

Figure 7. van der Waals area occupied by pyridine molecules coordinated to the surface of a single VOPO_4 layer, demonstrating the possibility of ligand interpenetration.

bonding model that has pyridine coordinated to vanadium with the ligand plane perpendicular to the layers. While it is difficult to predict exactly the c axes of these coordination intercalates without knowledge of the metal-ligand bond distance and the structural details of the oxide layer itself, it can be assumed that these factors remain constant as the ligand size increases. Thus, from CPK molecular models, the difference in van der Waals length along the coordination axis between pyridine and 4-phenylpyridine can be easily measured and compared directly to the observed c -axis differences. The 4.6-Å expansion observed on going from $\text{VOPO}_4(\text{py})$ to $\text{VOPO}_4(4\text{-Phpy})$ corresponds closely to the differences in length of the ligands (4.4 Å). This indicates that, in the VOPO_4 compounds, pyridine molecules from adjacent layers interpenetrate, since the total expansion is that caused by a

single ligand. On the VOPO_4 layer surface, the coordination sites are 6.2 Å apart. This is only a little less than the van der Waals width of pyridine, 6.4 Å, allowing the ligands to line up along the a axis as shown in Figure 7 and stack in an interlocking fashion along the c axis.

The ligand-packing arrangement in $\text{VOPO}_4(\text{py})$ is different from that of the analogous MoO_3 compound,⁴ which has coordination sites 5.3 Å apart. On the MoO_3 surface the pyridine molecules are more densely packed so no interpenetration of ligands from adjacent layers is possible. As a result the c -axis difference in $\text{MoO}_3(\text{py})$ and $\text{MoO}_3(4\text{-Phpy})$ is 8.8 Å, twice the difference in length of the ligands.

In summary, vanadyl phosphate and arsenate react with pyridine and 4-substituted pyridines to form coordination intercalation compounds. The pyridine molecules replace either a coordinated water molecule in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ or a vanadyl oxygen from an adjacent layer in the anhydrous hosts. In the compounds the pyridine molecules are perpendicular to the oxide layers and little or no reduction of the V^{5+} centers occurs. Reactions with 4-substituted pyridines are much slower than with pyridine itself, and the products are less crystalline than those formed with pyridine. These coordination intercalation compounds are analogous to those previously reported for MoO_3 and WO_3 . We are currently extending this general type of reaction to other MOXO_4 host lattices.

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Registry No. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, 12293-87-7; $\text{VOPO}_4 \cdot \text{H}_2\text{O}$, 61156-00-1; $\alpha\text{-VOPO}_4$, 12395-27-2; $\text{VOAsO}_4 \cdot 2\text{H}_2\text{O}$, 12291-57-5; $\text{VOPO}_4(\text{py})$, 82648-60-0; $\text{VOPO}_4(4,4'\text{-bpy})$, 82648-61-1; $\text{VOPO}_4(4\text{-Phpy})$, 82648-62-2; $\text{VOAsO}_4(\text{py})$, 82648-63-3.

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Eight-Coordinate Complexes of Molybdenum with 1,1-Dithio Ligands. Synthesis, Electrochemistry, and Spectroscopic Properties

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Syntheses, characterization, and electrochemical and spectroscopic properties are reported for a series of eight-coordinate molybdenum(V) complexes with 1,1-disubstituted ethylenedithiolate ($\text{Mo}(\text{S}_2\text{C}_2\text{R}_2)_4^{3-}$; $\text{R} = \text{CN}, \text{COOEt}$), dithiocarbamate ($\text{Mo}(\text{S}_2\text{CNEt}_2)_4^+$), and thioxanthate ($\text{Mo}(\text{S}_2\text{CS}-t\text{-Bu})_4^+$) ligands. The compounds each exhibit a reversible $\text{Mo(V)} \rightarrow \text{Mo(VI)}$ oxidation and a reversible $\text{Mo(V)} \rightarrow \text{Mo(IV)}$ reduction with the exception of $\text{Mo}(\text{S}_2\text{CS}-t\text{-Bu})_4^+$, for which no oxidation is observed. The half-wave potentials of these reversible processes span a range of +1.2 to -1.7 V vs. SCE in CH_3CN and CH_2Cl_2 . Irreversible oxidation of some of the Mo(VI) species and irreversible reduction of some of the Mo(IV) species also are observed. Thin-layer spectroelectrochemistry is used to obtain visible spectra of the oxidized and reduced complexes, establish the Nernstian character of the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox couples, and investigate the catalytic behavior of the electrogenerated Mo(VI) species, $\text{Mo}(\text{S}_2\text{CNEt}_2)_4^{2+}$.

Introduction

The occurrence of Mo-S bonding in molybdenum-containing enzymes² has generated current interest in complexes of this metal with sulfur-containing ligands.³ 1,1-Dithio ligands⁴ form sulfur-rich complexes with most transition

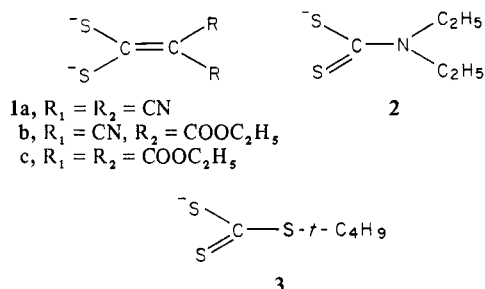
metals. Dithiocarbamates,⁵⁻⁷ thioxanthates,⁷ and dithiobenzoates⁷⁻⁹ form tetrakis complexes with the higher oxidation states of molybdenum and thereby provide an eight-sulfur (MoS_8) coordination environment for this element.

