Equation 3 shows the formation of the primary product.

$$3(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2 + 2\text{Zn} + 5\text{HCl} \rightarrow 3\text{ZnCl}_2 + \{[(\eta\text{-C}_5\text{Me}_5)\text{Mo}]_3(\mu\text{-OH})_5(\mu\text{-O})\}\text{Cl}_2 \quad (3)$$

The cluster $\{[(\eta\text{-C}_5\text{Me}_5)\text{Mo}]_3(\mu\text{-OH})_5(\mu\text{-O})\}^{2+}$ contains formally Mo_3^{XII} and therefore three Mo^{IV} centers. It was obtained by reducing the Mo^{VI} complex $(\eta\text{-C}_5\text{Me}_5)\text{MoCl(O)}_2$ with zinc. Poli and co-workers obtained the cluster $[(\eta\text{-C}_5\text{Me}_5)\text{MoCl}]_3(\mu\text{-Cl})_4(\mu_3\text{-O})$ (which also contains Mo_3^{XII}) by reducing the Mo^{V} complex $(\eta\text{-C}_5\text{Me}_5)\text{MoCl}_4$ with zinc.[13] Reduction of $(\eta\text{-C}_5\text{H}_5)\text{MoCl}_2(\text{O})$ with zinc gave the cluster $\{[(\eta\text{-C}_5\text{H}_5)\text{Mo}]_4(\mu\text{-O})_6\}\{(\mu\text{-Cl}_2)\text{ZnCl(thf)}\}$, containing $\text{Mo}_4^{\text{XVIII}}$ (a mixture of Mo^{IV} and Mo^{V}).[8] Thus it appears that zinc reduction of molybdenum(V) or -(VI) complexes leads to clusters containing molybdenum(IV).

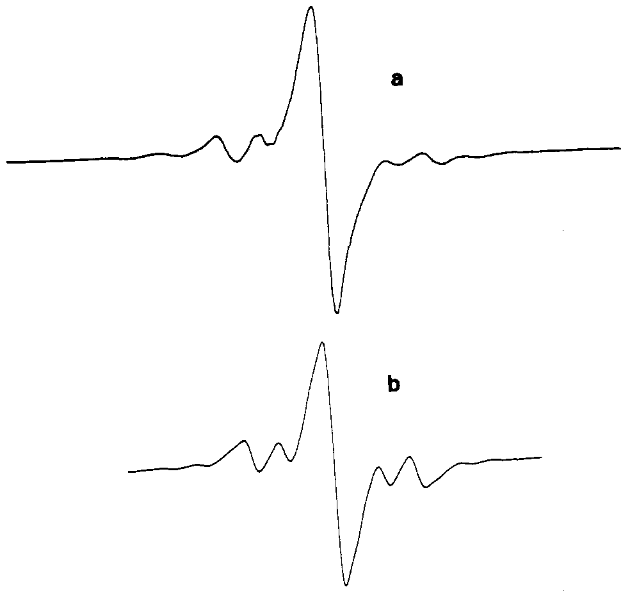

Figure 7. (a) EPR spectrum of $\{[(\eta\text{-C}_5\text{Me}_5)\text{Mo}]_3(\mu\text{-OH})_n(\mu\text{-O})_{6-n}\}^{2+}$ in toluene solution at 293 K. (b) Simulated spectrum. The resonance is centered at $g = 1.962$.

Related Clusters. The cluster $\{[(\eta\text{-C}_5\text{Me}_5)\text{Re}(\mu\text{-O})_2]_3\}^{2+}$, as the ReO_4^- salt, was obtained by reduction of $(\eta\text{-C}_5\text{Me}_5)\text{Re(O)}_3$

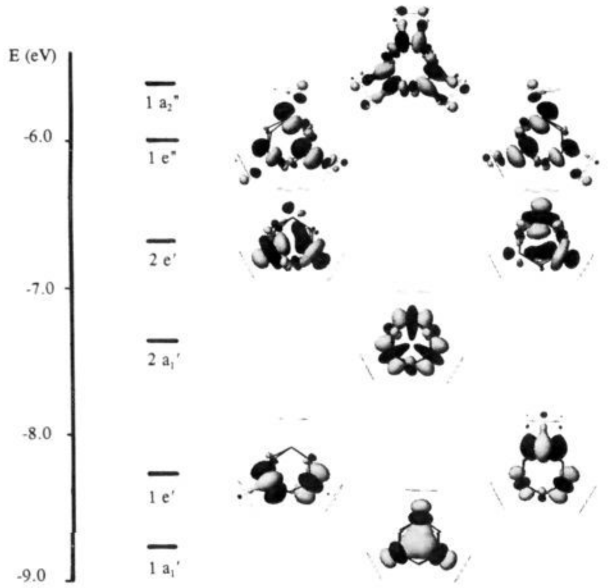

Figure 8. Molecular orbital energy level diagram for $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)_2]_3$.

