Contribution from the Department of Chemistry, Florida Atlantic University, Boca Raton, Florida 33431, and Contribution No. 621 from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387

Synthesis and Electrochemistry of Oxo- and Sulfido-Bridged Molybdenum(V) Complexes with 1,1-Dithiolate Ligands

FRANKLIN A. SCHULTZ,*[1a] VIRGINIA R. OTT,[1a] DEBRA S. ROLISON,[1a] DUDLEY C. BRAVARD,[1b] JOHN W. McDONALD,[1b] and WILLIAM E. NEWTON*[1b]

Received October 28, 1977

Syntheses are reported for a number of oxo- and sulfido-bridged molybdenum(V) complexes with the 1,1-dithiolate ligands *N,N*-diethyldithiocarbamate (dtc), diisopropyldithiophosphinate (dtp), and 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt). The dtc complexes constitute the first series of compounds in which bridging and terminal oxo groups have been sequentially replaced by sulfido in the binuclear $Mo_2X_4^{2+}$ core to yield all members of a single family from $Mo_2O_4(dtc)_2$ to $Mo_2S_4(dtc)_2$. Infrared spectra reveal the characteristic behavior of molybdenum–oxygen and molybdenum–sulfur stretching frequencies in the binuclear unit following O or S substitution at the bridging or terminal positions. Electrochemistry of the componds in dimethyl sulfoxide has been investigated by cyclic voltammetry, chronoamperometry, and controlled-potential coulometry. The sulfido-bridged dtc and *i*-mnt complexes undergo successive one-electron reductions to Mo(V)–Mo(IV) and $Mo^{IV}{}_2$ species. The ease of production and chemical stability of the one- and two-electron reduction products increase with increasing S substitution, although none of these products are stable on an extended time scale. The effect of ligand on electrochemical behavior, possible mechanisms for decomposition of the Mo(V)–Mo(IV) species, and comparisons to previous electrochemical studies of sulfido-bridged $Mo^V{}_2$ complexes in nonaqueous media are discussed.

Interest in the involvement of molybdenum in the function of the various redox-active molybdo enzymes[2] has led us to studies of complexes of molybdenum with bidentate sulfur donor ligands of the types dithiocarbamates,[3-11] xanthates,[12] dithiophosphinates,[3,10,13,14] and dithiophosphates[3,10,15,16] and with other ligands such as EDTA,[17] cysteine,[18] and ethylcysteine.[19] We have emphasized the oxidative addition chemistry of molybdenum(IV)[3,4,7,9] and molybdenum(II)[6,13] monomers, the interrelationship of the molybdenum atoms in dinuclear molybdenum(V) complexes[3,5,8,11,12] and the capability for transfer of oxo groups to and from molybdenum.[4,10,15,16] Herein, we describe the preparation and spectral characterization of dinuclear molybdenum(V) complexes of some of these ligands of the type $Mo_2X_2Y_2(LL)_2$ [LL = $S_2CN(C_2H_5)_2$, $S_2P(i\text{-}C_3H_7)_2$, $S_2C_2(CN)_2$; X = O, S; Y_2 = μ-O_2, μ-OS, μ-S_2], together with an investigation of their electrochemical behavior in dimethyl sulfoxide. These studies were prompted by the knowledge that molybdenum(V) is formed during the enzymic catalytic cycle and that all well-characterized molybdo enzymes contain two molybdenum atoms. We sought to determine the redox properties of a series of dinuclear molybdenum(V) complexes and thus elucidate the effect both of the successive substitution of sulfido for oxo in the bridging and/or terminal positions on molybdenum and of the ligating 1,1-dithiolate entity. Results such as these might have a bearing on the role and/or effect of sulfide on the properties of molybdenum in these enzymes as all are known to contain a wealth of sulfide.

Experimental Section

Materials and Physical Measurements. All reactions and physical measurements were carried out under an atmosphere of purified argon or nitrogen using degassed analytical reagent grade solvents. Molybdenum pentachloride was supplied by the Climax Molybdenum Co., and sodium *N,N*-diethyldithiocarbamate, dihydrate,[5] diisopropylphosphinodithioic acid,[14] and dipotassium 1,1-dicyanoethylene-2,2-dithiolate[20] were prepared as reported previously.

Infrared spectra were recorded as KBr disks with a Beckman IR-20A spectrophotometer; C, H, and N analyses were obtained with a Hewlett-Packard 185 CHN analyzer and S analysis was by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Analytical data are collected in Table I.

Electrochemical Measurements. Electrochemical experiments were carried out with instrumentation described previously.[17,18] Solutions were contained in a Brinkmann Model E615 cell at ambient temperature (22 ± 1 °C) and were deaerated with argon. Spectroquality dimethyl sulfoxide (Me_2SO, Aldrich Chemical Co.) was used as solvent with either 0.1 F tetraethylammonium perchlorate ($TEAClO_4$) or 0.1 F tetraethylammonium tetrafluoroborate ($TEABF_4$) from Southwestern Analytical Chemicals, Inc., Austin, Texas, as supporting electrolyte. No difference in behavior was observed between the two electrolytes. The working electrode for cyclic voltammetry and chronoamperometry experiments was either a Beckman Model 39273 Pt button electrode ($A = 0.20$ cm^2) or a piece of 18-gauge Pt wire ($A = 0.0133$ cm^2) sealed into glass tubing and polished flush to the surface. Normalized currents are reported to compensate for the difference in electrode area. The working electrode for controlled-potential coulometry was a large (~12 cm^2) hemicylindrical piece of Pt foil. Potentials are reported relative to an aqueous saturated calomel (SCE) reference electrode, which was separated from the test solution by a salt bridge containing supporting electrolyte.