In this paper we report the preparation and characterization of a new series of eight-coordinate molybdenum complexes with the dinegative ethylenedithiolate (ed) ligands 1,1-di-

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cyano-2,2-ethylenedithiolate (*i*-mnt) (**1a**), 1-cyano-1-carb-



ethoxy-2,2-ethylenedithiolate (*ced*) (**1b**), and 1,1-dicarbethoxy-2,2-ethylenedithiolate (*ded*) (**1c**). The redox and spectroscopic properties of these complexes and of those previously reported with *N,N*-diethyldithiocarbamate (Et_2dtc)⁵⁻⁷ (**2**) and *tert*-butyl thioxanthate (*t*-Butxn)⁷ (**3**) ligands are examined by cyclic voltammetry, controlled-potential coulometry, thin-layer spectroelectrochemistry, and visible absorption and EPR spectroscopy. The results establish the range of electrochemical and spectroscopic behavior associated with the MoS_8 center and the extent to which these properties are influenced by the structure of the 1,1-dithio ligand.

Experimental Section

Synthetic Procedures. The dipotassium salts of the three ethylenedithiolate ligands, $\text{K}_2(\text{i-mnt})$, $\text{K}_2(\text{ced})$, and $\text{K}_2(\text{ded})$, were prepared by known procedures.¹⁰ Sodium *tert*-butyl thioxanthate, $\text{Na}(\text{t-Butxn})$, was prepared as described by Hyde and Zubietta.⁷ Pyridinium oxopentachloromolybdate(V), $(\text{pyH})_2\text{MoOCl}_5$, was prepared as described by Sasaki et al.¹¹ Other starting materials were obtained commercially and used without purification. All syntheses were carried out in a fume hood, and the products were stored under vacuum. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$(n\text{-Bu}_4\text{N})_3\text{Mo}(\text{i-mnt})_4$. A solution of $(\text{pyH})_2\text{MoOCl}_5$ (3.6 g, 8.0 mmol) in 50 mL of ethanol/water (1:1) was purged with nitrogen for 10 min to remove HCl. This solution was added to $\text{K}_2(\text{i-mnt})$ (7.0 g, 32.0 mmol) dissolved in 50 mL of ethanol/water (1:1). The resulting red-brown solution was refluxed for 90 min. The solution was allowed to cool to room temperature, and tetra-*n*-butylammonium bromide, $n\text{-Bu}_4\text{NBr}$ (5.2 g, 16 mmol), was added. After overnight refrigeration, a green waxy solid precipitated and was isolated by filtration. This material was washed with 1:1 ethanol/water (4×25 mL), 4:1 ethanol/water (12×25 mL), and ethanol (4×25 mL) until the washings were no longer colored. Yield: 65%.

$(n\text{-Bu}_4\text{N})_3\text{Mo}(\text{ced})_4$. A solution of $(\text{pyH})_2\text{MoOCl}_5$ (6.8 g, 15 mmol) in 100 mL of ethanol/acetonitrile (1:1) was added to a suspension of $\text{K}_2(\text{ced})$ (16.0 g, 60 mmol) in 100 mL of the same solvent. The mixture was refluxed for 90 min, allowed to cool to room temperature, and filtered. After addition of $(n\text{-Bu}_4\text{N})_4\text{Br}$ (14.5 g, 45 mmol) to the filtrate, the mixture was filtered again. The solvent was allowed to evaporate from the filtrate, leaving a brown tar. Cyclic voltammetry of this material in CH_3CN solvent revealed the presence of several components. Attempts to isolate the desired $\text{Mo}(\text{ced})_4^{3-}$ complex by recrystallization were unsuccessful. Purification was accomplished by column chromatography (5 cm \times 12 cm) on alumina (Fisher A-540, 80–200 mesh) with dichloromethane/acetone mixtures as eluents. A broad, amber band eluted first with 2:1 CH_2Cl_2 /acetone. The $\text{Mo}(\text{ced})_4^{3-}$ complex eluted as a dark brown band with 1:2 CH_2Cl_2 /acetone. The solvent was evaporated under a stream of dry nitrogen. Recrystallization of the product was not necessary. Yield: 8%.

$(n\text{-Pr}_4\text{N})_3\text{Mo}(\text{ded})_4$. This compound was prepared by the procedure given for $(n\text{-Bu}_4\text{N})_3\text{Mo}(\text{ced})_4$, except that the materials used were $(\text{pyH})_2\text{MoOCl}_5$ (9.0 g, 20 mmol), $\text{K}_2(\text{ded})$ (25.0 g, 80 mmol), and tetra-*n*-propylammonium bromide, $n\text{-Pr}_4\text{NBr}$ (16.0 g, 60 mmol). The dark brown product was purified by chromatography on alumina using CH_2Cl_2 /acetone mixtures as eluents and recrystallized from acetone. Yield: 3%.

$\text{Mo}(\text{Et}_2\text{dtc})_4\text{PF}_6$. Procedure A reported in ref 6a for the preparation of $\text{Mo}(\text{Et}_2\text{dtc})_4\text{Br}$ was followed until the point of product isolation. Potassium hexafluorophosphate (5.5 g, 30 mmol) was added to the solution (30 mmol of $\text{Mo}(\text{Et}_2\text{dtc})_4\text{Br}$ in 100 mL of diglyme), and the mixture was heated until all solids dissolved. The solution was cooled to room temperature, and the brown product in quantitative yield was collected by filtration and recrystallized three times from acetone.

$\text{Mo}(\text{t-Butxn})_4$. A solution of $(\text{pyH})_2\text{MoOCl}_5$ (4.5 g, 10 mmol) in 50 mL of water was deoxygenated with argon and added to a deoxygenated solution of $\text{Na}(\text{t-Butxn})$ (15.1 g, 80 mmol) in 20 mL of water at 2 °C. Concentrated hydrochloric acid was added dropwise until a dark solid precipitated. This material was collected by filtration under nitrogen and dried under vacuum. The complex was purified by chromatography on Florisil (Fisher F-101, 100–200 mesh) and recrystallized from carbon disulfide/pentane as described in ref 7. UV-visible spectra and cyclic voltammetric traces obtained for the blue product were in good agreement with published data.⁷ Yield: 35%.