Table 3. Electron Configurations for $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ as a Function of *n*

n	oxidn no. (*A*) of $Mo_3{}^A$	no. of cluster electrons	configuration	no. of unpaired electrons	magnetism (spin only value)
0	XVII	1	$1a_1{}'^1$	1	paramag (1.73)
1	XVI	2	$1a_1{}'^2$	0	diamag (0)
2	XV	3	$1a_1{}'^2\ 1e'^1$	1	paramag (1.73)
3	XIV	4	$1a_1{}'^2\ 1e'^2$	2	paramag (2.84)
4	XIII	5	$1a_1{}'^2\ 1e'^3$	1	paramag (1.73)
5	XII	6	$1a_1{}'^2\ 1e'^4$	0	diamag (0)
6	XI	7	$1a_1{}'^2\ 1e'^4\ 2a_1{}'^1$	1	paramag (1.73)

with PPh_3 in the presence of air.[34,35] The magnetic properties of this cluster have not been investigated,[31] and the possibility that some of the oxide bridges are in fact OH cannot be discounted. The clusters $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$ and $\{[(\eta\text{-}C_5Me_5)Nb]_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3\}^+$ are diamagnetic.[32] Since clusters with all values of *n* except zero in the formula $\{[(\eta\text{-}C_5Me_5)Nb]_3(\mu\text{-}Cl)_3(\mu\text{-}OH)_n(\mu\text{-}O)_{3-n}\}^+$ will have unpaired electrons, the diamagnetism eliminates other formulations. Legzdins and Veltheer have prepared $\{[(\eta\text{-}C_5Me_5)W]_3(\mu\text{-}F)_2(\mu\text{-}Cl)(\mu\text{-}O)_3\}^{2+}$, with four cluster electrons.[36] Magnetic data are not available for this compound, which may therefore have the formula $\{[(\eta\text{-}C_5Me_5)W]_3(\mu\text{-}F)_2(\mu\text{-}Cl)(\mu\text{-}OH)_n(\mu\text{-}O)_{3-n}\}^{2+}$. Poli has prepared the cluster $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}Cl)_4(\mu\text{-}O)_n(\mu\text{-}OH)_{2-n}\}\{[Mo(O)Cl_4(H_2O)]_2\}$ (with five, six, or seven cluster electrons in the cation),[37] but in the absence of magnetic data, the formula must be regarded as unproven.

Conclusion

The clusters $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$ were prepared. In $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$, which is paramagnetic, the four cluster electrons are associated with the three basal Mo atoms of the $[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ core. For $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}^{2+}$, a combination X-ray crystallography, NMR and ESR spectroscopies, and magnetic moment measurements showed that the primary product, with $n = 5$, undergoes disproportionation to the clusters with $n = 4$ and $n = 6$. This is the first example of a redox equilibrium in a cluster of this type.

Experimental Section

A standard double manifold vacuum line was used for the manipulation of air-sensitive compounds. Solvents were predried over molecular sieves and dried over $LiAlH_4$ (THF), Na (toluene, hexane), or P_2O_5 (CH_2Cl_2, $CHCl_3$). The starting materials $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$, $(\eta\text{-}C_5Me_5)MoCl(O)_2$, and $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ were prepared as described previously.[17] Instruments used were Varian XL200 and Unity 400 for ^1H NMR spectra, Perkin-Elmer 683 for infrared spectra, Kratos MS50 for mass spectra, and locally modified versions of Varian E-4 and E-12 spectrometers for EPR spectra. Extended Hückel molecular orbital calculations were performed using the CAChe system. Microanalyses (C, H, Cl) were by Beller Laboratorium, Göttingen, Germany. Molybdenum was determined by atomic absorption spectroscopy in the department of Geology, UNB.