Preparations. $Mo_2O_4(LL)_2$. (a) For LL = $S_2CN(C_2H_5)_2$, the complex was prepared either as previously reported,[5] but with additional purification by chromatography of the precipitated product on silica gel using dichloromethane as eluent, or by one of the following methods. (i) A mixture of *cis*-dioxobis(*N,N*-diethyldithiocarbamato)molybdenum(VI) [$MoO_2(LL)_2$] (3.00 g, 7.08 mmol) and zinc dust (3 g) was heated under reflux in a solution of thiophenol (0.15 mL, 1.46 mmol) in 1,2-dichloroethane for 3 h. The reaction mixture was allowed to cool and then was filtered, and the dark orange filtrate was evaporated to ~20 mL in vacuo. Ether (50 mL) was added with stirring to give the yellow *product* (1.26 g; 65% yield) which was collected by filtration, washed with acetone (3 × 5 mL) and ether (3 × 10 mL) and dried in vacuo. (ii) A solution of sodium *N,N*-diethyldithiocarbamate dihydrate (0.84 g, 4.0 mmol) in methanol (45 mL) was added dropwise to a stirred solution of molybdenum pentachloride (1.10 g, 4.0 mmol) in water (15 mL). The resulting reddish precipitate was heated under reflux for 10 min to give the bright yellow *product* (0.77 g; 70% yield) which was cooled, collected by filtration, washed with methanol–water (3:1; 20 mL), methanol (25 mL), and ether (2 × 25 mL), and dried in vacuo.

(b) For LL = $S_2P(i\text{-}C_3H_7)_2$, a solution of molybdenum pentachloride (5.1 g, 18.7 mmol) in water (80 mL) was stirred while a solution of diisopropylphosphinodithioic acid (3.0 mL, 3.4 g, 18.7 mmol) in ethanol (30 mL) was added dropwise. The mixture was then stirred for 0.5 h and the precipitated yellow *product* (4.81 g, 84% yield) collected by filtration, washed with water, ethanol, benzene, and ether, and dried in vacuo.

$Mo_2O_3S(LL)_2$. Two methods were used for both ligand types. (a) Gaseous hydrogen sulfide (1 mmol) was injected via a gastight syringe into a solution of μ-oxo-di-μ-thiophenolato-bis[oxo(LL)-molybdenum(V)][8,11] (1 mmol) in dichloromethane (20 mL) and the resultant solution stirred for 18 h. The solution was evaporated to ~5 mL and ether (50 mL) added to precipitate the yellow *product* (~70% yield) which was collected by filtration, washed with ether (3 × 30 mL), and dried in vacuo. The filtrate was evaporated to ~5 mL and diluted to 25 mL with carbon tetrachloride. Iodine/ethanol titration and gas chromatography indicated the presence of thiophenol (2.1 mmol).

0020-1669/78/1317-1758$01.00/0

Table I. Analytical and Selected Infrared[a] Spectral (cm^{-1}) Data

	% calcd				% found					
Compound	C	H	N	S	C	H	N	S	ν(Mo=X)[b]	(MoX_2Mo)[b]
$Mo_2O_4(S_2P\text{-}i\text{-}Pr_2)_2$	23.4	4.6			23.3	4.8			980 vs, 961 m	732 s, 714 w, 475 m
$Mo_2O_3S(S_2P\text{-}i\text{-}Pr_2)_2$	22.7	4.5		25.3	22.8	4.5		25.2	977 vs, 962 s	712 s, 514 w, 458 m, 376 w
$Mo_2O_3S(S_2CNEt_2)_2$	21.1	3.6	4.9	28.2	20.9	3.5	4.7	28.4	969 vs, 952 s	708 m, 515 m, 462 m, 353 m
$Mo_2O_2S_2(S_2CNEt_2)_2$	20.6	3.5	4.8	32.9	20.6	3.7	4.7	32.8	965 vs, 952 m	477 m, 340 m
$Mo_2OS_3(S_2CNEt_2)_2$[c]	20.0	3.4	4.7	37.4	19.9	3.4	4.6	36.8	962 s, 956 sh, 544 s	471 m, 337 m
$Mo_2S_4(S_2CNEt_2)_2$	19.5	3.3	4.5	41.6	19.1	3.1	4.3	40.8	546 s, 535 m	463 m, 331 m
$K_2[Mo_2O_2S_2(i\text{-mnt})_2]\cdot H_2O$	14.5	0.3	8.4		14.4	0.4	8.2		952 s, 940 sh	483 m, 340 m
$[(n\text{-Bu})_4N]_2[Mo_2O_2S_2(i\text{-mnt})_2]$	45.6	6.8	8.0	18.2	45.8	7.2	7.9	18.0	970 s, 955 m	485 m, 345 m

[a] As KBr disks. [b] ν(Mo=X) are the assignments for the terminal molybdenum–X stretching vibrations and (MoX_2Mo) are the various bridge modes with X = O or S.[23] [c] O analysis: calcd, 2.7%; found, 2.7%.