$\text{Mo}(\text{t-Butxn})_4^+$. Solutions of this $\text{Mo}(\text{V})$ -thioxanthate complex were generated in two ways: (i) controlled-potential oxidation of $\text{Mo}(\text{t-Butxn})_4$ at +0.7 V vs. SCE in 0.1 M $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ and (ii) oxidation of $\text{Mo}(\text{t-Butxn})_4$ in CH_2Cl_2 by stoichiometric addition of a spectrophotometrically standardized¹² solution of Br_2 in CH_3CN . Cyclic voltammetric traces of the resulting red solutions confirmed complete oxidation to the $\text{Mo}(\text{V})$ state. We were unable to isolate a pure solid sample of the $\text{Mo}(\text{t-Butxn})_4^+$ complex as had been reported previously for $\text{Mo}(\text{i-Prtn})_4\text{PF}_6$.⁷

$(n\text{-Pr}_4\text{N})_2\text{S}_2\text{C}_2\text{R}_2$ ($\text{R} = \text{CN}, \text{COOC}_2\text{H}_5$). Tetra-*n*-propylammonium salts of the ethylenedithiolate ligands were prepared by adding the dipotassium salt of each ligand (10 mmol) to 20 mmol of $n\text{-Pr}_4\text{NBr}$ in 20 mL of water. The product was extracted into an equal volume of dichloromethane, which was evaporated to yield $(n\text{-Pr}_4\text{N})_2(\text{i-mnt})$ and $(n\text{-Pr}_4\text{N})_2(\text{ced})$ as yellow solids and $(n\text{-Pr}_4\text{N})_2(\text{ded})$ as a viscous yellow oil.

Instrumentation. Cyclic voltammetric experiments were conducted with a solid-state operational amplifier potentiostat constructed in this laboratory. Traces were recorded on a Hewlett-Packard Model 7035B X-Y recorder. Voltammetric experiments were conducted in a Brinkmann E615 cell using a Beckman 39273 Pt-button working electrode (area 0.20 cm²), a Pt-wire auxiliary electrode, and a commercial aqueous saturated calomel reference electrode (SCE). The reference electrode was isolated from the test solution by a salt bridge containing supporting electrolyte and solvent. All potentials are reported vs. the aqueous SCE.

Controlled-potential coulometric experiments were conducted by use of an EG&G Princeton Applied Research (PAR) Model 173/179 potentiostat and digital coulometer. Current was measured during coulometry by use of a Fluke 8010A digital multimeter connected to the current output terminal of the 179. The working electrode for coulometry was a 12-cm² piece of Pt foil. The reference electrode was described above. The auxiliary electrode was a Pt coil separated from the sample solution by a 4–8- μm glass frit. Cells, glassware, supporting electrolyte, and the Pt electrodes were dried overnight at 100 °C before each electrochemical experiment. All solutions were deoxygenated and blanketed with dry nitrogen or argon that had passed through a solvent washing tower. All electrochemical experiments were carried out at ambient temperature (22 ± 2 °C).

Thin-layer electrochemistry and spectroelectrochemistry were accomplished by use of an optically transparent, thin-layer electrode (OTTLE) cell, which has been described previously¹³ and is based on the design of Anderson et al.¹⁴ In the present experiments the OTTLE cell incorporated a gold-minigrid (1.0 \times 1.5 cm, 100 lines/in., Buckbee-Mears Co., St. Paul, MN) working electrode and a Pt-needle auxiliary electrode; a saturated calomel reference electrode was connected to the cell by a nonaqueous salt bridge. Deoxygenated sample solutions were transferred to the cell under pressure of inert gas through Teflon tubing.

In spectroelectrochemical experiments, visible absorption data at 350–700 nm were obtained as a function applied potential with the

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Table I. Analytical, Conductivity, and Infrared and EPR Spectroscopic Data

complex	% found (% calcd)				
	C	H	N	Mo	S
Mo(Et ₂ dtc) ₄ PF ₆	28.66 (28.80)	4.75 (4.83)		11.43 (11.50)	
(<i>n</i> -Bu ₄ N) ₃ Mo(<i>i</i> -mnt) ₄	55.35 (55.54)	7.97 (7.87)	10.98 (11.13)	6.83 (6.93)	18.43 (18.53)
(<i>n</i> -Bu ₄ N) ₃ Mo(ced) ₄	54.78 (55.00)	8.20 (8.21)	6.14 (6.24)	6.29 (6.10)	16.12 (16.31)
(<i>n</i> -Pr ₄ N) ₃ Mo(ded) ₄	51.46 (51.30)	7.95 (7.85)	2.68 (2.64)	5.83 (6.03)	15.98 (16.11)

complex	Λ_M^a , cm ² Ω ⁻¹ mol ⁻¹	freq, cm ⁻¹ ^c				g^d	10 ⁴ A- (^{95,97} Mo), cm ⁻¹ ^d
		Mo-S	X=CS ₂ (X = N, C)	C=O	C≡N		
Mo(Et ₂ dtc) ₄ PF ₆	140	359 m	1505 s (1472 s)			1.980	34.1
(<i>n</i> -Bu ₄ N) ₃ Mo(<i>i</i> -mnt) ₄	313	346 w	1385, 1405 s (1360 s)		2199 s (2174, 2199, 2225 s)	1.979	32.7
(<i>n</i> -Bu ₄ N) ₃ Mo(ced) ₄	291	341 w	1394 s (1363 s)	1660 s (1654 s)	2187 s (2177, 2194 s)	1.982	32.0
(<i>n</i> -Pr ₄ N) ₃ Mo(ded) ₄	363 ^b	338 w	1374, 1397 s (1365 s)	1654 m (1658 m)		1.983	32.2

^a At 10⁻³ M in CH₃CN. ^b 2.5 × 10⁻⁴ M. ^c Values in parentheses are for the *n*-Pr₄N⁺ salts of the ligands. ^d In CH₂Cl₂ at room temperature. For Mo(*i*-Butxn)₄⁺, $g = 1.981$ and $A = 30.4 \times 10^{-4}$ cm⁻¹ were observed upon oxidation of Mo(*i*-Butxn)₄ in CH₂Cl₂ with Br₂.