Preparation of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. A mixture of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ (0.085 g, 0.16 mmol), $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ (0.093 g, 0.16 mmol), and toluene (25 cm³) was placed in a 100-cm³ side-arm flask under argon. The flask was equipped with a greased connector joint for attachment to the vacuum line. The flask was evacuated to a pressure of approximately 2 cmHg, closed, and then heated until the toluene refluxed. Refluxing was continued for 6 days, during which time the solution changed color from red to green. The solution was filtered and the residue extracted with CH_2Cl_2 (5 cm³). The combined extract and filtrate were concentrated to 5 cm³ under vacuum, giving an oil. Addition of hexane (15 cm³) gave green crystals of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ (0.13 g, 68%) and a yellow solution which, on concentration, yielded 0.025 g (14%) of $[(\eta\text{-}C_5Me_5)Mo(O)_2]_2(\mu\text{-}O)$ (identified by comparison of its spectroscopic properties and mass spectrum with those of an authentic sample[4]). Characterization of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ follows. Anal. Calcd for $C_{43.5}H_{64}Mo_5O_{11}$ ($(\eta\text{-}C_5Me_5)_4Mo_5O_{11}\cdot 0.5\ C_6H_5Me$): C, 42.0; H, 5.2. Found: C, 42.2; H, 5.0. ^1H NMR (200 MHz, $[^2H_6]C_6H_6$ solution): δ 1.78 (sharp singlet), assigned to the protons of the $(\eta\text{-}C_5Me_5)Mo(O)_2(\mu\text{-}O)$ group; 11.72 (v broad), assigned to the protons of the $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(\mu\text{-}O)$ cluster. The ratio of the intensities was approximately 1:3. In $[^2H_1]CHCl_3$ the signals were at 2.01 and 10.3 ppm. In this solvent there were also weak signals at 2.15 and 7.10 ppm, assigned to toluene. Infrared spectrum (KBr pellet): 932 (s); 909 (vs); 897 (s); 876 cm⁻¹ (s), assigned to $\nu(Mo{=}O)$ vibrations. The mass spectrum (FAB, Cleland's reagent ($C_4H_{10}S_2O_2$) as matrix) showed major clusters of peaks at *m/e* 1190 ($\{(C_5Me_5)_4{}^{98}Mo_5O_{10}\}^+$), 1055 ($\{(C_5Me_5)_3{}^{98}Mo_5O_{10}\}^+$), 941 ($\{(C_5Me_5)_3{}^{98}Mo_4O_9\}^+$), 925 ($(C_5Me_5)_3{}^{98}Mo_4O_8\}^+$), 909 ($\{(C_5Me_5)_3{}^{98}Mo_4O_7\}^+$), 774 ($\{(C_5Me_5)_2{}^{98}Mo_4O_7\}^+$), and 758 ($\{(C_5Me_5)_2{}^{98}Mo_4O_6\}^+$). Full details and assignments are given in the supplementary material. Magnetic moment (Evan's method,[29] $CHCl_3$ solution, 18 °C) was 3.16 μ_B. The crystals were also characterized by X-ray diffraction.

Preparation of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$. Method 1 (from $(\eta\text{-}C_5Me_5)MoCl(O)_2$). To a solution of $(\eta\text{-}C_5Me_5)MoCl(O)_2$ (0.30 g, 1.01 mmol) in $CHCl_3$ (30 cm³) were added zinc powder (2 g) and concentrated hydrochloric acid (1 cm³). The mixture was stirred under argon at room temperature for 4 days, during which time the color changed from yellow through orange to green. The $CHCl_3$ was removed completely under vacuum, giving a green residue which was extracted twice with benzene (50 cm³). The combined extracts (which were yellow) were evaporated to dryness under vacuum. The residue was recrystallized from THF/hexane (1:5 v/v), giving $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$ (0.025 g, 10%). This was identified by comparison of its analytical and physical properties with those of an authentic sample.[17] The green residue was dissolved in dilute hydrochloric acid (2 M, 100 cm³) and the solution extracted three times with benzene (50-cm³ portions). The resultant turquoise solution was dried over Na_2SO_4, and then the solvent was removed under vacuum. The turquoise residue was dissolved in THF (50 cm³), and the solution was filtered and concentrated to 20 cm³. Addition of hexane (30 cm³) gave turquoise crystals of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ (0.11 g, 37% based on molybdenum). The physical and chemical properties of the product were identical to those of samples prepared as described in method 2 below.

