The only capped-octahedral clusters other than the two $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ species for which X-ray diffraction studies have been reported are $Os_7(CO)_{21}$[19] and $Rh_7(CO)_{16}^{13-}$,[20] both of which are electronic analogues of the $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ systems and hence conform to the skeletal-electron paradigm alluded to earlier.

Conclusion. The $[\eta^5\text{-}C_5(CH_3)_5]_3Co_3B_4H_4$ molecule is, to our knowledge, the only structurally characterized species containing three mutually bonded $M[\eta^5\text{-}C_5(CH_3)_5]$ groups. As we note in the Introduction, prior to the crystal structure determination it was questionable whether such an arrangement would be viable, given the unavoidably severe interligand steric crowding. The fact that this structure is nonetheless adopted even at the expense of cobalt–cobalt bond lengthening and considerable bending of the methyl groups out of the C_5 ring planes implies strong thermodynamic preference for this particular cluster geometry as opposed to other, less sterically crowded arrangements. In principle, there exists a possibility

that the observed structure is kinetically rather than thermodynamically dictated, but this is quite unlikely given (1) the high symmetry, (2) the fact that the same geometry is observed for both the C_5H_5- and the $C_5(CH_3)_5$-containing species, and (3) the failure to detect any other isomer. Indeed, it is probable that the formation of the $(\eta^5\text{-}C_5R_5)_3Co_3B_4H_4$ complexes from $B_5H_8^-$ involves rearrangement of other, less stable species that form in earlier stages of the reactions.

The present work indicates that the capped-*closo*-Co_3B_4 polyhedron is an electronic system of exceptional stability, which persists even in the face of strong steric inducement to adopt a different geometry. When quantitative molecular orbital treatments are conducted on this system, it will be surprising if they do not reveal a clear preference for the observed cage structure in relation to other conceivable alternatives.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, thermal parameters, and selected mean planes (16 pages). Ordering information is given on any current masthead page.

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Investigations of the Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N₂S₂ Donor Sets. 2.[1] Preparation, Chemical Characterization, and Electrochemical Study of the Molybdenum(IV)-, Molybdenum(V)-, and Molybdenum(VI)-Oxo Complexes

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The chemistry of the tetradentate N₂S₂ donor ligands *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine (LH₂) and *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine (L'H₂) with molybdenum in the VI, V, and IV oxidation states is described. In methanol solution Mo(VI)–oxo reagents combine with LH₂ and L'H₂ to give [MoO₂L] and [MoO₂L']. Reduction of these complexes with HSPh in methanol yields [Mo₂O₃L₂] and [H₂Mo₂O₄L'₂]. The more common mono-oxo-bridged Mo(V) dimer [Mo₂O₃L'₂] may be prepared by the reaction of [MoO₂L'] with PMe₂Ph in dry THF. The Mo(IV) species [MoOL] and [MoOL'] are obtained by treatment of the Mo(VI) species with excess PMe₂Ph in THF solution. The sulfido-bridged dimers [Mo₂S₄L'₂]²⁻ and [MoO₂S₂L'₂]²⁻ have also been prepared. The infrared, electronic, and proton magnetic resonance spectra of these complexes are noted. The electrochemical properties of the complexes are discussed in detail. The significant differences in the redox characteristics of [MoO₂L] and [MoO₂L'] are reflected in the contrasting reactivity patterns with substituted hydrazines. Whereas [MoO₂L] reacts with H₂NNR₂ and H₂NNHR species to give the common monosubstituted derivatives [MoO(N₂R₂)L] and the disubstituted diazene complexes [Mo(N₂R)₂L], [MoO₂L'] reacts only with benzoylhydrazides (C₆H₅CONHNH₂) to yield the potentially seven-coordinate species [MoO-(C₆H₅CONNH)L'].

Introduction

There has been much recent interest in the synthesis and characterization of molybdenum–sulfur complexes.[3,4] This attention by coordination chemists stems largely from the recognition that molybdenum is a necessary cofactor for a number of redox-active enzymes.[5,6] On the basis of electron

paramagnetic resonance studies[7–9] and, more recently, EXAFS investigations,[10–13] a number of these enzymes, other than nitrogenase, have been shown to possess molybdenum coordinated to both terminal oxo ligands and to sulfur groups, a

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number of which are most likely thiolato sulfur from cysteinyl residues. In order to provide a set of structurally defined molybdenum-oxo species containing thiolate-sulfur ligands and to study the effects of chelate-ring constraints on the general spectroscopic and redox properties of these species, we initiated a program into the synthesis and structural characterization of complexes of Mo(VI), Mo(V), and Mo(IV) with tetradentate S_2N_2 donor ligands with flexible backbones.[1,14,15] Similar investigations have been reported by other investigators in the field,[3,16-18] and these results will be discussed and compared to those observed for the system with L and L' in this and subsequent papers in the series.

In the present paper we describe an improved synthesis of the Mo(VI) complexes with the ligands L and L',[19] the syn-

LH₂

L'H₂
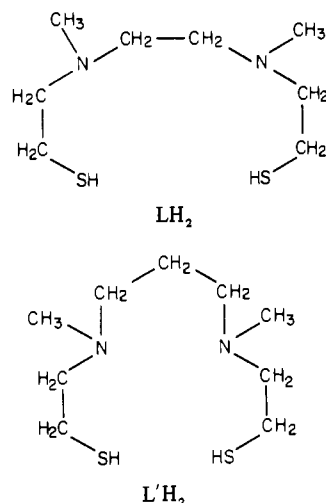
thesis of Mo(V) complexes with the $Mo_2O_3^{4+}$, $Mo_2O_4^{2+}$, $Mo_2O_2S_2^{2+}$, and $Mo_2S_4^{2+}$ cores, the preparation of the Mo-(IV)-oxo monomers, and the detailed spectroscopic properties of these complexes. Since geometric considerations suggest that the complexes of L would be more strained than those of L',[19] we anticipated some difference in the properties of the analogous Mo(VI) species. The constraints imposed by the five-membered ethylenediamine chelate ring of [moO₂L] or, alternatively, by the relative instability of the six-membered ring of [MoO₂L'] may be responsible for the contrasting electrochemical behavior of these species, which is discussed in detail in the present paper. The differences in reactivity patterns of [MoO₂L] and [MoO₂L'] toward condensation reactions with substituted hydrazines are also noted. Three subsequent papers report the results of detailed structural studies of the complexes with MoO_2^{2+} core, a comparison of the structures exhibiting the $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ cores, and the results of structural investigations of hydrazido(2-) and diazenido derivatives, [MoO(N₂R₂)L] and [Mo(N₂R)₂L].

Experimental Procedure

Material and Methods. All compounds were prepared from commercially available starting materials used without further purification. The syntheses were carried out under inert atmosphere with use of carefully dried solvents.

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Mr. A. G. Olney (University of Sussex). Analytical data are given in Table I.

Proton nuclear magnetic spectra were recorded on a Varian Associates A-60A spectrometer. Tetramethylsilane (Me₄Si) was added as an internal chemical shift calibrant, and all shifts are reported in parts per million downfield from Me₄Si (δ).

Molecular weights were determined with a Hitachi-Perkin-Elmer 115 osmometer on dichloromethane solutions of the complexes.

Cyclic voltammetric studies[20] were performed on a Princeton Applied Research (PAR) Model 170 electroanalytical system using a three-electrode configuration in CH₂Cl₂|0.1 M [n-Bu₄N]PF₆ or THF|0.2 M [n-Bu₄N]BPh₄ solution vs. Ag wire reference. Ferrocene was used as an internal calibrant, and all potentials are referred to the first one-electron oxidation FeCp₂/FeCp₂⁺.[21] Controlled-potential electrolyses were performed in an H-type three-electrode, three-compartment cell. Platinum working and auxiliary electrodes of 1 cm² gauge were employed. Electrolyses were carried out on 50-150 μmol of complex under dinitrogen atmosphere, and the charge passed was measured graphically or with use of a Chemical Electronics integrator.

The preparation and properties of the starting material [n-Bu₄N]₂Mo₆O₁₉ have been discussed elsewhere.[22] The ligands N,-N'-dimethyl-N,N'-bis(2-mercaptoethyl)ethylenediamine (LH₂) and N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)propanediamine (L'H₂) were prepared according to the procedure of Karlin and Lippard.[19]

[MoO₂(C₈H₁₈N₂S₂)], [MoO₂L]. (a) To a stirred suspension of [MoO₂(C₅H₇O₂)₂] (3.6 g, 0.01 mol) in 60 mL of methanol, N,N'-dimethyl-N,N'-bis(2-mercaptoethyl)ethylenediamine (2.3 g, 0.01 mol) was added dropwise over a period of 10 min. The yellow precipitate that formed immediately was collected, washed with CH₃OH/ether, and recrystallized from CH₂Cl₂/CH₃OH to give 0.5 g of product (15% yield).