OTTLE cell located in the sample compartment of a Harrick RSS-C rapid-scan spectrophotometer and attached to the PAR 173 potentiostat. Spectral data were digitized and processed by a Nova 2 minicomputer and were plotted on the Hewlett-Packard recorder. Cell thickness and cell volume were calibrated with solutions of potassium ferricyanide in water.

Electronic spectra from 350 to 900 nm also were recorded on a Cary 14 or Perkin-Elmer 575 spectrophotometer. The latter instrument was used to obtain charge-transfer spectra of the Mo(VI)-ed complexes since the absorptions were outside the range of the RSS-C. Dichloromethane solutions of Mo(*i*-mnt)₄³⁻ and Mo(ced)₄³⁻, oxidized with Br₂, and of Mo(ded)₄³⁻, oxidized with I₂, were used for this purpose.

Room-temperature EPR spectra of dichloromethane solutions of the isolated Mo(V) complexes were recorded at 9.52 GHz by use of a Varian Model 4502 spectrometer. The EPR spectrum of Mo(*i*-Butxn)₄⁺ was acquired after oxidizing a solution of Mo(*i*-Butxn)₄ in CH₂Cl₂ with Br₂.

Infrared spectra of the Mo(V) complexes and the *n*-Pr₄N⁺ salts of the ligands were obtained on a Perkin-Elmer 621 spectrometer. Solid samples were run as KBr disks; (*n*-Pr₄N)₂(ded) was run as a neat liquid between AgCl plates.

Conductance measurements were made with a Yellow Springs Instruments Model 31 conductivity bridge with aqueous solutions of KCl as standards.

Reagents. Spectrophotometric grade acetonitrile and dichloromethane (Aldrich) were stored over activated molecular sieves and used as electrochemical and spectroscopic solvents. The supporting electrolytes were tetraethylammonium tetrafluoroborate ((TEA)BF₄) and tetra-*n*-butylammonium hexafluorophosphate ((TBA)PF₆) from Southwestern Analytical Chemicals.

Results and Discussion

Preparation and Characterization. Analytical, conductivity, and infrared and EPR spectroscopic data (Table I), electrochemical data (Table II), and visible absorption data (Table III) indicate that the ed complexes are isolated as trinegative ions containing the Mo(V) oxidation state. Preparation of these complexes demonstrates that the ethylenedithiolates parallel other 1,1-dithio ligands in their ability to form eight-coordinate complexes with early transition elements.^{4,15} Particularly notable is the capacity of these ligands to stabilize non-oxo molybdenum in its highest formal oxidation states. As suggested by the redox potentials in Table II, isolation of non-oxo Mo^{VI}S₈ species should be possible with ed ligands.

Previous syntheses of MoS₈ complexes have utilized oxidative decarbonylation of Mo(CO)₆ or Mo(CO)₅X⁻ (X = Cl⁻, Br⁻, I⁻) by the disulfide form of the ligand⁵⁻⁷ as well as ligand

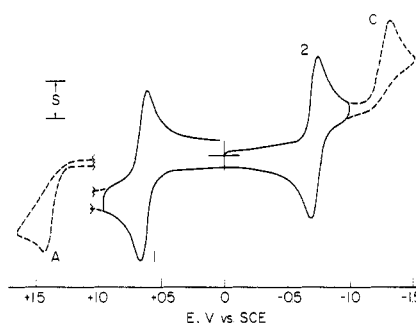


Figure 1. Cyclic voltammogram of 0.23 mM (*n*-Bu₄N)₃Mo(*i*-mnt)₄ in CH₃CN (0.1 M (TEA)BF₄); $v = 0.2$ V s⁻¹. $S = 50$ μA cm⁻² for waves 1, 2, and C; $S = 200$ μA cm⁻² for wave A.

displacement from oxo^{7,16} and non-oxo^{8,9} complexes of molybdenum. Not having the oxidized forms of the ligands in hand, we chose to prepare the ed complexes by ligand displacement from readily synthesized¹¹ (pyH)₂MoOCl₅. This approach is effective in the preparation of Mo(*i*-mnt)₄³⁻, where the oxo group is readily cleaved from Mo(V), even in the presence of H₂O, and the desired complex is isolated in good yield. Preparation of the ced and ded complexes by this route proved to be more difficult. Ligand displacement provided these complexes in low yield, and chromatographic separation from mixtures with unidentified side products was required. Improved synthetic procedures are being sought for the ced and ded complexes.

In the infrared spectrum (Table I) the frequency of the C=CS₂ vibration is seen to increase by 25–45 cm⁻¹ upon coordination of the ed dianion. This increment is similar to the shift of ca. 35 cm⁻¹ in ν (N=CS₂) upon coordination of Et₂dtc⁻ as Mo(Et₂dtc)₄⁺. Our values for ν (C=CS₂) are consistent with strong bands observed at ~1400 cm⁻¹ in Ni(*i*-mnt)₂²⁻, Cu(*i*-mnt)₂²⁻, and Fe(*i*-mnt)₃³⁻¹⁷ but differ significantly from a recent tabulation¹⁸ that assigns ν (C=CS₂) at ≥1450 cm⁻¹ for analogous ded complexes.