Method 2 (Directly from $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$). A solution of $[(\eta\text{-}C_5Me_5)Mo(CO)_2]_2$ (0.42 g, 0.73 mmol) in $CHCl_3$ (120 cm³) was oxidized by H_2O_2 (30%, 3 cm³) in the presence of concentrated HCl (1.5 cm³) and air for 2 h. The chloroform solution was extracted twice with 250-cm³ portions of water and then with 100 cm³ of 5% aqueous $FeSO_4$ and then degassed under vacuum. To the resultant bright yellow solution of (η-

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Table 4. Crystal Data, X-ray Diffraction Results, and Refinement Details for $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$

	$(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$	$\{[(\eta\text{-}C_5Me_5)Mo]_3\text{-}(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$
mol formula	$C_{40}H_{60}Mo_5O_{11}$	$C_{44}H_{66}Cl_2Mo_3O_6$[a]
M_r	1196.61	1049.82
system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	10.851(2)	27.97(4)
b, Å	12.450(4)	11.260(6)
c, Å	18.153(3)	16.865(15)
α, deg	91.07(2)	90
β, deg	102.04(1)	117.93(8)
γ, deg	109.27(2)	90
V, Å^3	2253.9(9)	4692(8)
Z	2	4
$F(000)$ electrons	1195.5	2151.3
D_x, Mg m^{-3}	1.76	1.48
T, K	295	295
cryst dimens, mm	0.48 × 0.40 × 0.12	0.45 × 0.36 × 0.08
μ, cm^{-1}	13.7	9.3
2θ range, deg	2–46	2–44
total no. of reflns	6231	2859
unique reflns	6228	2859
obsd reflns	4575	921
obsd criteria	$I > 1\sigma(I)$	$I > 1\sigma(I)$
no. of refined params	505	61
obsd/param ratio	9.1	15.1
R[b]	0.063	0.147
R_w	0.073[c]	0.398[d]
GOF[e]	1.58	1.26
max residual, e Å^{-3}	1.80	1.37
min residual, e Å^{-3}	–1.40	–0.80
max shift, Δ/σ	0.021	0.026

[a] For $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_5(\mu\text{-}O)\}Cl_2\cdot 2C_6H_5CH_3$. [b] $R = (\sum|\Delta F|/(\sum F_o)$. [c] $R_w = [(\sum w(\Delta F)^2)/\sum w(F_o)^2]^{1/2}$. [d] $R_w = [(\sum w(\Delta F^2)^2)/\sum w(F_o^2)^2)]^{1/2}$. [e] GOF $= \sum w(\Delta F)^2/[(\text{no. of reflns}) - (\text{no. of params})]$.

$C_5Me_5)MoCl(O)_2$ were added zinc powder (3 g) and concentrated hydrochloric acid (1.5 cm^3). The mixture was stirred for 4 days, giving a green precipitate and a red-brown solution. The green precipitate was removed by filtration, and the red-brown filtrate evaporated to dryness. Recrystallization of the residue from THF/hexane (1:5 v/v) gave 0.082 g (21%) of $[(\eta\text{-}C_5Me_5)Mo(O)(\mu\text{-}O)]_2$. The product was identified by comparison of its spectroscopic properties with those of a sample prepared as described previously.[17] The green precipitate was wash twice with chloroform (25 cm^3) and then dissolved in aqueous hydrochloric acid (2 M, 100 cm^3) to give a turquoise solution. The solution was extracted with benzene (3 × 100 cm^3) until the aqueous layer was colorless. The combined benzene extracts were dried with Na_2SO_4, the mixture was filtered, and the benzene was removed under vacuum. The crude green residue was recrystallized by dissolving it in THF (20 cm^3), concentrating the solution to 5 cm^3 in vacuum, and layering the solution with toluene (15 cm^3). On setting the solution aside at –30°C, turquoise crystals of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ formed in 14 days. Yield 0.26 g, 63%. Anal. Calcd for $C_{30}H_{50}Cl_2Mo_3O_6$ (n = 5, see text): C, 41.6; H, 5.8; Cl, 8.2; Mo, 33.3. Found: C, 41.3; H, 5.7; Cl, 8.6; Mo, 33.0. ^1H NMR: δ ($[^2H_6]C_6H_6$ solution, 400 MHz) 0.29 (broad), 1.59 (sharp); ($[^2H_8]C_6H_5Me$ solution, 400 MHz) 0.28 (broad), 1.62 (sharp); ($^2H_2$ CH_2Cl_2 solution, 200 MHz) 0.07 (broad), 2.08 (sharp). The signals were assigned to $\eta\text{-}C_5Me_5$ attached to paramagnetic and diamagnetic molybdenum centers, respectively. Infrared spectrum (KBr pellet): very broad, intense absorption from 3400–2400 cm^{-1}, with a spike at 2950 cm^{-1}; the absorptions were assigned to ν(OH) and ν(CH) vibrations, the OH group being strongly hydrogen bonded. The mass spectrum is shown in Figure 5, the magnetic moment in Figure 6, and the EPR spectrum in Figure 7. The salt was also characterized by X-ray crystallography.