(b) In an improved synthesis, [Bu₄N]₄Mo₈O₂₆[52] (10 g, 0.004 mol) was dissolved in 250 mL of hot methanol. To the cooled solution was added LH₂ (6.9 g, 0.03 mol) dropwise with stirring. The yellow microcrystalline precipitate was collected and purified as above to give 6.3 g of product (67% yield).

[MoO₂(C₉H₂₀N₂S₂)], [MoO₂L']. The complex was prepared in an analogous manner to that for [MoO₂L]. The yield with procedure a was 19% while that for method b was 60%.

[Mo₂O₃(C₈H₁₈N₂S₂)₂], [Mo₂O₃L₂]. (a) A solution of [MoO₂L] (0.66 g, 0.002 mol) in 30 mL of CH₂Cl₂ was added to PPh₃ (0.26 g, 0.001 mol) in 10 mL of CH₂Cl₂. Over a 12-h period the solution proceeds through a red-brown stage to an intensely purple product. Addition of 50% by volume CH₃OH yields prismatic crystals in 30% yield.

(b) With use of the ability of thiol groups to reduce molybdenum-oxo species, a suspension of MoO₂L (3.0 g, 0.009 mol) in 50 mL of dry CH₃OH was treated with PhSH (1.00 g, 0.009 mol) and stirred with gentle heating overnight. From the intensely purple solution that resulted, prismatic crystals formed upon cooling. The crystals were collected and washed with CH₃OH and ether (40% yield).

(c) In a similar fashion, an excess of LH₂ (13.8 g, 0.06 mol) was added to [n-Bu₄N]₄Mo₈O₂₆ (10 g, 0.0046 mol) in 250 mL of hot methanol. A deep red-brown solution resulted, which was stirred overnight with gentle heating. When the solution cooled, large purple prisms were formed (63% yield based on Mo).

H₂[Mo₂O₄(C₉H₂₀N₂S₂)₂], [H₂Mo₂O₄L'₂]. Attempts to prepare [Mo₂O₃L'₂] by conventional methods led to the isolation of [H₂Mo₂O₄L'₂]. (a) L'H₂ (1.31 g, 0.006 mol) was added dropwise with stirring to 1.97 g of [MoO₂(acac)₂] (0.006 mol) in 75 mL of CH₃OH. The solution was filtered and an additional 0.65 g of ligand added to the filtrate, which was allowed to stand in a stream of nitrogen overnight. The cubic crystals that formed overnight were found to be air-stable but insoluble in most common organic solvents. Me₂SO solutions of the complex were found to decolorize over a period of 2-3 h (5% yield). (b) A solution of [MoO₂L'] (1.00 g) in 30 mL of

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Table I. Summary of Analytical and Relevant Spectroscopic Data for the Molybdenum Complexes

compd	$M_r{}^a$	color	IR, cm^{-1}	^{1}H NMR^b L or L'	^{1}H NMR^b hydrazido	elemental anal., %^{c} C	H	N	X
[MoO$_2$(C$_8$H$_{16}$N$_2$S$_2$)]	362 (334)	yellow	892 (s), 917 (s) [ν(Mo-O$_t$)]	6.83 br (6, s), 7.08 (12, m)		30.0 (28.7)	5.2 (5.4)	8.6 (8.4)	
[MoO$_2$(C$_9$H$_{20}$N$_2$S$_2$)]	332 (348)	yellow	888 (s), 921 (s) [ν(Mo-O$_t$)]	6.96 (6, s), 6.73, 7.?4 (12, m)		30.9 (31.0)	5.6 (5.7)	8.3 (8.0)	
[Mo$_2$O$_3$(C$_8$H$_{16}$N$_2$S$_2$)$_2$]	681 (652)	purple	936 (s) [ν(Mo-O$_t$)]; 442 (m), 730 (m) [ν(Mo$_2$O$_b$)]	6.48 (3, s), 7.12 (3, s), 6.93 (12, m)		29.4 (29.2)	5.7 (5.5)	8.6 (8.6)	
[Mo$_2$O$_3$(C$_9$H$_{20}$N$_2$S$_2$)$_2$]	d	purple	941 (s) [ν(Mo-O$_t$)]; 440 (m), 729 (m) [ν(Mo$_2$O$_b$)]	6.56 (3, s), 6.83 (3, s), 7.00 (12, m)		32.1 (31.8)	6.0 (5.9)	8.2 (8.2)	
[Mo$_2$O$_4$(C$_9$H$_{21}$N$_2$S$_2$)$_2$]	e	orange	952 (s) [ν(Mo-O$_t$)]; 495 (m), 740 (m) [ν(Mo$_2$O$_b$)]			30.8 (30.9)	6.0 (6.0)	8.2 (8.0)	
[Mo(N$_2$C$_6$H$_4$CH$_3$)$_2$(C$_9$H$_{18}$N$_2$S$_2$)]	555 (540)	purple	1515, 1589 (s) [ν(NN)]	f	f	49.0 (48.9)	5.8 (5.9)	15.7 (15.6)	
[Mo(N$_2$C$_6$H$_4$OCH$_3$-p)$_2$(C$_8$H$_{18}$N$_2$S$_2$)]	558 (572)	purple-black	1531, 1602 (s) [ν(NN)]	7.11 (s), 7.08 (s), 6.88 (m)	6.18 (s), 4.72 (q)	46.4 (46.2)	5.7 (5.6)	14.4 (14.7)	
[Mo(N$_2$C$_6$H$_5$)$_2$(C$_9$H$_{20}$N$_2$S$_2$)]	539 (526)	purple	1510 (s), 1563 (m), 1600 (m), 1630 (m) [ν(NN)]	f	f	48.1 (47.9)	6.0 (5.7)	16.1 (16.0)	
[Mo(N$_2$C$_6$H$_4$OCH$_3$-p)$_2$(C$_9$H$_{20}$N$_2$S$_2$)]	603 (586)	purple	1508, 1553 (m), 1603, 1645 (m) [ν(NN)]	f	f	47.0 (47.1)	5.6 (5.8)	14.0 (14.3)	
[Mo(N$_2$C$_6$H$_4$OCH$_3$)(NNHC$_6$H$_4$OCH$_3$)(C$_8$H$_{18}$N$_2$S$_2$)] [BPh$_4$]	436 (892)	purple	1490 (s), 1625 (s) [ν(NN)]	f	f	61.5 (61.9)	6.0 (5.9)	9.6 (9.4)	
[Mo(N$_2$C$_6$H$_4$OCH$_3$)(NNCH$_3$C$_6$H$_4$OCH$_3$)(C$_8$H$_{18}$N$_2$S$_2$)] [BPh$_4$]	437 (906)	purple	1492 (s), 1579 (m), 1630 (s) [ν(NN)]	f	f	62.4 (62.3)	6.0 (6.1)	9.1 (9.3)	
[MoOC$_6$H$_5$CONNH)(C$_9$H$_{20}$N$_2$S$_2$)]	447 (466)	red	870 (s) [ν(Mo-O$_t$)]; 1545 (m), 1590 (m) [ν(NN), ν(CO)]	f	f	42.0 (41.2)	5.1 (5.6)	11.8 (18.0)	
[MoO(p-CH$_3$OC$_6$H$_4$CONNH)(C$_9$H$_{20}$N$_2$S$_2$)]	475 (495)	red-brown	882 (s) [ν(Mo-O$_t$)]; 1550, 1600 (m) [ν(NN), ν(CO)]	f	f	40.7 (41.1)	5.6 (5.6)	11.4 (11.3)	
(n-Et$_4$N)$_2$[Mo$_2$S$_4$(C$_9$H$_{20}$N$_2$S$_2$)$_2$]	...	red-brown	481 (s) [ν(Mo-S$_b$)]	f	f	40.3 (40.0)	8.0 (7.8)	8.0 (8.2)	25.8 [S] (25.1)
(n-Et$_4$N)$_2$[Mo$_2$S$_2$O$_2$(C$_9$H$_{20}$N$_2$S$_2$)$_2$]	...	red-orange	920 (s) [ν(Mo-O$_t$)]	f	f	40.7 (41.3)	7.6 (8.1)	8.3 (8.5)	18.6 [S] (19.4)
[MoO(C$_9$H$_{18}$N$_2$S$_2$)]	304 (318)	red	948 (s) [ν(Mo-O$_t$)]	f	f	30.7 (30.2)	5.7 (5.7)	8.3 (8.8)	
[MoO(C$_9$H$_{20}$N$_2$S$_2$)]	348 (332)	red	953 (s) [ν(Mo-O$_t$)]	f	f	32.1 (32.5)	6.2 (6.0)	7.9 (8.4)	
[MoO(C$_8$H$_{18}$N$_2$S$_2$)](BPh$_4$)	...	green-brown	910 (s) [ν(Mo-O$_t$)]	g	g	59.8 (60.3)	6.4 (6.0)	4.2 (4.4)	
[MoO(C$_9$H$_{20}$N$_2$S$_2$)](BPh$_4$)	...	emerald green	915 (s) [ν(Mo-O$_t$)]	g	g	60.3 (60.8)	5.8 (6.1)	4.1 (4.3)	
[MoO(N$_2$Ph$_2$)(C$_9$H$_{18}$N$_2$S$_2$)]	478 (500)	red	890 (s) [ν(Mo-O$_t$)]; 1581 (m) [ν(NN)]	f	6.87 (3, s), 2.60 (10, m), 6.80 (3, s), 7.00 (12, m)	48.6 (48.0)	5.4 (5.6)	11.8 (11.2)	
[MoO(N$_2$PhMe)(C$_8$H$_{18}$N$_2$S$_2$)]	418 (438)	red	888 (s) [ν(Mo-O$_t$)]; 1590 (m) [ν(NN)]	f		40.7 (41.1)	6.0 (5.9)	13.2 (12.8)	
[Mo(N$_2$Ph)$_2$(C$_9$H$_{18}$N$_2$S$_2$)]	539 (512)	purple	1525 (s), 1598 (s) [ν(NN)]	f		43.9 (44.5)	5.3 (5.5)	16.1 (16.4)	
[Mo(N$_2$C$_6$H$_4$NO$_2$-p)$_2$(C$_8$H$_{18}$N$_2$S$_2$)]	584 (602)	purple	1531 (s), 1596 (s) [ν(NN)]	f		40.2 (39.9)	4.1 (4.3)	18.7 (18.6)	
[Mo(N$_2$C$_6$H$_4$Cl-p)$_2$(C$_8$H$_{18}$N$_2$S$_2$)]	595 (581)	purple	1530, 1601 (s) [ν(NN)]	f		40.7 (41.3)	4.3 (4.5)	14.3 (14.5)	
[MoO(p-ClC$_6$H$_4$CONNH)(C$_9$H$_{20}$N$_2$S$_2$)]	529 (500)	brown	875 (s) [ν(Mo-O$_t$)]; 1543, 1601 [ν(NN), ν(CO)]	f		37.9 (38.4)	4.6 (5.0)	11.0 (11.2)	