Cyclic Voltammetry and Controlled-Potential Coulometry. Electrochemical behavior of the MoS₈ complexes is represented by the cyclic voltammogram of Mo(*i*-mnt)₄³⁻ shown in Figure 1. Starting in the Mo(V) oxidation state, we observed one reversible oxidation (wave 1) and one reversible reduction (wave 2) for this compound. Waves 1 and 2 occur for all five

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Table II. Electrochemical Data^a

complex	wave A			wave 1		
	E_p , V ^b	$i_p/v^{1/2}AC^d$	n^e	$E_{1/2}$, V ^c	$i_p/v^{1/2}AC^d$	n^e
Acetonitrile (0.2 M (TEA)BF ₄)						
Mo(<i>t</i> -Butxn) ₄ ⁺				+1.153 (68)	950	0.95
Mo(Et ₂ dtc) ₄ ⁺				+0.654 (66)	828	1.02
Mo(<i>i</i> -mnt) ₄ ³⁻	+1.433 (73)	3162	4	+0.304 (64)	812	1.00
Mo(ced) ₄ ³⁻	+1.208 (78)	2788	4	-0.132 (62)	705	1.02
Mo(ded) ₄ ³⁻	+0.800 (45)	1665	2			
Dichloromethane (0.1 M (TBA)PF ₆)						
Mo(<i>t</i> -Butxn) ₄ ⁺				+1.129 (113)	885	1
Mo(Et ₂ dtc) ₄ ⁺				+0.519 (85)	870	1
Mo(<i>i</i> -mnt) ₄ ³⁻	+1.510 (71)	1768	2	+0.175 (113)	730	1
Mo(ced) ₄ ³⁻	+1.060 (74)	1571	2	-0.302 (101)	710	1
Mo(ded) ₄ ³⁻	+0.830 (56)	1650	2			
complex	wave 2			wave C		
	$E_{1/2}$, V ^c	$i_p/v^{1/2}AC^d$	n^e	E_p , V ^b	$i_p/v^{1/2}AC^d$	n^e
Acetonitrile (0.2 M (TEA)BF ₄)						
Mo(<i>t</i> -Butxn) ₄ ⁺	+0.494 (63)	<i>f</i>	<i>f</i>	-0.730 (82)	<i>f</i>	<i>f</i>
Mo(Et ₂ dtc) ₄ ⁺	-0.444 (66)	965	1	-1.141 (66)	969	1
Mo(<i>i</i> -mnt) ₄ ³⁻	-0.715 (64)	888	1	-1.295 (65)	767	1
Mo(ced) ₄ ³⁻	-1.024 (63)	800	1			
Mo(ded) ₄ ³⁻	-1.472 (67)	773	1			
Dichloromethane (0.1 M (TBA)PF ₆)						
Mo(<i>t</i> -Butxn) ₄ ⁺	+0.369 (78)	985	0.99	-0.953 (87)	1673	2
Mo(Et ₂ dtc) ₄ ⁺	-0.550 (105)	915	1	-1.283 (122)	811	1
Mo(<i>i</i> -mnt) ₄ ³⁻	-0.843 (84)	740	1	-1.723 (123)	566	1
Mo(ced) ₄ ³⁻	-1.178 (144)	850	1			
Mo(ded) ₄ ³⁻	-1.672 (139)	1060 ^f	1			

^a 0.2–1 mM complexes; data for waves 1 and 2 averaged over $v = 0.01$ – 0.2 V s⁻¹; data for waves A and C at $v = 0.1$ V s⁻¹. ^b Irreversible peak potential; number in parentheses is $|E_p - E_p|$ in mV. ^c Reversible half-wave potential = $(E_{pa} + E_{pc})/2$; number in parentheses is ΔE_p in mV. ^d Units of A s^{1/2} cm V^{-1/2} mol⁻¹. ^e Number of electrons determined by controlled-potential coulometry or comparison of voltammetric peak current parameters (see text). ^f Concentration of complex unknown due to low solubility. ^g $i_p/v^{1/2}AC$ increases and i_{pr}/i_{pf} decreases as v decreases.

Table III. Electronic Spectral Data^a

complex	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
Mo(<i>t</i> -Butxn) ₄ ⁺ ^b	424 sh (8800), 480 (6610), 524 (6200), 561 (6030), 604 sh (4800)
Mo(<i>t</i> -Butxn) ₄ ^b	472 sh (3040), 513 (3900), 633 (5250)
Mo(Et ₂ dtc) ₄ ²⁺	459 (2020), 670 (11 200)
Mo(Et ₂ dtc) ₄ ⁺	397 (5360), 450 (5510), 460 (5580), 492 sh (2820), 525 (1890)
Mo(Et ₂ dtc) ₄	400 sh (2100), 448 sh (2000), 480 (2440), 515 (2290), 567 (1770)
Mo(<i>i</i> -mnt) ₄ ²⁻	475 sh (4300), 860 (9830) ^c
Mo(<i>i</i> -mnt) ₄ ³⁻	408 sh (12 800), 464 (14 800), 572 (9450), 628 sh (3040), 672 (3320)
Mo(<i>i</i> -mnt) ₄ ⁴⁻	418 sh (11 400), 452 (12 400), 528 (5250), 638 (2620)
Mo(ced) ₄ ²⁻	450 sh (6650), 823 (13 700) ^c
Mo(ced) ₄ ³⁻	412 sh (16 400), 467 (15 200), 554 (9900), 634 (3920)
Mo(ced) ₄ ⁴⁻	558 (6450), 656 (7380)
Mo(ded) ₄ ²⁻	455 sh (6300), 792 (10 700) ^d
Mo(ded) ₄ ³⁻	463 (15 500), 545 (8340), 638 (3490)
Mo(ded) ₄ ⁴⁻	580 (4500), >680 sh (4800)

^a In CH₃CN (0.2 M (TEA)BF₄). ^b In CH₂Cl₂ (0.2 M (TBA)PF₆).

^c Recorded in CH₂Cl₂ after oxidation of Mo(V) complex with Br₂.

^d Recorded in CH₂Cl₂ after oxidation of Mo(V) complex with I₂.

complexes with the exception of Mo(*t*-Butxn)₄⁺, for which no oxidation is observed. At more positive potentials an irreversible oxidation (wave A) occurs also in the case of the *i*-mnt, ced, and ded complexes, and at more negative potentials an irreversible reduction (wave C), in the case of the *i*-mnt, Et₂dtc, and *t*-Butxn complexes. Electrochemical data for these redox processes in CH₃CN and CH₂Cl₂ solvents are summarized in Table II.