(b) Hydrogen sulfide was passed through a solution of $Mo_2O_4(LL)_2$ (1 mmol) heated under reflux in 1,2-dichloroethane (30 mL) for 1 h. The solution was evaporated to half-volume and ether (40 mL) added. The precipitated *product* (~80% yield) was collected by filtration, washed with ether (3 × 30 mL) and dried in vacuo.

$Mo_2O_2S_2(S_2CNEt_2)_2$. $Mo_2O_4(S_2CNEt_2)_2$ (0.16 g, 0.29 mmol) was heated under reflux in chloroform (30 mL) containing 4 drops of concentrated HCl in a stream of H_2S for 1 h. The reaction mixture was then reduced to half-volume in vacuo and ether (40 mL) added with stirring. The yellow *product* (0.15 g, 88% yield) was collected by filtration, washed with ether (3 × 10 mL), and dried in vacuo. A similar reaction occurred with $Mo_2O_3S(S_2CNEt_2)_2$. Alternatively, the same product is formed on heating a H_2S-saturated, 1,2-dichloroethane solution (40 mL) of Mo_2O_4 $(S_2CNEt_2)_2$ (0.28 g, 0.5 mmol) at 80 °C in a bomb, followed by a similar workup of the product (91% yield).

$Mo_2OS_3(S_2CNEt_2)_2$. This compound was prepared from $Mo_2O_3(S_2CNEt_2)_4$ and H_2S as described in ref 21 and crystallized from dichloromethane solution by pentane addition.

$Mo_2S_4(S_2CNEt_2)_2$. Using a modification of a literature procedure,[22] $Mo_2O_4(S_2CNEt_2)_2$ (0.50 g, 0.91 mmol) and P_4S_{10}(0.20 g, 0.45 mmol) were heated under reflux in xylene (35 ml) for 3 h. The red precipitate was filtered off and extracted with dichloromethane (4 × 25 mL), which, on evaporation to ~20 mL and addition of ether (50 mL), gave red-orange crystals of the *product* (0.2 g, 36% yield).

$[(n\text{-}C_4H_9)_4N]_2Mo_2O_2S_2[S_2C{=}C(CN)_2]_2$. A solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1.0 g) and $K_2S_2C{=}C(CN)_2$ (K_2(*i*-mnt); 5.2 g) in water (80 mL) was heated under reflux for 1 h. The yellow crystals of $K_2[Mo_2O_2S_2(i\text{-mnt})_2]\cdot H_2O$ (0.35 g, 56% yield), which were deposited after cooling at 0 °C overnight, were isolated by filtration, washed with water, and dried in vacuo. To a solution of $K_2[Mo_2O_2S_2(i\text{-mnt})_2]\cdot H_2O$ (0.20 g) in water (40 mL) was added $[(n\text{-}C_4H_9)_4N]I$ (0.5 g) in ethanol (20 mL) to give a yellow oil which crystallized when additional ethanol (30 mL) was added. The yellow *product* (0.3 g, 97% yield) was collected by filtration, washed with ethanol and ether, and dried in vacuo. The same product can be obtained without isolation of the intermediate by adding $[(n\text{-}C_4H_9)_4]I$ in ethanol to the cooled reaction mixture obtained after the reflux step.

Results

Preparation and Characterization of Compounds. A new method to prepare the parent compound of the *N*,*N*-diethyldithiocarbamate (dtc) series, $Mo_2O_4(dtc)_2$, was realized from studies of the mercaptan-catalyzed reactions of *cis*-dioxomolybdenum(VI) species with zinc. On heating of $MoO_2(dtc)_2$ and zinc in 1,2-dichloroethane under reflux in the presence of a small quantity of thiophenol, good yields of $Mo_2O_4(dtc)_2$ are obtained. The reaction probably proceeds via the following scheme:[5,8,10,11]

$$MoO_2(dtc)_2 + 2PhSH \rightarrow OMo(dtc)_2 + PhS\text{-}SPh + H_2O$$

$$OMo(dtc)_2 + MoO_2(dtc)_2 \rightleftarrows Mo_2O_3(dtc)_4$$

$$Mo_2O_3(dtc)_4 + 2PhSH \rightarrow Mo_2O_3(SPh)_2(dtc)_2 + 2dtcH$$

$$Mo_2O_3(SPh)_2(dtc)_2 + H_2O \rightarrow Mo_2O_4(dtc)_2 + 2PhSH$$

$$Zn + PhS\text{-}SPh + H_2O \rightarrow ZnO + 2PhSH$$

$Mo_2O_4(dtc)_2$ prepared both in this way and by a modification of our previously published method[5] was used in the electrochemical studies. The modification involves methanol–water as the solvent for the reaction which gives pure $Mo_2O_4(dtc)_2$ after only 10 min of heating under reflux.