^{a} By vapor pressure osmometry; calculated values in parentheses. ^{b} In CD$_2$Cl$_2$ solution. Abbreviations: s, singlet; m, multiplet; q, quartet. ^{c} Calculated values in parentheses. ^{d} Solutions decompose. ^{e} Insoluble. ^{f} Limited solubility in CD$_2$Cl$_2$. ^{g} Paramagnetic.

CH_2Cl_2 to which 1 mL of acetic acid (0.5 N) was added was stirred overnight. Amber crystals were found to have formed in the reaction vessel (yield 0.4 g, 39%).

$[Mo_2O_3(C_9H_{20}N_2S_2)_2]$, $[Mo_2O_3L'_2]$. The complex with the $Mo_2O_3^{4+}$ core could only be synthesized by exploiting the ability of PMe_2Ph to abstract oxo groups from Mo(VI) species. To a solution of $[MoO_2L']$ (3.0 g, 0.009 mol) in 100 mL of dry THF was added PMe_2Ph (0.6 g, 0.005 mol) dropwise. The deep purple solution that resulted was concentrated under vacuum to 10 mL and kept at 4 °C until purple crystals formed on the surface of a dark oil (yield 0.4 g, 13%). The complex is extremely moisture-sensitive and readily reacts upon exposure to moist air to give $[Mo_2O_4(L'H)_2]$.

$[MoO(C_8H_{18}N_2S_2)]$, $[MoOL]$. Upon addition of a large excess of PhSH (5.0 g, 0.045 mol) to a solution of $[MoO_2L]$ (1.0 g, 0.003 mol) in 30 mL of THF at -20 °C, the characteristic yellow color of the solution is rapidly discharged and a chinese red color evolved. The solution was concentrated to 5 mL and hexane added to induce crystallization. After 5 days at -20 °C, light red needle-shaped crystals formed (yield 0.1 g, 10%). Attempts to grow X-ray quality crystals were unsuccessful as solutions of the complex in common organic solvents rapidly decompose to produce purple residues characteristic of the dimeric species $[Mo_2O_3L_2]$.

$[MoO(C_9H_{20}N_2S_2)]$, $[MoOL']$. The complex with the MoO^{2+} core was synthesized by an analogous preparation to that employed for $[MoOL]$ (yield 15%).

$[MoO(C_8H_{18}N_2S_2)(OPMe_2Ph)]$. Addition of an excess of PMe_2Ph (2.0 g, 0.018 mol) to a solution of $[MoO_2L]$ (2.0 g, 0.006 mol) in 50 mL of THF at 0 °C resulted in the evolution of an intense emerald-green color. A fine precipitate was formed upon concentration of the solvent to 5 mL (yield 1.2 g, 63%).

$[MoO(C_8H_{18}N_2S_2)(NNPh_2)]$, $[MoOL(NNPh_2)]$. To a stirred suspension of $[MoO_2L]$ 2.00 g, 0.006 mol) in 50 mL of CH_3OH was added 5 mL of $H_2NNPh_2\cdot HCl$. Stirring at room temperature was continued overnight, and the precipitate obtained was filtered, washed with ether, and air-dried. Recrystallization from CH_2Cl_2/CH_3OH produced lustrous red needles of $MoOL(NNPh_2)$ (yield 1.6 g, 53%). The $[MoOL(NNMePh)]$ analogue was synthesized in a similar fashion.

$[Mo(N_2C_6H_4OCH_3-p)_2(C_8H_{18}N_2S_2)]$, $[Mo(N_2PhOCH_3)_2L]$. A solution of $H_2NNHC_6H_4OCH_3\cdot HCl$ (2.5 g, 0.014 mol) in 5 mL of CH_3OH was added to a suspension of $[MoO_2L]$ (1 g, 0.003 mol) in 50 mL of CH_3OH. Refluxing for 2 h produces a deep red solution from which black microcrystals precipitate upon cooling overnight (yield 0.9 g, 52%).

The analogous complexes $[MoL(N_2Ph)_2]$, $[MoL(N_2C_6H_4CH_3)_2]$, $[MoL(N_2C_6H_4Cl)_2]$, and $[MoL(N_2C_6H_4NO_2)_2]$ were prepared by an identical route. The derivatives of L', $[Mo(N_2C_6H_4OCH_3)_2L']$ and $[Mo(N_2C_6H_5)_2L']$, were obtained in a similar fashion.

$[Mo(N_2C_6H_4OCH_3)(NNCH_3C_6H_4OCH_3)(C_8H_{18}N_2S_2)]BPh_4$. $[Mo(N_2C_6H_4OCH_3)_2L]$ (2.5 g, 0.004 mol) was dissolved in 50 mL of dry CH_2Cl_2 under an argon atmosphere and treated with 1.0 g of $(CH_3)_3OBF_4$. After 0.5 h of stirring, the solution was evaporated to dryness and the residue taken up in CH_3OH. Addition of $NaBPh_4$ yielded a purple precipitate, which was recrystallized from CH_2Cl_2/CH_3OH (yield 1.5 g, 41%).

$[Mo(N_2C_6H_4OCH_3)(NNHC_6H_4OCH_3)(C_8H_{18}N_2S_2)]BPh_4$. Concentrated HCl (0.5 mL) was added to $[Mo(N_2C_6H_4OCH_3)_2L]$ (0.5 g) suspended in 20 mL of CH_3OH. The solution was heated under reflux for 15 min and the solvent removed under vacuum. The residue was taken up in a minimum of CH_3OH, and $NaBPh_4$ was added to give a purple precipitate (yield 0.22 g, 28%).