Waves 1 and 2 are judged to be reversible, diffusion-controlled, one-electron transfers on the basis of the cyclic voltammetric data. Values of $i_p/v^{1/2}AC$ are constant to within $\pm 5\%$, and $i_{pr}/i_{pf} = 1.00 \pm 0.05$ over the range $v = 0.01$ – 0.2 V s⁻¹ for waves 1 and 2 in both solvents. The only exception to this behavior occurs in the case of Mo(ded)₄³⁻ in CH₂Cl₂, for which wave 2 lies close to the background discharge of the solvent. The peak potential separations (ΔE_p) in CH₃CN range from 62 to 68 mV, which is close to the expected value for a reversible one-electron transfer.¹⁹ The larger values of ΔE_p observed in CH₂Cl₂ are attributed in part to the larger amount of uncompensated solution resistance in this solvent.

The number of electrons transferred in wave 1 for the ded, ced, *i*-mnt, and Et₂dtc complexes and in wave 2 for the *t*-Butxn complex was confirmed by controlled-potential coulometry. Coulometric oxidation of Mo(ded)₄³⁻ (at +0.10 V), Mo(ced)₄³⁻ (+0.50 V), and Mo(*i*-mnt)₄³⁻ (+0.85 V) in CH₃CN produced currents that decayed smoothly to background levels and provided linear log i vs. t plots. Values of $n = 1.02$, 1.00, and 1.02, respectively, were obtained from the coulometric data. Oxidation of Mo(Et₂dtc)₄⁺ at +1.30 V in CH₃CN resulted after 45 min in a steady-state current which was ca. one-third of the initial current. Treatment of the data as described previously^{20,21} for a catalytic chemical reaction in controlled-potential coulometry gave $n = 0.95$. Apparently, the oxidation product of Mo(Et₂dtc)₄⁺ reacts catalytically with the solvent medium on the time scale of bulk-solution coulometry, although the oxidation of Mo(Et₂dtc)₄⁺ is reversible and dif-

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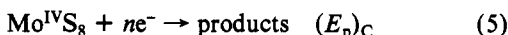
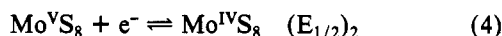
fusion controlled on the shorter time scale of cyclic voltammetry. Coulometric oxidation of $\text{Mo}(t\text{-Butxn})_4$ was accomplished at +0.6 V in CH_2Cl_2 . Current was almost constant initially but decayed smoothly to the background level after 30 min. A value of $n = 0.99$ was calculated from the total coulombs passed in the experiment.

Values of n for the other redox steps were estimated by comparing voltammetric peak current parameters. A value of $n = 1$ was assigned to the remaining reversible electron transfers, because $(i_p/v^{1/2}AC)_1$ and $(i_p/v^{1/2}AC)_2$ have nearly the same magnitudes for all complexes in a given solvent. For the irreversible processes, n was estimated by comparing peak current parameters of waves A and C to those of the corresponding reversible reactions by using relationship 1,²² where

$$n_{\text{irrev}} = \frac{0.90(i_p/v^{1/2}AC)_{\text{irrev}}}{(i_p/v^{1/2}AC)_{\text{rev}}} \frac{n^{3/2}_{\text{rev}}}{(\alpha n_a)^{1/2}_{\text{irrev}}} \quad (1)$$

$\alpha n_a = 0.0477/(E_p - E_{p/2})$ (in V). The electron stoichiometries determined in this manner for waves 1, 2, A, and C are listed in Table II.

The electrochemical behavior of the MoS_8 complexes is described by the series of reactions (2)–(5). Reactions 3 and



4 (waves 1 and 2) are assigned to reversible, metal-centered electron transfers, which constitute $\text{Mo}(\text{VI})/\text{Mo}(\text{V})$ and $\text{Mo}(\text{V})/\text{Mo}(\text{IV})$ redox couples. Reactions 2 and 5 (waves A and C) are assigned to oxidations above or reductions below these levels. These steps are irreversible and result in the transfer of either single or multiple electrons, which may imply substantial ligand character to the redox orbital.

The notable electrochemical feature of the MoS_8 complexes is the large sensitivity of the metal-centered redox processes to changes in ligand structure; indeed, the reversible half-wave potentials in Table II exhibit a total range of nearly 3 V. The shifts in $E_{1/2}$ are consistent with the expectation that electron-withdrawing substituents favor reduction and electron-donating substituents favor oxidation of the metal center. In a separate paper²³ we present a detailed interpretation of the shifts in $E_{1/2}$ and their correlation with ligand substituent parameters, molecular structural features, and spectroscopic properties of the MoS_8 complexes. The ability to predictably adjust reversible, metal-centered redox potentials over such a wide range suggests possible useful applications for these compounds as electron-transfer mediators or homogeneous catalysts.

Electronic Spectra. Visible absorption data for stable oxidation levels of all five MoS_8 complexes are reported in Table III. Except where noted, these spectral results were obtained under potentiostatic control in the OTTLE cell. The experimentally demonstrated reversibility of the redox conversions under these conditions confirms the spectroscopic features assigned to the various oxidation states. Our spectral results agree well with previous reports for $\text{Mo}(\text{Et}_2\text{dte})_4^{4+}$,^{6b,24} $\text{Mo}(\text{Et}_2\text{dte})_4^{6+}$,^{6c} and $\text{Mo}(t\text{-Butxn})_4^{4+}$ but we note some differences between our results and those reported in CHCl_3 for $\text{Mo}(t\text{-Butxn})_4^{4+}$.⁷ Some uncertainty is associated with the spectral parameters reported for $\text{Mo}(\text{Et}_2\text{dte})_4^{2+}$, because of the catalytic

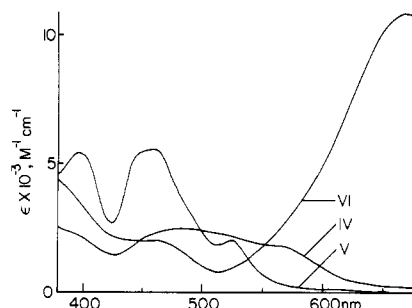


Figure 2. Visible absorption spectra of $\text{Mo}(\text{Et}_2\text{dte})_4^{2+,+0}$ species in CH_3CN (0.2 M $(\text{TEA})\text{BF}_4$) obtained under constant potential conditions in the OTTLE cell. Potentials used to generate the oxidation states: $\text{Mo}(\text{VI})$, +1.4 V; $\text{Mo}(\text{V})$, 0.0 V; $\text{Mo}(\text{IV})$, -0.7 V.