By careful adjustment of the reaction conditions, three of the four other possible members of the series $Mo_2O_nS_{4-n}(dtc)_2$ (n = 0–3; dtc = Et_2NCS_2) are prepared from the parent compound[5] $Mo_2O_4(dtc)_2$, i.e., with n = 4. When a 1,2-dichloroethane solution of $Mo_2O_4(dtc)_2$ is heated under reflux in a stream of hydrogen sulfide for 1 h, substitution of only *one* bridging oxo by sulfido occurs,[8] while a similar reaction in chloroform in the presence of a few drops of concentrated hydrochloric acid gives the di-μ-sulfido complex

$$Mo_2O_4(dtc)_2 + \text{excess } H_2S \left\{ \begin{array}{l} \xrightarrow{C_2H_4Cl_2} Mo_2O_3S(dtc)_2 \\ \xrightarrow[+HCl]{CHCl_3} Mo_2O_2S_2(dtc)_2 \end{array} \right.$$

Total substitution of all oxo groups by sulfido is accomplished[8,22] by boiling a mixture of $Mo_2O_4(dtc)_2$ and P_4S_{10} in xylene and extracting the precipitate with dichloromethane.

$$Mo_2O_4(dtc)_2 + P_4S_{10} \rightarrow Mo_2S_4(dtc)_2$$

The last member of this series is prepared[21] from the reaction of hydrogen sulfide with the linear oxo-bridged dinuclear species $Mo_2O_3(dtc)_4$.

$$Mo_2O_3(dtc)_4 + 3H_2S \rightarrow Mo_2OS_3(dtc)_2 + 2H_2O + 2dtcH$$

The compound $Mo_2O_4(S_2P\text{-}i\text{-}Pr_2)_2$ is most simply prepared by the addition of an ethanolic solution of diisopropylphosphinodithioic acid[14] to an equimolar aqueous molybdenum pentachloride solution. If the reaction is carried out in a totally aqueous environment, a mixture containing the reduction product, $OMo(S_2P\text{-}i\text{-}Pr_2)_2$,[10] in addition to the required compound, is obtained. Again, reaction with H_2S in refluxing 1,2-dichloroethane gives the μ-O,S product, $Mo_2O_3S(S_2P\text{-}i\text{-}Pr_2)_2$.

The reaction of ammonium paramolybdate with K_2(*i*-mnt) in boiling water results in the formation of yellow $[Mo_2O_2S_2(i\text{-mnt})_2]^{2-}$. Both the potassium and tetra-*n*-butylammonium salts of this anion were isolated either by direct means from the reaction mixture or by metathesis. It is of interest to note that the *i*-mnt ligand acts not only as a bidentate, dinegative chelate but also as the reductant and a source of bridging sulfide in the preparation of $[Mo_2O_2(\mu\text{-}S)_2(i\text{-mnt})_2]^{2-}$ from ammonium paramolybdate.

Analytical and infrared data (Table I) are consistent with all these formulations, some of which have been confirmed by recent X-ray structural determinations. Those compounds containing terminal molybdenyl moieties are characterized[23] by strong infrared absorption at ~970 cm^{-1}, while terminal molybdenum–sulfur stretching modes are observed at ~545 cm^{-1}. The characteristic modes for the di-μ-sulfido bridge occur at ~475 and ~340 cm^{-1}, for the di-μ-oxo bridge at ~730, ~710, and ~475 cm^{-1}, and for the μ-oxo-μ-sulfido bridge at ~710, ~515, ~460, and ~360 cm^{-1}.

Table II. Electrochemical Data for Reduction of Dithiocarbamate Complexes[a]

Compound	$E_1^{f,b}$ V	$E_{p1} - E_{p/2}$, mV	ΔE_{p1}, mV	$E_2^{f,b}$ V	$i_{p1}/\nu^{1/2}AC$, A cm s$^{1/2}$ V$^{-1/2}$ mol^{-1}		$(it^{1/2})_1/AC$, A cm s$^{1/2}$ mol^{-1}		Process
					$\nu \rightarrow \infty$	$\nu \rightarrow 0$	$t \rightarrow 0$	$t \rightarrow \infty$	
$Mo_2O_4(dtc)_2$	(−1.46)	52			582		148		2e$^-$
$Mo_2O_3S(dtc)_2$	−1.41	71	79	(−1.74)	313	500	80	128	1e$^-$ → 2e$^-$
$Mo_2O_2S_2(dtc)_2$	−1.30	69	72	(−1.61)	333	465	73	106	1e$^-$ → 2e$^-$
$Mo_2OS_3(dtc)_2$	−0.97	86	80	−1.34	338[c]	422[c]	78[c]	98[c]	1e$^-$ → 2e$^-$
$Mo_2S_4(dtc)_2$	−0.84			−1.27	302	365	74		1e$^-$ → 2e$^-$

[a] Data recorded for 0.3–2 mM solutions of complexes in 0.1 F $TEAClO_4$ or $TEABF_4$ in Me_2SO. [b] E_1^f and $E_2^f = (E_{pc} + E_{pa})/2$ under conditions where a reverse wave is observed. If no reverse wave is observed, E_{pc} at $\nu = 0.1$ V s^{-1} is given in parentheses. [c] Calculated on the basis of 70% purity.