$[MoO(C_6H_5CONNH)(C_8H_{20}N_2S_2)]$, $[MoO(PhCON_2H)L']$. A suspension of $[MoO_2L']$ (1.0 g, 0.003 mol) and $PhCON_2H_3$ (0.4 g, 0.003 mol) in 60 mL of CH_3OH was refluxed for 1.5 h. The brilliant red precipitate was collected, air-dried, and recrystallized from CH_2Cl_2/CH_3OH (yield 0.6 g, 43%). The $[MoO(ClC_6H_4CON_2H)L']$ and $[MoO(CH_3OC_6H_4CON_2H)L']$ derivatives were prepared by analogous procedures.

$(Bu_4N)_2[Mo_2S_4(C_9H_{20}N_2S_2)]$, $(R_4N)_2[Mo_2S_4L'_2]$. $(NH_4)_2[Mo_2(S-S)_6]\cdot2H_2O$ was prepared by the procedures reported by Muller and co-workers[23] and used without further purification. $(NH_4)_2[Mo_2(S-S)_6]\cdot2H_2O$ (2 g, 0.004 mol) was heated with $C_9H_{22}N_2S_2$ (17.8 g,
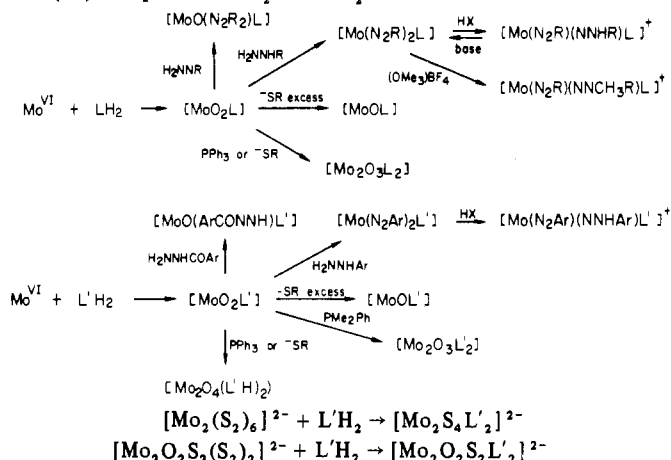
0.08 mol) in 30 mL of CH_3CN containing $(C_2H_5)_4NBr$ for 2 h. Upon addition of isopropyl alcohol, a red precipitate formed, which was subsequently recrystallized from CH_2Cl_2/CH_3OH (yield 1.9 g, 39%).

$(Et_4N)_2[Mo_2S_2O_2(C_9H_{20}N_2S_2)_2]$. $[(C_2H_5)_4N]_2[Mo_2O_2S_2(S_2)_2]$ was prepared as described in the literature.[24] To a solution of the above complex (2.4 g, 0.0035 mol) in CH_3CN was added $C_9H_{22}N_2S_2$ (1.6 g, 0.007 mol) with stirring and gentle heating, followed by the addition of triethylamine (1.4 g, 0.14 mol). Addition of isopropyl alcohol resulted in precipitation of orange crystals (yield 2.4 g, 81%).

$[MoO(C_8H_{18}N_2S_2)](BPh_4)$, $[MoOL]BPh_4$. $[(C_6H_4CH_2)(C_6H_5)_3-P][MoO(SC_6H_5)_4]^{50}$ was prepared from the reaction of $[(n-C_4H_9)_4N]_4Mo_8O_{26}$ with HSC_6H_5 in methanol in the presence of $(C_6H_4CH_2)(C_6H_5)_3PBr$.[22] To a solution of $[(C_6H_4CH_2)-(C_6H_5)_3P][MoO(SPh)_4]$ (1 g, 0.001 mol) in 25 mL of acetonitrile was added $C_8H_{20}N_2S_2$ (0.23 mL) in 10 mL of dry, degassed acetonitrile. The solution was refluxed for 1 h, when a deep green color was obtained. Addition of excess $NaBPh_4$ in methanol yielded a green-brown precipitate. The analogous complex of L', $[MoOL']BPh_4$, was synthesized in a similar fashion (yield 20%).
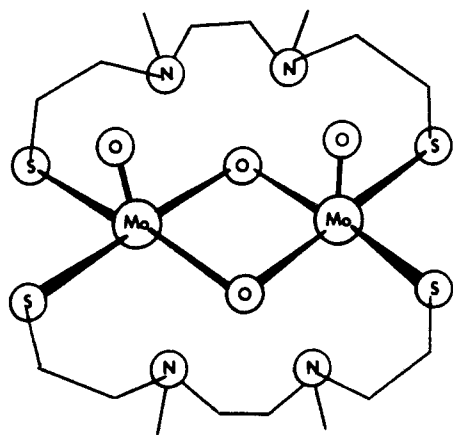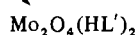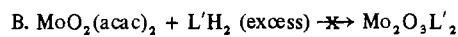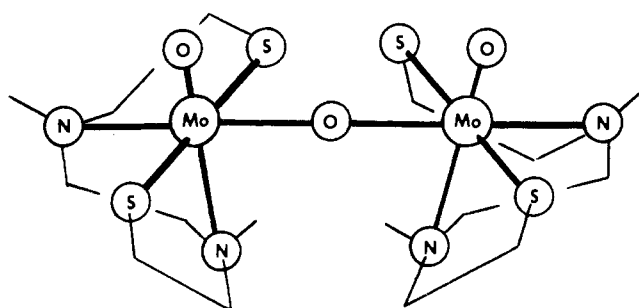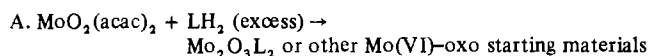
Results and Discussion

Syntheses. The ligands LH_2 and $L'H_2$ have been found to yield a full range of complexes of Mo(IV), Mo(V), and Mo(VI) as summarized in Scheme I.

The molybdenum(VI) complexes $[MoO_2L]$ and $[MoO_2L']$ were synthesized by either of two possible routes: (1) reaction of $MoO_2(acac)_2$ with the appropriate ligand or (2) reaction of $(n-Bu_4N)_4Mo_8O_{26}$ with a stoichiometric amount of the ligand. The nature of the heptamolybdate starting material in methanol is not yet certain, and full details of the preparation and structure of the yellow crystalline material that forms in methanol will be given in a forthcoming publication.[22] The alkylammonium heptamolybdate has proved a useful

Scheme I. Reaction Chemistry of the Mo(IV), Mo(V), and Mo(VI) Complexes of LH_2 and $L'H_2$

$$[Mo_2(S_2)_6]^{2-} + L'H_2 \rightarrow [Mo_2S_4L'_2]^{2-}$$
$$[Mo_2O_2S_2(S_2)_2]^{2-} + L'H_2 \rightarrow [Mo_2O_2S_2L'_2]^{2-}$$

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(37) Dahlstrom, P.; Dilworth, J. R.; Schulman, P.; Vella, P.; Zubieta, J. *Inorg. Chem.*, third following paper in this issue.
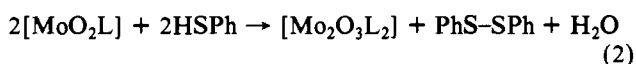
Scheme II. Preparation of Oxo-Bridged Bridged Dimers and Schematic Representations of the Structure

A. $MoO_2(acac)_2$ + LH_2 (excess) →

   $Mo_2O_3L_2$ or other Mo(VI)–oxo starting materials

B. $MoO_2(acac)_2$ + $L'H_2$ (excess) —×→ $Mo_2O_3L'_2$

   $Mo_2O_4(HL')_2$

starting material in a variety of reactions because of its ready solubility in organic solvents and its ease of preparation and purification.

[MoO₂L] and [MoO₂L'] are obtained as light yellow microcrystalline solids, which require no special precautions in handling. Solid samples show no signs of decomposition after storage for 2 years in air at room temperature. [MoO₂L] is quite soluble in dichloromethane, chloroform, THF, and dimethylformamide; it is sparingly soluble in benzene and toluene and insoluble in all other common organic solvents. Solutions of [MoO₂L] stored in the cold (4 °C) are indefinitely stable as judged by electronic spectroscopy. [MoO₂L'] is much less soluble in all solvents under any conditions.