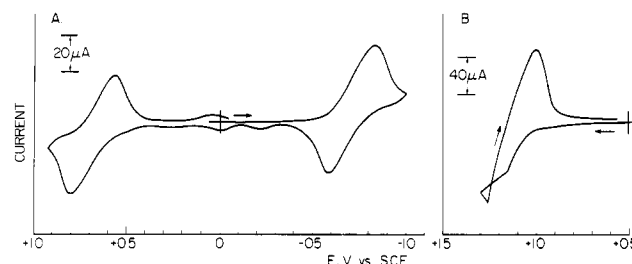


Figure 3. Thin-layer cyclic voltammograms in the OTTLE cell of (A) 1.21 mM $(n\text{-Bu}_4\text{N})_3\text{Mo}(i\text{-mnt})_4$ and (B) 1.95 mM $\text{Mo}(\text{Et}_2\text{dte})_4\text{PF}_6$. $v = 4 \text{ mV s}^{-1}$, and the solvent is CH_3CN (0.2 M $(\text{TEA})\text{BF}_4$).

reaction of this species with the solvent medium. However, conversion to the $\text{Mo}(\text{VI})$ oxidation state must be nearly quantitative under the conditions of thin-layer electrolysis because spectral features characteristic of $\text{Mo}(\text{V})$ are absent from the $\text{Mo}(\text{Et}_2\text{dte})_4^{2+}$ spectrum. Spectra of the $\text{Mo}(\text{Et}_2\text{dte})_4^{2+,+0}$ oxidation states obtained in the OTTLE cell are shown in Figure 2.

The prominent spectral feature of the $\text{Mo}(\text{VI})$ complexes is a single intense absorption at 670–860 nm, which is assignable to ligand-to-metal charge transfer on the basis of the d^0 configuration of the metal. The molybdenum(V)–ethylenedithiolate complexes exhibit a distinctive pattern of charge-transfer absorptions, observable as a progression of three bands at 463–467, 545–572, and 643–672 nm (see Figure 4 for an example). Similar, but less perfectly ordered, absorptions are observed for the $\text{Mo}(\text{Et}_2\text{dte})_4^{4+}$ and $\text{Mo}(t\text{-Butxn})_4^{4+}$ species. The $\text{Mo}(\text{IV})$ complex $\text{Mo}(i\text{-mnt})_4^{4-}$ also displays a series of three charge-transfer bands, but this feature is absent from the spectra of $\text{Mo}(\text{ced})_4^{4-}$ and $\text{Mo}(\text{ded})_4^{4-}$. Absorption bands for the $\text{Mo}(\text{ed})_4^{2-}$ and $\text{Mo}(\text{ed})_4^{3-}$ complexes shift to lower energy as their redox potentials become more positive (stronger electron-withdrawing substituents). This trend is consistent with $L \rightarrow M$ charge transfer. However, the effect of ligand structure on these spectral properties (Table III) is small in comparison to the effect on redox potentials (Table II).

Thin-Layer Electrochemistry and Spectroelectrochemistry. The technique of spectroelectrochemistry in thin layers of solution²⁵ has been applied increasingly to the study of inorganic redox systems.^{13,26} Benefits of this methodology include

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Table IV. Thin-Layer Electrochemical and Spectroelectrochemical Data^a

complex	process	2.3RT/nF, ^b mV	n ^b	E° _{SE} , ^b V	E° _{TL} , ^c V	E _{1/2} , ^d V
Mo(<i>i</i> -mnt) ₄ ³⁻	V → VI	63.2 ± 1.1	0.94	+0.680 ± 0.001	+0.680 (237)	+0.654
	V → IV	65.2 ± 2.5	0.91	-0.719 ± 0.002	-0.715 (248)	-0.715
Mo(ced) ₄ ³⁻	V → VI	61.1 ± 1.3	0.97	+0.318 ± 0.001	+0.327 (210)	+0.304
	V → IV	58.1 ± 2.0	1.02	-1.034 ± 0.003	-1.035 (230)	-1.024
Mo(ded) ₄ ³⁻	V → VI	59.9 ± 2.7	0.99	-0.124 ± 0.003	-0.125 (140)	-0.132
	V → IV	61.5 ± 2.3	0.96	-1.493 ± 0.001	-1.505 (172)	-1.472

^a In CH₃CN (0.2 M (TEA)BF₄), with 0.4–1.0 mM complex, at 24 ± 2 °C; results were averaged over four data sets. ^b Determined by application of eq 6 using a monitoring wavelength of 464 nm. ^c Average of E_{pc} and E_{pa} from thin-layer cyclic voltammetry at *v* = 4 mV s⁻¹; ΔE_p in mV is shown in parentheses. ^d Half-wave potential determined by bulk-solution cyclic voltammetry at Pt electrode; from Table II.

the abilities to (i) derive additional information from the electrochemical part of the thin-layer experiment,²⁷ (ii) generate and obtain spectroscopic information about potentially reactive species within a period of a few minutes, and (iii) determine the formal potential (E°_{SE}) and electron stoichiometry (*n*) of a redox couple from simultaneous spectroscopic and electrochemical measurements by use of the Nernst equation.^{25,26} We have used these approaches to further characterize the reversible electron-transfer steps of the MoS₈ complexes and to obtain the spectral information reported in Table III.