X-ray Crystallography. X-ray diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å). Data were collected using the $\omega/2\theta$ scan method. Crystal data are given in Table 4.

$(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$. An empirical absorption correction (ψ scan data) was applied to the data. Refinement used the NRCVAX suite of programs.[38] The weighting scheme was of the form $w = 1/(\sigma^2(F)^2 + 0.001(F)^2)$. Scattering factors for the neutral atoms were taken from the program. Structure solution and refinement were uneventful, with all atoms anisotropic, except fixed hydrogen atoms (C–H = 0.96 Å). Important angles and distances are given in Table 1, and the structure is shown in Figures 1 and 2. Tables of atomic coordinates, displacement parameters, and a complete list of distances and angles are available in the supplementary material.

$\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$. The crystals were thin plates which diffracted weakly; the intensity of the standards decreased by 15% over the 48 h required to collected the data. Thus the intensity data were of very poor quality and quantity. They were corrected for the decomposition and empirically (ψ scan) for absorption. Only 32% of the data could be considered observed. During the refinement it became apparent that the crystals contained solvent molecules, presumed to be toluene, although they were very ill-defined. The Mo, Cl, and O atom positions were found using direct methods. All of the carbon atom positions for the C_5Me_5 bonded to Mo(1) were found from difference maps, but the atoms would not refine individually to chemically reasonable positions. The C_5Me_5 bonded to Mo(2) was disordered by at least the crystallographic 2-fold axis and possibly an additional general positional disorder. Only a four atom fragment of this C_5Me_5 made chemical sense. This was used to find an idealized rigid group, assuming only the crystallographically imposed disorder. Both ligands were refined as "variable metric"[39] rigid groups. The toluene was fitted to a regular hexagon (C–C = 1.39 Å) and the position of the methyl group restrained during refinement. Due to the paucity of data, no attempt was made to include hydrogens in the model. The refinement was performed on F_o^2 using SHELXL-93[39] with a weighting scheme of the form $w = [\sigma^2(F_o^2) + (0.1691P)^2 + 1137.69P]^{-1}$, where $P = 0.33[F_o^2 + 2F_c^2]$. In general, refinements on F_o^2 give much larger residuals than refinements on F_o. In this case the values of R and R_w (see Table 4) indicated a poorly determined structure where only the heaviest atom positions can be considered meaningful. However, the cluster was clearly defined as $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$. Some important average distances and angles are given in Table 2. Tables of atomic coordinates, displacement parameters, and distances are available as supplementary material.

Magnetic Moment. Magnetic susceptibilities were measured over the temperature range 4.4–85 K employing the Princeton Applied Research Model 155 vibrating-sample magnetometer described previously.[40] The molar magnetic susceptibility of $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2$ was corrected for the background diamagnetism of the sample holder, for the diamagnetic contribution of all atoms (total -500×10^{-6} cm^3 mol^{-1}), and for temperature-independent paramagnetism (150×10^{-6} cm^3 mol^{-1}). The latter was estimated from the work of French and Garside.[41] Uncertainties in χ_m are estimated to range from ±2% at 4.4 K to ±11% at 85 K.

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Supplementary Material Available: X-ray diffraction data and mass spectral data for $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and tables of atomic coordinates, U_{ij} values, and bond distances and angles for $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $\{[(\eta\text{-}C_5Me_5)Mo]_3(\mu\text{-}OH)_n(\mu\text{-}O)_{6-n}\}Cl_2\cdot 2C_6H_5Me$ (24 pages); listing of observed and calculated structure factors (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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