[MoO₂L] provides a convenient starting point for the snythesis of [Mo₂O₃L₂] exploiting either (1) the ability of tertiary phosphines to abstract oxo groups and thereby reduce Mo(VI) to Mo(V) or (2) the reducing ability of thiols. Thus, stoichiometric reactions with these reagents yield [Mo₂O₃L₂] in moderate yields:

$$2[MoO_2L] + PPh_3 \rightarrow [MoO_3L_2] + OPPh_3 \quad (1)$$

$$2[MoO_2L] + 2HSPh \rightarrow [Mo_2O_3L_2] + PhS-SPh + H_2O \quad (2)$$

The dimeric complex [Mo₂O₃L₂] may also be prepared in good yield and most conveniently by direct reaction of a Mo(VI) starting material and excess thiolate ligand, LH₂, which acts both as the reductant and as a ligand in the reaction.

Attempts to prepare [Mo₂O₃L'₂] by similar procedures rather surprisingly produced [Mo₂O₄(L'H)₂]¹, a Mo(V) species displaying the Mo₂O₄²⁺ core (see Scheme II). This suggests that in protic solvents coordinated L' may protonate to produce a bidentate ligand coordinating through thiol groups only. The

structural study of [Mo₂O₄(L'H)₂] confirms this, and the recently determined structure of [Fe(L'H)(NO)₂][38] provides an additional example of this unusual behavior.

The complex with the Mo₂O₃²⁺ core was successfully synthesized by the reaction of [MoO₂L'] with PMe₂Ph in rigorously dried THF. [Mo₂O₃L'₂] is soluble in dichloromethane, chloroform, and acetonitrile and insoluble in other common organic solvents. The purple color of the solutions of this complex is rapidly discharged on exposure to air or addition of CH₃OH to give light yellow solutions from which [Mo₂O₄(L'H)₂] slowly precipitates.

The Mo(IV) complexes [MoOL₂] and [MoOL'₂] were prepared by exploiting the reducing power of thiol groups. Addition of an excess of PhSH to a cold solution of the parent Mo(VI) species, [MoO₂L] or [MoO₂L'], in rigorously dried THF produced low yields of the chinese red Mo(IV) species. Both [MoOL] and [MoOL'] are soluble in methylene chloride and THF; solutions of these complexes rapidly discharge their characteristic red color to produce unidentified insoluble yellow residues. Solid microcrystalline samples are stable for several hours in air.

The unusual electrochemical behavior of [MoO₂L] and [MoO₂L'] (vide infra) prompted an investigation of the Mo(V) chemistry of these ligands. A recent publication by Spence et al.[51] suggested a convenient route to Mo(V) monomeric species through the exploitation of the lability of the ⁻SPh ligands of [MoO(SPh)₄]⁻.[50] It was, thus, observed that LH₂ and L'H₂ react with [MoO(SPh)₄]⁻ to yield complexes isolated as the tetraphenylboron salts. The green solids analyzed for [MoOL]BPh₄ and [MoOL']BPh₄, respectively. These solids were paramagnetic, and dimethylformamide solutions displayed conductivities in the range of 70 Λ⁻¹ M⁻¹ cm², confirming the formulation of these complexes as Mo(V) monomers.

The continuing interest in molybdenum sulfide entities[39,40] and our own desire to exploit the chemistry of LH₂ and L'H₂ with the full range of Mo(V) structural types encouraged the syntheses of complexes in the thiomolybdate series $MoO_xS_{4-x}^{2-}$ ($x = 0-3$). As reported previously by Stiefel and co-workers,[4] $(NH_4)_2[Mo_2(S-S)_6] \cdot 2H_2O$[23] provides a remarkably useful starting material for the preparation of complexes containing the Mo₂S₄²⁺ core. Direct reaction of this material with excess L'H₂ in acetonitrile in the prsence of an appropriate alkylammonium salt, R₄NBr, yields the complex [R₄N]₂[Mo₂S₄L'₂] in good yield. Analytical and spectroscopic properties (Table I) are consistent with this formulation. In this preparation, the excess thiolate ligand once again functions as both reductant and ligand, according to eq 3. The complex [R₄N]₂[Mo₂S₄L'₂] is deep red and soluble in dichloromethane and dimethylformamide.

$$[(S_2)_2Mo(S_2)_2Mo(S_2)]^{2-} + 8L'^{2-} \rightarrow$$
$$[Mo_2S_4(L')_2]^{2-} + 3(L')_2 + 8S^{2-} \quad (3)$$
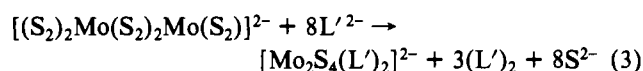
Recently, Muller and co-workers[24] have reported another in the series of binuclear molybdenum complexes containing disulfide S₂²⁻ ligands, namely, [R₄N]₂[MoO₂S₂(S₂)₂]. This species provides a convenient starting point for the preparation of complexes containing the MoO₂S₂²⁺ core. Reaction of [R₄N]₂[MoO₂S₂(S₂)] with 2 equiv of L'H₂ in the presence of base (triethylamine) gives high yields of the red-orange crystalline complex [R₄N][MoO₂S₂L'₂]. The failure of LH₂ to produce analogous species suggests that L'²⁻ functions as a bridging bidentate in these complexes, as observed in

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[Mo₂O₄(L'H)₂], a coordination mode apparently unavailable to the more sterically hindered L^{2-} group.

In order to investigate the contrasting reactivities of the complexes of L and L', we studied the reactions of [MoO₂L] and [MoO₂L'] with substituted hydrazines extensively. The monohydrazido(2-) complexes [MoO(N₂R₂)L] are readily prepared by the usual condensation type reaction[32] of the appropriate disubstituted hydrazine, H₂NNR₂ (ca. 1 equiv), with [MoO₂L] in dry methanol. The compounds discussed here are those for which R = alkyl and/or aryl. Attempts to prepare analogous complexes with benzoyl- or (thio-benzoyl)hydrazides, RC(O)NHNH₂, were unsuccessful. Likewise, the bis[hydrazido(2-)] analogues [Mo(N₂R₂)₂L] could not be synthesized, although complexes of the type [Mo(N₂R₂)₂(LL)₂] are well-known when the coligand LL is dithiocarbamate.[41]

In contrast, [MoO₂L'] does not react under these conditions with disubstituted hydrazines, H₂NNR₂, with R = alkyl or aryl groups. It does, however, react readily with benzoyl-hydrazines in methanol to yield monodiazene complexes [MoO(RCONNH)L'] in which the diazene ligand apparently coordinates both through the nitrogen and through the carbonyl oxygen to produce a seven-coordinate complex.

Both [MoO₂L] and [MoO₂L'] react readily with 2 equiv of monosubstituted hydrazines H₂NNHR, R = aryl, in methanol to give bis(organodiazenido) complexes of the type [Mo(N₂R)₂L] or [Mo(N₂R)₂L']. These are monomeric, diamagnetic, air-stable crystalline solids (Table I). When the hydrazine is carbazate, C₆H₅OCONHNH₂, a complex formulated as [Mo(N₂H₂CO₂R)(N₂CO₂R)L] is isolated. This microcrystalline material is stable in the solid state and in solution in the absence of air. Upon exposure of the solution to air, the complex converts quantitatively to [Mo(N₂CO₂R)L]. The mixed hydrazido—diazenido complex is most likely seven-coordinate, exhibiting the η^2-hydrazido(1-) coordination mode common to these species.[42,43]

The diazenido ligand, when acting as a three-electron donor, should be susceptible to electrophilic attack at the nitrogen remote from the metal. It has been observed recently that the complexes [Mo(N₂R)(dtc)₃] react readily with acids, HX, to yield hydrazido(2-) complexes [Mo(N₂HR)(dtc)₃]X or [Mo(N₂HR)(dtc)₃X], depending on X.[44] However, attack is not invariably observed, as suggested by the lack of reactivity toward protons of [ReCl₂(N₂Ph)₃].[45] The complex [Mo(N₂R)L] does react with HCl in the presence of NaBPh₄ to yield the 1:1 electrolyte [Mo(N₂R)(NNHR)L]BPh₄. The proton can be removed by bases, a behavior closely paralleling the reversible protonation of [Mo(N₂H)(Ph₂PH₂PPh₂)₂X].[46] The complex [Mo(N₂R)₂L] also reacts with [OMe₃][BF₄] in an analogous fashion to yield the disubstituted hydrazido(2-) complex [Mo(N₂R)(NNRR')L]⁺.

Spectroscopic Properties. Infrared Spectra. The infrared spectra of the complexes with the MoO₂²⁺, MoO²⁺, Mo₂O₃⁴⁺, and Mo₂O₄²⁺ cores are unexceptional and similar to those observed for dithiocarbamate complexes of molybdenum—oxo species.[25-27] The Mo(VI) species [MoO₂L] and [MoO₂L'] exhibited the characteristic bands at ~890 and ~920 cm⁻¹ associated with ν(Mo=O).