The thin-layer cyclic voltammogram in Figure 3A shows the reversible Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox couples of the Mo(*i*-mnt)₄³⁻ complex in CH₃CN. On the time scale of this experiment a small amount of electrode product decomposition is indicated by the presence of extraneous anodic peaks at -0.2 and 0.0 V following Mo(IV) generation and a cathodic peak at +0.05 V following Mo(VI) generation. Spectroscopic monitoring of the Mo(V) state indicates ~3–5% decomposition upon each cyclic Mo(V)/Mo(IV) or Mo(V)/Mo(VI) conversion. A similar amount of decomposition is noted following one-electron reduction of Mo(ded)₄³⁻ in CH₃CN, but no decomposition is detectable in the case of the Mo(ced)₄^{2-/3-}, Mo(ced)₄^{3-/4-}, and Mo(ded)₄^{2-/3-} couples in CH₃CN or the Mo(*t*-Butxn)₄⁺⁰ couple in CH₂Cl₂.

Thin-layer cyclic voltammetric oxidation of Mo(Et₂dtc)₄⁺ in CH₃CN produces an atypical current plateau at potentials more positive than +1.15 V as shown in Figure 3B. This result is attributed to catalytic oxidation of solvent or solvent impurities by the Mo(VI) electrode product, as observed also in the coulometric oxidation of Mo(Et₂dtc)₄⁺ in bulk solution. After the electrode potential was returned in to 0 V the OT-TLE experiment, spectroscopic measurements showed that Mo(Et₂dtc)₄⁺ is regenerated with ≥85% efficiency. Thus, loss of material is less than would be expected if the Mo(VI) complex were to be irreversibly consumed during its chemical reaction. This result suggests possible application of Mo(Et₂dtc)₄²⁺ and other highly oxidized MoS₈ species as oxidative redox catalysts.

Formal potentials and *n* values were determined for the ethylenedithiolate complexes in CH₃CN by means of spectropotentiostatic experiments in the OTTLE cell and the following form of the Nernst equation:^{25,26}

$$E_{\text{applied}} = E^{\circ}_{\text{SE}} + \frac{2.3RT}{nF} \log \frac{[\text{O}]}{[\text{R}]} \quad (6)$$

The ratio [O]/[R] was determined spectrophotometrically at several applied potentials as the quantity (A - A_R)/(A_O - A), where A is the absorbance measured for a mixture of O and R and A_O and A_R are the absorbances of the fully oxidized and fully reduced species. These quantities were corrected in appropriate cases for the small amounts of product decomposition noted above. A spectropotentiostatic experiment

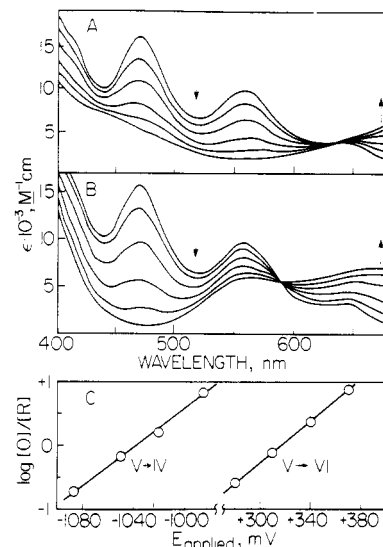


Figure 4. Spectropotentiostatic experiments for 0.94 mM (*n*-Bu₄N)₃Mo(ced)₄ in CH₃CN (0.2 M (TBA)PF₆): (A) spectra recorded during oxidation at 0, +0.280, +0.310, +0.340, +0.370, and +0.600 V; (B) spectra recorded during reduction at 0, -0.990, -1.020, -1.050, -1.080, and -1.350 V; (C) Nernst plots for Mo(V) → Mo(VI) and Mo(V) → Mo(IV) redox processes monitored at 464 nm.

monitoring Mo(V) → Mo(VI) oxidation and Mo(V) → Mo(IV) reduction for Mo(ced)₄³⁻ is illustrated in Figure 4. A clearly defined isosbestic point is observed in each case, as expected for the reversible conversion of one species to another. Values of E°_{SE} and *n* determined from the intercept and slope of eq 6 are presented in Table IV. The results further substantiate the reversible, one-electron character of the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) couples for the ethylenedithiolate complexes.

Table IV also contains formal potentials determined simultaneously by thin-layer cyclic voltammetry (E°_{TL}). Agreement between the spectroelectrochemically and voltammetrically determined E°'s at the Au minigrid in the OTTLE cell is excellent. Agreement between these formal potentials and half-wave potentials determined by bulk-solution cyclic voltammetry at a Pt electrode (E_{1/2}, Table IV) also is good, but small systematic differences exist between E°_{SE} or E°_{TL} and E_{1/2} (E°_{SE} = 1.021 E_{1/2} + 0.010 V, *r* = 0.9999). The cause of this small discrepancy has not been identified.

Acknowledgment. Support of this research by the National Science Foundation under Grant CHE 80-20442 is gratefully acknowledged.

Registry No. (*n*-Bu₄N)₃Mo(*i*-mnt)₄, 81643-67-6; (*n*-Bu₄N)₃Mo(ced)₄, 81642-88-8; (*n*-Pr₄N)₃Mo(ded)₄, 81642-90-2; Mo(Et₂dtc)₄PF₆, 81655-19-8; Mo(*t*-Butxn)₄, 63576-35-2; Mo(*t*-Butxn)₄⁺, 82614-50-4; Mo(Et₂dtc)₄²⁺, 82614-51-5; Mo(Et₂dtc)₄, 41947-30-2; Mo(*i*-mnt)₄²⁻, 81643-64-3; Mo(*i*-mnt)₄⁴⁻, 81643-61-0; Mo(ced)₄²⁻, 81643-65-4; Mo(ced)₄⁴⁻, 81643-62-1; Mo(ded)₄²⁻, 81643-63-2; Mo(ded)₄⁴⁻, 82614-52-6.