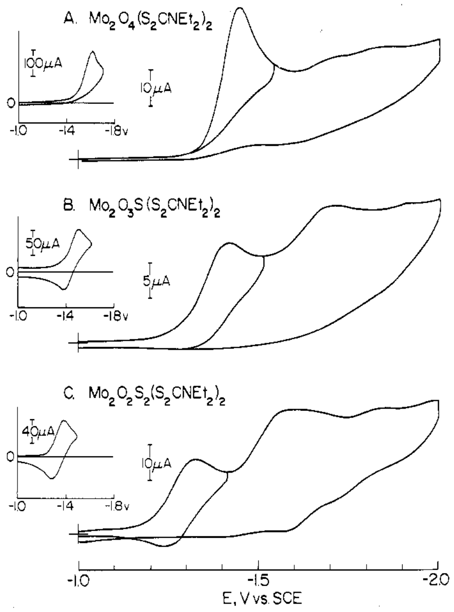


Figure 1. Cyclic voltammetric traces for dinuclear oxo- and sulfido-bridged molybdenum(V)–dithiocarbamate complexes in 0.1 F $TEABF_4/Me_2SO$. Concentrations (mM) and scan rates (V s^{-1}) as follows: main figures, (A) 0.99, 0.1; (B) 0.58, 0.1; (C) 0.93, 0.1; insets, (A) 1.22, 2; (B) 0.87, 5; (C) 0.81, 1.

Electrochemistry. Electrochemical results for reduction of the dithiocarbamate complexes are presented in Figure 1 and Table II. No oxidation waves are observed for these compounds in Me_2SO. The di-μ-oxo species, $Mo_2O_4(dtc)_2$, displays a single irreversible reduction wave at −1.46 V, and the voltammetric ($i_p/\nu^{1/2}AC$) and chronoamperometric ($it^{1/2}/AC$) current parameters for this process are constant over the entire range of scan rates (ν = 0.02–20 V s^{-1}) and measurement times (t = 0.01–2.0 s) employed. The remaining compounds exhibit two reduction waves, which are separated by 0.3–0.4 V. The first reduction wave is irreversible and larger than the second at slow scan rates, but the two waves become approximately equal in height at fast scan rates. For complexes substituted with sulfur in only the bridging positions, the first electron-transfer step but not the second becomes reversible at fast scan rates (see insets to Figure 1). If sulfur is placed in one or both terminal positions in addition to the bridging positions, both electron-transfer steps become reversible at fast scan rates. The formal redox potentials, E_1^f and E_2^f, shift in the positive direction with increasing sulfur substitution. Thus, replacement of bridging and terminal oxygens by sulfur enhances the ease of reduction of the binuclear Mo(V) center.

At fast measurement times, the first reduction wave of all S-substituted complexes achieves reversible behavior. The ratio of the reverse-to-forward peak current approaches unity, the peak potential becomes independent of scan rate, and the current parameters reach constant limiting values of $i_{p1}/\nu^{1/2}AC \simeq 320$ A cm s$^{1/2}$ V$^{-1/2}$ mol^{-1} and $(it^{1/2})_1/AC \simeq 77$ A cm s$^{1/2}$ mol^{-1}. As scan rate is decreased or measurement time increased, the first wave increases in size at the expense of the second, the reverse wave diminishes, and the two-wave system collapses to a single irreversible wave of approximately twice the original magnitude. The extent of this change depends on the particular complex and its concentration, but the upper limiting values in Table II (chosen arbitrarily at ν = 0.02 V s^{-1} or t = 2 s for ~1 mM solutions of the complexes) appear to approach those of $Mo_2O_4(dtc)_2$. Coulometric reduction of the sulfido-bridged complexes [$Mo_2O_3S(dtc)_2$ and $Mo_2O_2S_2(dtc)_2$] at a potential 100–150 mV negative of the first reduction wave yields values of n = 1.8–2.1, as determined from plots of log i vs. t over the first 60 min of electrolysis.[24] Coulometric reduction of $Mo_2O_4(dtc)_2$ at −1.55 V provides variable n values between 2 and 4.

Several pieces of evidence suggest that the initial reduction step for the sulfur-substituted members of the dithiocarbamate series [$Mo_2O_3S(dtc)_2$ through $Mo_2S_4(dtc)_2$] is a one-electron process. The lower limits of $i_{p1}/\nu^{1/2}AC$ and $(it^{1/2})_1/AC$ in Table II compare favorably with similar values for the ethyl cysteinate complexes, $Mo_2O_2X_2(Etcys)_2$ (X_2 = μ-O_2, μ-OS, or μ-S_2), which have been shown to undergo one-electron reduction in aprotic solvents.[19] If the value $it^{1/2}/AC$ = 77 A cm s$^{1/2}$ mol^{-1}, which is common to all complexes save $Mo_2O_4(dtc)_2$ in dimethyl sulfoxide, is used with n = 1 to solve for D in the Cottrell equation,[25] a diffusion coefficient of 2.0

$$i = nFAC(D/\pi t)^{1/2} \tag{1}$$

× 10^{-6} cm^2 s^{-1} is obtained. A similar value of $D = 2.2 \times 10^{-6}$ cm^2 s^{-1} has been obtained for the μ-oxo-bridged 8-quinolinol complex, $Mo_2O_3Q_4$, from chronopotentiometric measurements in Me_2SO.[26] Selection of other values of n yields diffusion coefficients which are unreasonable for molecules of this size in dimethyl sulfoxide. Under conditions where forward and reverse peaks are observed for the dtc complexes, values of the peak width ($E_p - E_{p/2}$) and peak separation (ΔE_p) are ~70 and 70–80 mV, respectively. These quantities agree reasonably well with the expected values of 57 and 59 mV for a reversible one-electron transfer,[27] considering the fact that contributions from charge-transfer irreversibility and uncompensated solution resistance are likely to be present to some degree under the experimental conditions. The latter factors, however, do introduce an uncertainty of about ±0.01 V to the E^f values in Table II.