Table II

complex	ν, cm⁻¹	ϵ	complex	ν, cm⁻¹	ϵ
MoOL	19 400	350	Mo₂O₃L₂	19 600	600
	25 900	845		26 400	1832
MoO₂L	26 600	1480			

[a] In CHCl₃ Solution.

The strong band at ~940 cm⁻¹, observed in both [Mo₂O₃L₂] and [Mo₂O₃L₂'], is unique to the spectra of purple compounds displaying the Mo₂O₃⁴⁺ core and is assigned to the molybdenum—terminal oxygen vibration ν(Mo=O). The weak absorptions at ~740 and ~440 cm⁻¹ are attributed to the antisymmetric and symmetric vibrations of the Mo–O–Mo bridge.[26] These assignments agree with those proposed for Mo₂O₃(S₂CNEt₂)₄.

In the [Mo₂O₄(L'H)₂] complex, ν(Mo=O) is shifted to higher frequency, 952 cm⁻¹, a trend similar to that observed for the dithiocarbamate series and the thioxanthate series,[20,28-30] although in this case the band is not split into two absorptions. The Mo–O₂–Mo bridge vibrations may be the medium bands observed at 740 cm⁻¹ and 495 cm⁻¹, an assignment consistent with those made for other complexes possessing the Mo₂O₄²⁺ core.

The Mo(IV) species [MoOL] and [MoOL'] exhibit a single strong sharp band at ~950 cm⁻¹ assigned to ν(M=O).

The sulfido-bridged dimers with the Mo₂O₂S₂²⁺ core show a strong band at ~920 cm⁻¹ associated with ν(Mo=O). This band disappears in the analogous species with the MoS₄²⁺ core, [R₄N]₂[MoS₄L'₂], but a strong band associated with ν(Mo=S) is observed at 515 cm⁻¹. This assignment is consistent with the assignment of ν(Mo=S) in similar complexes such as (R₄N)₂[Mo₂S₄(SC₆H₅)₄]⁴ and (R₄N)₂[Mo₂S₄(SCH₂CH₂S)₂].³

The monohydrazido-substituted complexes [MoO(N₂R₂)L] are characterized by a strong band attributed to ν(Mo=O) but shifted to lower frequencies, ~890 cm⁻¹, than those observed for parent Mo(VI)—oxo complexes. This trend appears to be characteristic for the monohdyrazido derivatives with the MoO(N₂R₂)²⁺ core.[32,33] The spectra of these species are also characterized by strong bands in the ~1590-cm⁻¹ region attributed to ν(N=N).

The benzoylhydrazido complexes [MoO(ArCONNH)L'] derived exclusively from the reaction of [MoO₂L'] and the appropriate hydrazine display similar behavior in the low frequency of the ν(Mo=O) band (~890 cm⁻¹). The complexes also exhibit a band at ~1550 cm⁻¹ attributed to ν(N=N) and a band at ~1600 cm⁻¹, which most likely arises from the coordinated carbonyl group ν(C=O). The infrared evidence suggests that the benzoylhydrazide coordinates through the carbonyl oxygen and the nitrogen to form a five-membered ring with the seven-coordinate molybdenum.

Visible Spectra. Visible spectral data for the oxo derivatives of LH₂ is given in Table II. The oxo species are characterized by a band at ~26 500 cm⁻¹, which has been associated with a molybdenum—oxygen transition.[26] The value of the molar absorptivity of this transition appears to be a direct function of the number of oxo ligands per molybdenum, an observation previously reported for a similar series of dithiocarbamate complexes.

The spectra of the [Mo₂O₃L₂] complex also displayed an intense band at 19 600 cm⁻¹, which has been attributed to a transition involving the Mo–O–Mo bridge. This interpretation has been previously proposed to explain the origin of similar bands in the electronic spectra of analogous xanthate[34] and dithiocarbamate dimers.[26] In contrast to the non Beer's law behavior of the 19 600-cm⁻¹ band in the dithiocarbamate dimers, we found that the analogous band in [Mo₂O₃L₂] does

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Table III. Summary of Electrochemical Data for Molybdenum Complexes[a] of LH_2 and $L'H_2$

complex	solvent	E, V	$\|E_p^{ox} - E_p^{red}\|$, mV	i_p^{ox}/i_p^{red}	$i_p/\nu^{1/2}C$, A^{-3} $V^{-1/2}$ $s^{1/2}$ M^{-1}	n_{app}
[MoO$_2$L]	THF	−1.28	100	1.0	2.4	1 (1.25)
	CH$_2$Cl$_2$	−1.34	70	1.0	2.0	1 (1)
[MoO$_2$L']	THF	−1.18	b		1.4	1 (0.7)
	CH$_2$Cl$_2$	−1.09	b		1.5	1 (0.8)
[Mo$_2$O$_3$L$_2$]	THF	+0.18	84	0.4	2.9	1 (1.5)
		−1.65	75	1.0	2.9	1 (1.5)
	CH$_2$Cl$_2$	+0.15	77	1.3	3.0	1 (1.5)
		−1.69	69	1.0	2.9	1 (1.5)
[Mo$_2$O$_4$(L'H)$_2$]	DMF	−0.72	b		2.3	1 (1.2)
[n-Bu$_4$N] [Mo$_2$S$_4$L$_2$]	CH$_2$Cl$_2$	−1.75	78	1.0	2.1	1 (1.0)
[Me$_4$N] [Mo$_2$O$_2$S$_2$L$_2$]	CH$_2$Cl$_2$	−1.90	b		1.3	1 (0.7)

[a] Redox-potential–current data determined by cyclic voltammetry in 0.1 M [n-Bu$_4$N] [PF$_6$]/CH$_2$Cl$_2$ or 0.2 M [n-Bu$_4$N] [BF$_4$]/THF at a platinum electrode, scan rate 200 mV s^{-1}. The values of the apparent number of electrons involved in the irreversible or quasi-reversible electron-transfer steps, n_{app}, were determined by comparison of their current functions at 200 mV s^{-1} with that for ferrocene oxidation at the same electrode, for which $i_p\nu^{-1/2}$[Fc]$^{-1}$ = 1.9 A^{-3} V$^{-1/2}$ s$^{1/2}$ M. [b] No wave observed on anodic sweep.

not deviate from Beer's law, suggesting that the dimer does not dissociate into Mo(VI) and Mo(IV) monomeric units under these conditions.

Proton Magnetic Resonance Spectra. The ^{1}H NMR spectra of the various complexes of LH$_2$ and L'H$_2$ are in general unexceptional (Table I). However, the methyl groups of the L ligand appear as a broadened singlet or as two singlets in all complexes containing L that were studied by NMR. The L methyls are thus rendered chemically inequivalent, suggesting that bridging the amine nitrogens by only two methylene groups, and thus forming three constrained five-membered chelate rings with the metal, may induce structural distortions sufficiently severe to prevent averaging of the methyl environments in solution. X-ray crystallographic studies of the structures of [Mo$_3$O$_3$L$_2$][36] and {MoO(N$_2$R$_2$)L}[37] confirm the chemical and structural inequivalence of the amine methyl groups. In contrast structural studies of {MoO$_2$L'}[35] and [Mo$_2$O$_4$(L'H)$_2$] clearly demonstrate the equivalence of the amine methyl groups in these complexes, thus confirming model studies suggesting that the three-methylene-group bridge between the amine nitrogens in L' allows an unconstrained ligand conformation about the metal such that the amine methyl groups are structurally identical. The structural results are discussed in detail in accompanying papers.[35-37]

Electrochemical Studies. The relevant electrochemical data for the molybdenum complexes of L and L' are summarized in Table III. Figure 1 illustrates representative voltammograms for the Mo(V)– and Mo(VI)–oxo species.

An unusual feature of the electrochemistry of this system is the quasi-reversibility of the redox processes for [MoO$_2$L] and [Mo$_2$O$_3$L$_2$], whereas the analogous complexes with delocalized ligand systems such as dithioacid groups[47] yield irreversible voltammetric patterns or complex behavior as a result of disproportionation reactions.