The electrochemical behavior of the analogous di-μ-sulfido complex, $[Bu_4N]_2[Mo_2O_2S_2(i\text{-mnt})_2]$, supports the proposal that initial reduction of the dtc complexes proceeds by one electron. Cyclic voltammetric traces and electrochemical data for the first reduction step of $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$ in Me_2SO are shown in Figure 2 and Table III, respectively. The values of i_{pa}/i_{pc}, $E_p - E_{p/2}$ and ΔE_p in Table III indicate that $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$ is reduced by a reversible, one-electron transfer to a stable product at the scan rates investigated. Values of $i_p/\nu^{1/2}AC$ and $it^{1/2}/AC$ for $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$ reduction are constant and are in excellent agreement with

Table III. Electrochemical Data for First Reduction Step of $[Bu_4N]_2[Mo_2O_2S_2(i\text{-mnt})_2]^a$

Cyclic Voltammetry

Scan rate, V s^{-1}	E_{pc}, V	$E_p - E_{p/2}$, mV	ΔE_p, mV	$E_1{}^{f,b}$ V	$i_p/v^{1/2}AC$, A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1}	i_{pa}/i_{pc}
0.02	−1.460	62	60	−1.429	318	1.00
0.05	−1.452	63	63	−1.420	324	0.97
0.10	−1.458	66	64	−1.426	313	0.98
0.20	−1.455	66	66	−1.422	316	0.98

Chronoamperometry^c

Time, s	$it^{1/2}/AC$, A cm $s^{1/2}$ mol^{-1}	Time, s	$it^{1/2}/AC$, A cm $s^{1/2}$ mol^{-1}
0.04	78	0.50	76
0.10	77	1.00	78
0.20	74	1.50	78
0.40	74	2.00	78

^{a} 0.82 mM complex/0.1 F $TEAClO_4/Me_2SO$. $^b E_1{}^f = (E_{pc} + E_{pa})/2$. $^c E_{step} = -1.25$ to -1.55 V.

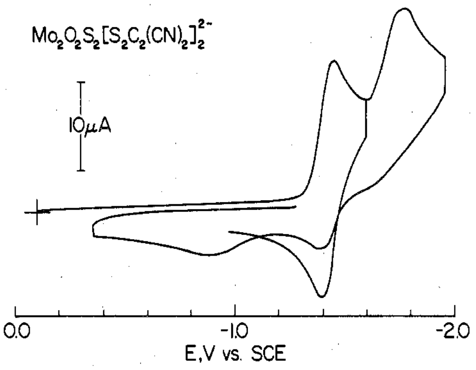


Figure 2. Cyclic voltammetric trace for 0.82 mM $[Bu_4N]_2[Mo_2O_2S_2(i\text{-mnt})_2]$ in 0.1 F $TEAClO_4/Me_2SO$. $\nu = 0.1$ V s^{-1}.

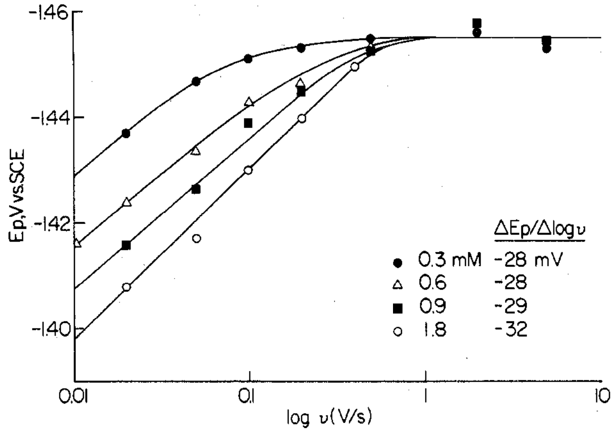


Figure 3. Dependence of peak potential on scan rate for cyclic voltammetric reduction of $Mo_2O_3S(dtc)_2$ at various concentrations.

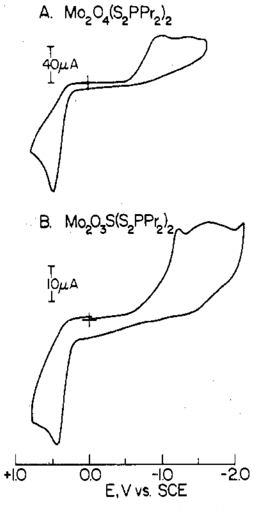


Figure 4. Cyclic voltammetric traces for dinuclear oxo- and sulfido-bridged molybdenum(V)–dithiophosphinate complexes in 0.1 F $TEABF_4/Me_2SO$ at $\nu = 0.2$ V s^{-1}. Concentrations (mM) are as follows: (A) 1.79; (B) 0.68.

the lower limits for the sulfur-substituted complexes in Table II. Coulometric reduction at a potential 150 mV beyond the first wave yields $n = 1.5$. The one-electron product of this compound, which is stable on the time scale of the voltammetry experiments, appears to undergo slow reaction to a further electroactive species during controlled-potential coulometry.

The data presented above indicate that the four S-substituted dithiocarbamate complexes undergo a transition from one-electron to two-electron behavior during the voltammetric and chronoamperometric experiments. Chemical reaction of the primary electrode product to a more easily reduced species is the usual cause of such behavior. Attempts to fit the normalized current parameters and reverse-to-forward current ratios to working curves for a first-order ECE mechanism[28,29] in possible explanation of these observations were not successful. Such attempts did reveal that changes in the current parameters and current ratios were dependent on the concentration of the complex. The data in Figure 3 clearly illustrate the concentration dependence of the chemical process. At fast scan rates, the peak potential for $Mo_2O_3S(dtc)_2$ reaches a value corresponding to the reversible one-electron reduction of the complex, which is independent of scan rate and concentration. At slower scan rates, the chemical process consuming the electrode product exerts its influence, and the peak potential shifts in the positive direction with decreasing ν and with increasing concentration of $Mo_2O_3S(dtc)_2$. For the data in Figure 3, the shift in peak potential is $\Delta E_p/\Delta \log C = +33 \pm 3$ mV at constant ν and $\Delta E_p/\Delta \log \nu = -29 \pm 2$ mV at constant C. These results suggest that the chemical reaction is second order in concentration of reduced molybdenum dimer. Equivalent behavior is observed for the remaining S-substituted dithiocarbamates. However, the scan rate needed to achieve reversible behavior of the first reduction wave for each compound decreases with increasing sulfur substitution. Therefore, the chemical stability of the one-electron reduction products of the $Mo_2X_4(dtc)_2$ complexes increases in the order: $Mo_2O_3S < Mo_2O_2S_2 < Mo_2OS_3 < Mo_2S_4$.

Electrochemical results for the dithiophosphinate complexes $Mo_2O_4(dtp)_2$ and $Mo_2O_3S(dtp)_2$ are presented in Figure 4 and Table IV. Each complex yields a broad, irreversible reduction wave at −1.0 to −1.2 V and an irreversible oxidation wave at ca. +0.5 V. Controlled-potential coulometry experiments could not be completed because the electrode products rapidly

Table IV. Electrochemical Data for Dithiophosphinate Complexes[a]

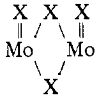
Compound	E_p, V	$E_p - E_{p/2}$, mV	$i_p/\nu^{1/2}AC$, A cm $s^{1/2}$ $V^{-1/2}$ mol^{-1}	$it^{1/2}/AC$, A cm $s^{1/2}$ mol^{-1}
	Cathodic Wave			
$Mo_2O_4(dtp)_2$	−1.02	188	380	115
$Mo_2O_3S(dtp)_2$	−1.22	170	372	145
	Anodic Wave			
$Mo_2O_4(dtp)_2$	+0.51	131	705	221
$Mo_2O_3S(dtp)_2$	+0.47	117	437	131

[a] 0.3–2 mM complexes/0.1 F $TEABF_4/Me_2SO$.

formed a film on the electrode surface. This filming probably is responsible for the poorly shaped reduction waves and poor reproducibility of electrochemical data for these compounds in general. Comparison of $it^{1/2}/AC$ values with those in Tables II and III suggests that the reduction of both phosphinate complexes and the oxidation of $Mo_2O_3S(dtp)_2$ involve two electrons, whereas the oxidation of $Mo_2O_4(dtp)_2$ appears to involve an unlikely four electrons.

Discussion

Preparation and Characterization of Compounds. The principal compounds prepared and investigated are a series of *N,N*-diethyldithiocarbamate ($Et_2NCS_2^-$ = dtc) complexes in which bridging and terminal oxo groups have been sequentially replaced by sulfido in the $Mo_2X_4^{2+}$ core. These



X = O, S

compounds constitute the first series of compounds in which all members of a single family from $Mo_2O_4(LL)_2$ to $Mo_2S_4(LL)_2$ (excluding those in which terminal substitution precedes bridging substitution) have been prepared. Certain of these compounds have been claimed to be prepared by other means and in some cases, were probably wrongly formulated.[22,30] However, by extensive infrared studies, including oxygen-18 substitution,[23] and by X-ray structural investigations,[21,31–34] it is now certain that the initial fairly facile substitution by sulfide occurs at the bridging oxo groups, while more stringent reaction conditions using P_4S_{10} are usually necessary to effect terminal oxo substitution. The synthetic procedures presented in this paper with their easy workup and *single* product are preferred to those published earlier[22,33,35] all of which produce mixtures of compounds with varying degrees of substitution of sulfido for oxo groups.