The cyclic voltammetry of [MoO$_2$L] at platinum or vitreous carbon electrodes in 0.2 M [n-Bu$_4$N] [BF$_4$]/tetrahydrofuran or 0.1 M [n-Bu$_4$N] [PF$_6$]/CH$_2$Cl$_2$ shows a single one-electron reduction process at moderately negative potentials. The process is electrochemically quasi-reversible at scan rates of 200 mV s^{-1} as judged by the ratio of peak heights for the cathodic and anodic processes and the peak to peak separation of 59 mV. Although the peak height ratio i_p^{ox}/i_p^{red} approaches 1.0 for higher scan rates, the peak to peak separation ΔE_p increases with increasing sweep rate, consistent with a quasi-reversible process characterized by slow electron transfer. The one-electron reduction product is somewhat unstable as
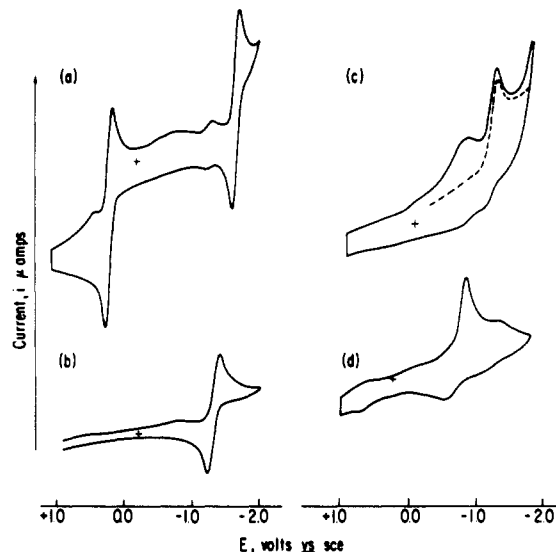
(47) DeHayes, L. J.; Faulkner, H. C.; Doub, W. H., Jr.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 2110.

Figure 1. Cyclic voltammograms recorded at 200 mV s^{-1} scan speed at a Pt wire electrode vs. a Ag(s)–electrolyte pseudo reference electrode. The solutions are 0.1 M in [n-Bu$_4$N][PF$_6$]/CH$_2$Cl$_2$ and 0.001 M in (a) Mo$_2$O$_3$L$_2$, (b) MoO$_2$L, (c) MoO$_2$L', and (d) Mo$_2$O$_4$(L'H)$_2$.
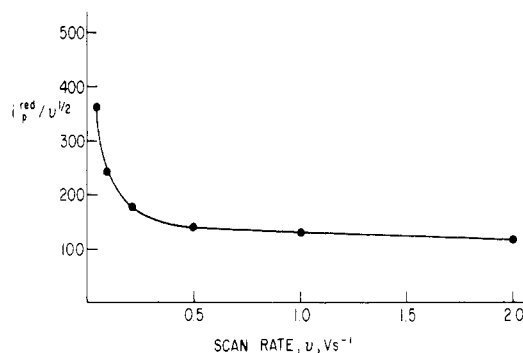

Figure 2. Peak current function $i_p^{red}/\nu^{1/2}$ vs. scan rate, ν, from cyclic voltammograms of MoO$_2$L, 3.0 mM, in 0.2 M [n-Bu$_4$N](BF$_4$)/THF at a Pt wire electrode.

suggested by the deviation of the peak current ratio from unity at slower scan rates while concomitantly the peak current function $i_p^{red}\nu^{1/2}$ approaches that for an overall two-electron reduction (Figure 2).

Since the one-electron product was not indefinitely stable in the electrolyte media at ambient temperatures, the half-life being in the order of several seconds, a stable solution of the one-electron reduction product was prepared by controlled-
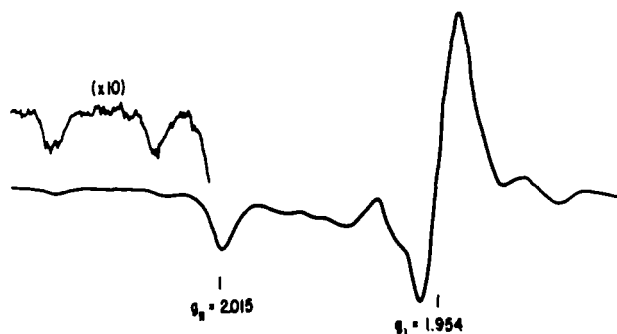
Figure 3. Frozen-solution spectrum of $[MoO_2L]^-$ taken on a Varian E-4 spectrometer with the following parameters: scan range 400 G, field setting 3340 G, time constant 1 s, scan time 2 min, modulation amplitude 5 G, modulation frequency 100 kHz, power 10 mW, microwave frequency 9.223 GHz.
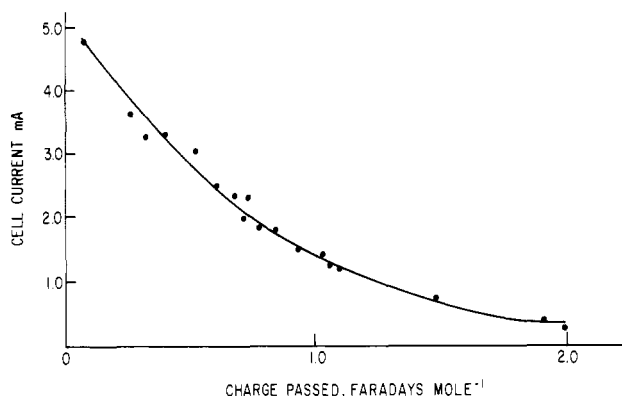

CHARGE PASSED, FARADAYS MOLE⁻¹

Figure 4. Charge passed vs. cell current plot for the electrolysis of MoO_2L in 0.2 M $[n\text{-}Bu_4N][PF_6]/THF$ at a Pt gauge electrode. The electrolysis was at −1.40 V vs. SCE on a 56.2-mg sample in 25 mL of catholyte under N_2 at room temperature.

potential electrolysis of $[MoO_2L]$ at 0 °C at −1.40 V in THF/0.2 M $[n\text{-}Bu_4N][BF_4]$ treated with neutral alumina. The current decayed after the passage of approximately 1 faraday mol⁻¹ to a background level while the solution changed in color from yellow to deep green. Examination of the catholyte CV after the 1 faraday mol⁻¹ reduction indicates the formation of $[MoO_2L]^-$. A sample of the frozen catholyte solution was examined by electron paramagnetic resonance at −145 °C and revealed a paramagnetic signal attributed to $[MoO_2L]^-$, characterized by $g_\perp = 1.954$ and $g_\parallel = 2.015$ (Figure 3). The spectrum suggests that the unpaired electron density is located on the Mo center; the observed molybdenum hyperfine lines, $A_\parallel = 56 \times 10^{-4}$ cm⁻¹, are consistent with an interaction with ^{97}Mo and ^{95}Mo, spin $^5/_2$. The spectrum of the reduced species suggests predominantly axial symmetry, consistent with the retention of the pseudooctahedral geometry of the precursor. This spectrum is qualitatively quite different from that reported for the Mo(V)–chloro–oxo analogue $[MoOClL]$.[16]

At room temperature, controlled-potential electrolysis of $[MoO_2L]$ at −1.4 V tends toward a two-electron overall reduction with nonlinear current vs. charge passed plots (Figure 4), consistent with the cyclic voltammetric behavior. During the course of the electrolysis, the characteristic yellow color of the solution of $[MoO_2L]$ was discharged, a green-brown color developed after approximately 1 faraday mol⁻¹ had been

Figure 5. Frozen-solution spectrum of $[MoOL]^+$, taken on a Varian E-4 spectrometer with the following parameters: scan range 400 G, field setting 3400 G, time constant 1 s, scan time 8 min, modulation amplitude 0.63 G, modulation frequency 100 kHz, power 5 mW, microwave frequency 9.472 GHz.

passed, and finally the solution developed a bright pink-red color, which persisted after complete electrolysis with the consumption of 2 faradays mol⁻¹ Examination of the catholyte by CV after the two-electron reduction indicated that a single major product characterized by an oxidation process at −0.4 V had been formed. The potential of this oxidation is identical with that observed for the oxidation of $[MoOL]$ in THF solution, indicating that the final product of the reduction of $[MoO_2L]$ is $[MoOL]$ produced according to the scheme

$$[MoO_2L] \xrightarrow[e^-]{-1.28\ V} [MoO_2L]^- \xrightarrow{+2H^+}$$

$$[MoOL]^+ + H_2O \xrightarrow{e^-} [MoOL] \quad (4)$$
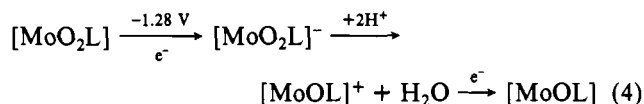
The pink-red solution of $[MoOL]$ oxidizes rapidly on exposure to air to give a deep violet solution characteristic of $[Mo_2O_3L_2]$. The rapid conversion to $[MoOL]$ is accomplished by the presence of residual water in the electrolyzing solvent. In cold solution with neutral alumina suspended in the solvent, the one-electron process is favored, while upon addition of 0.1 mL of H_2O the electrolysis appears to proceed directly to the two-electron product with no intermediate green species observable.

This behavior is consistent with the previously observed instability of Mo(V) monomers with respect to both the Mo(IV) and the Mo(VI) oxidation states.[51]

Controlled-potential electrolysis of $[MoO_2L]$ at 0 °C in THF/0.2 M $[n\text{-}Bu_4N][BF_4]$ in the absence of neutral alumina produced a stable bright green solution after the passage of 1 faraday mol⁻¹. However the EPR of the frozen solution is not identical with that observed for $[MoO_2L]^-$ but shows a three-line spectrum with $g_x = 1.960$, $g_y = 1.970$, $g_z = 2.014$, and $A_z = 58 \times 10^{-4}$ cm⁻¹ (Figure 5). This spectrum is identical with that observed for $[MoOL]BPh_4$ under similar conditions and confirms that, in the presence of trace amounts of H_2O, $[MoO_2L]^-$ rapidly protonates and expels H_2O to produce the five-coordinate species $[MoOL]^+$. The observed three-line spectrum is consistent with the loss of axial symmetry in the five coordinate complex.

In contrast, the electrochemical behavior of $[MoO_2L]$ in DMF solution exhibits none of this complexity. Controlled-potential electrolysis at −1.4 V proceeds smoothly to the two-electron reduction product with linear current vs. charge

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(49) (a) Hu, W. J.; Barton, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 1170. (b) Hu, W. J.; Lippard, S. J. *Ibid.* **1974**, *96*, 2366.

(50) Boyd, I. W.; Dance, I. G.; Murray, K. S.; Wedd, A. G. *Aust. J. Chem.* **1978**, *31*, 279.

(51) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538.

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plots. This indicates that the reduction proceeds according to

$$[MoO_2L] \xrightarrow[+2H^+]{+2e^-} [MoOL] + H_2O$$
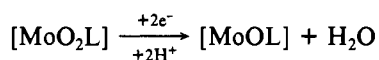
The dimeric species $[Mo_2O_3L_2]$ exhibits both a pseudo-reversible reduction and a pseudoreversible oxidation. The reduction at -1.65 V in THF is characterized by a peak-to-peak separation of 75 mV, which remains constant at all scan rates. The peak current ratio i_p^{ox}/i_p^{red}, however, does fall below 1 at slow scan rates with the appearance of [MoOL] and other processes in the voltammetric scan. The peak current function tends decidedly toward a two-electron process, and controlled-potential electrolysis confirms that 2 faradays mol^{-1} are consumed upon exhaustive electrolysis at -1.75 V. Upon electrolysis the purple color is discharged and a bright red color evolved. The cyclic voltammogram of the catholyte is complex but shows the presence of some [MoOL] at -0.1 V and the formation of traces of $[MoO_2L]$, presumably from dimer disproportionation during electrolysis. Evidently, the overall process may be described by

$$[Mo_2O_3L] \xrightarrow[-1.65 V]{2e^-} \text{``}[Mo_2O_3L_2]^{2-}\text{''} \xrightarrow{2H^+}$$
$$2[MoOL] + H_2O \quad (5)$$
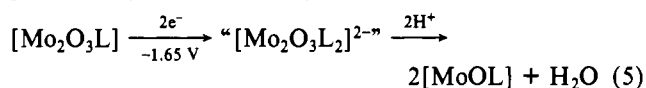
The instability of [MoOL] in solution with respect to oxidation or dimerization results in decomposition of the product and complexity in subsequent voltammograms.

The quasi-reversible oxidation observed in CV of $[Mo_2O_3L_2]$ at $+0.18$ V also tends toward a two-electron process. The process is not well-behaved, and electrolysis at $+0.28$ V results in decomposition and precipitation of intractable precipitates.

The redox behavior of $[MoO_2L']$ contrasts sharply with that observed for $[MoO_2L]$. Cyclic voltammograms of $[MoO_2L']$ exhibit a totally irreversible reduction at potentials 0.1–0.2 V more positive than that observed for $[MoO_2L]$, depending on the solvent/electrolyte system. This contrasting redox behavior may reflect both the relative thermodynamic instability of the six-membered $MoNCH_2CH_2CH_2N$ ring in $[MoO_2L']$ and the steric constraints imposed by the five-membered $MoNCH_2CH_2N$ ring in $[MoO_2L]$. Thus, the crystal structure of $[MoO_2L']^{35}$ displays a relatively unconstrained N–Mo–N angle of 81.1° but a significantly lengthened Mo–N distance of 2.486 (5) Å, suggesting that this weakened Mo–N interaction, together with the relative instability of the six-membered chelate ring, accounts for the preferential chemical reduction of $[MoO_2L']$ to $[MoO_2O_4-(L'H)_2]$ rather than $[Mo_2O_3L'_2]$ and for the total irreversibility of the cathodic process in the electrochemistry. On the other hand, $[MoO_2L]$ is unusual for *cis*-dioxo–Mo(VI) species in displaying well-behaved, quasi-reversible electrochemistry. As discussed in an accompanying paper of this series, $[MoO_2L]$ and $[MoO_2L']$, which also displays reversibility in its electrochemistry, are found to possess severely constrained five-membered $MoNCH_2CH_2N$ chelate rings as reflected in N–Mo–N angles of 74.8 (1) and 74.7 (1)°, respectively. These ring constraints may produce a geometry distorted to an intermediate between the pseudooctahedral limits favored for the Mo(VI) and Mo(V) partners in the redox couple, thus promoting the reversibility of the cathodic process by minimizing the reorganizational barriers. This conclusion is highly speculative but does receive support from the detailed structural studies.[35]

Subsequent cathodic sweeps on $[MoO_2L']$ result in the appearance of an electrode process at -0.7 V in $CH_2Cl_2/0.1$ M $[n\text{-}Bu_4N][PF_6]$. The potential for this process is coincident with that observed for the reduction of $[Mo_2O_4(L'H)_2]$ (Table III). This behavior is attributed to the presence of residual water in the solvent. Methylene chloride dried by conventional methods was found to contain 20–25 nM H_2O. Addition of neutral alumina directly into the electrochemical cell reduced the H_2O concentration to 1–5 mM and caused the disappearance of the -0.7-V peak in the voltammograms of $[MoO_2L']$. The electrochemical behavior of $[MoO_2L']$ in untreated CH_2Cl_2 is consistent with the scheme shown in eq 6.

$$[MoO_2L'] \xrightarrow[e^-]{-1.09 V} [MoO_2L']^-$$

$$2[MoO_2L']^- + 2H^+ \rightarrow [Mo_2O_4(L'H)_2]$$

$$[Mo_2O_4(L'H_2)] \xrightarrow[2e^-]{-0.7 V} [Mo_2O_4(L'H)_2]^{2-} \quad (6)$$
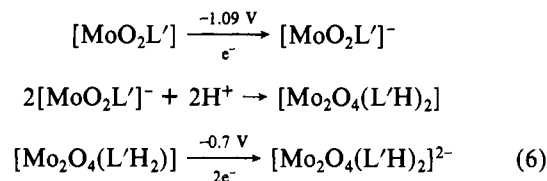
Conclusions. Although not as versatile as dithiocarbamate ligands in stabilizing a variety of Mo(IV)–, Mo(V)–, and Mo(VI)–oxo and –sulfido complexes, the ligands L^{2-} and L'^{2-} display a remarakable range of chemistry with molybdenum in the higher oxidation states. The reaction chemistry and the electrochemical properties of the molybdenum complexes of these ligands are quite different and reflect both the influence of ligand steric constraints on the geometries of these complexes, as discussed in the accompanying paper, and the relative thermodynamic instability of the six-membered chelate ring in $[MoO_2L']$. Models and previous structural studies[1,49] indicate that, while complexes of L^{2-} will have constrained N,N'- and N,S-chelate ring angles, the extra methylene group in the N,N'-chelate ring of complexes of L'^{2-} relieves these steric constraints. This, relative ring stabilities and steric constraints have a profound influence in the reactivity patterns of the complexes and account for the absence of parallel reaction trends for molybdenum complexes of L and L'. A detailed investigation of the structures of a range of complexes of molybdenum with L^{2-} and L'^{2-} is presented in the accompanying papers.