The compound formulated[22] as $Mo_2OS(\mu\text{-}O)_2(dtc)_2$ is certainly $Mo_2O_2(\mu\text{-}O\text{-}\mu\text{-}S)(dtc)_2$ with a bridging, rather than terminal, sulfido group. Those authors were misled by assigning an infrared absorption at 520 cm^{-1} to a terminal molybdenum–sulfur stretch. We have shown,[23] however, that this absorption is due to a molybdenum–oxygen bridging mode by oxygen-18 substitution studies. This same compound was also isolated[33,35] from the several products of the *aerobic* reaction of $MoO_2(dtc)_2$ with P_4S_{10} but not from the similar reaction with H_2S in air. In contrast, we isolate[21] *only* $Mo_2OS_3(dtc)_2$ from the *anaerobic* reaction of $MoO_2(dtc)_2$ (which is initially reduced to $Mo_2O_3(dtc)_4$) with H_2S. This compound probably constitutes[36] the major product in the sample used by De Hayes et al.[30] in their electrochemical studies of "$Mo_2O_2(\mu\text{-}S)_2(dtc)_2$".

This series of *N,N*-diethyldithiocarbamate complexes of various dinuclear molybdenum(V) cores allows a systematic study of the effects of sulfur substitution on the electron-transfer properties of these entities to be made. In addition, we have also prepared several members of the $Mo_2X_4(LL)_2$ series with LL = diisopropylphosphinodithioate ($i\text{-}Pr_2PS_2^-$ = dtp) and 1,1-dicyanoethylene-2,2-dithiolate [$(NC)_2C{=}CS_2^{2-}$ = *i*-mnt] to make, together with previous studies,[19] a partial comparison of ligand effects on electrochemical behavior.

Electrochemistry. The electrochemical data show that the reduction of sulfido-bridged dinuclear molybdenum(V)–dithiocarbamate complexes may be described by two successive one-electron-transfer reactions.

$$Mo_2X_4(dtc)_2 + e^- \rightleftharpoons Mo_2X_4(dtc)_2^{-\cdot} \qquad E_1^f \tag{2}$$

$$Mo_2X_4(dtc)_2^{-\cdot} + e^- \rightleftharpoons Mo_2X_4(dtc)_2^{2-} \qquad E_2^f \tag{3}$$

$$X_4 = O_3S \text{ through } S_4$$

The first step is reversible at fast scan rates for complexes containing at least a bridging S atom, while both steps become reversible at fast scan rates for complexes with bridging and terminal sulfido groups. Several pieces of evidence support the transfer of a single electron as the initial step in these processes. (1) The first reduction wave reduces at fast scan rates to a simple reversible process having a peak potential independent of concentration and scan rate and a peak width and peak separation only slightly larger than expected for a one-electron transfer. (2) Values of $i_{p1}/\nu^{1/2}AC$ and $(it^{1/2})_1/AC$ at short measurement times are similar for all sulfido-bridged dinuclear Mo(V) complexes containing dtc, *i*-mnt, and Etcys ligands. The reversible one-electron behavior of $Mo_2O_2S_2(i\text{-}mnt)_2^{2-}$ is demonstrated in Table III and Figure 2, while the behavior of $Mo_2O_2X_2(Etcys)_2$ complexes was reported previously.[19] (3) A reasonable value for the diffusion coefficient of dinuclear Mo complexes in Me_2SO is obtained from the short-time chronoamperometric results only when $n = 1$. (4) Current parameters for the sulfido-bridged dtc complexes approximately double in magnitude over the range of measurement times, and a limiting value of $n = 2$ is substantiated by controlled-potential coulometry.

De Hayes et al.[30] also have investigated the electrochemistry of $Mo_2O_4(dtc)_2$ in Me_2SO and *N,N*-dimethylformamide (DMF) and of $Mo_2O_2S_2(dtc)_2$ in DMF. Whereas there is agreement that the di-μ-oxo compound is reduced in an irreversible two-electron process at ca. −1.5 V, De Hayes and co-workers suggest that the di-μ-sulfido compound is reduced in two reversible $^1/_2$-electron steps at potentials ($E_1^{f'} = -1.00$ V and $E_2^{f'} = -1.35$ V) substantially different than observed by us.

$$2Mo_2O_2S_2(dtc)_2 + e^- \rightleftharpoons Mo_4O_4S_4(dtc)_4^{-\cdot} \qquad E_1^{f'} \tag{4}$$

$$Mo_4O_4S_4(dtc)_4^{-\cdot} + e^- \rightleftharpoons Mo_4O_4S_4(dtc)_4^{2-} \qquad E_2^{f'} \tag{5}$$

We also investigated the electrochemistry of $Mo_2O_2S_2(dtc)_2$ in DMF and found at $\nu > 0.1$ V s^{-1} a reversible reduction at −1.375 V and an irreversible reduction at −1.7 V. Voltammetric peak currents were representative of a one-electron transfer in this solvent. Aside from a small shift in reduction potential there seems to be little difference in the electrochemical behavior of $Mo_2O_2S_2(dtc)_2$ in DMF and Me_2SO.

In addition to the values cited earlier for the voltammetric and chronoamperometric current parameters, there is considerable evidence that electrochemical reduction of $Mo_2O_2S_2(dtc)_2$ in Me_2SO does not proceed by a reversible $^1/_2$-electron dimerization. If reduction were to take place by a reaction such as eq 6, values of $E_p - E_{p/2} = 81$ mV and

$$2A + e^- \rightleftharpoons A_2^{-\cdot} \tag{6}$$

$\Delta E_p/\Delta \log C = +60$ mV should be observed at the limit of thermodynamic reversibility.[37–41] We find that when the first voltammetric wave for $Mo_2O_2S_2(dtc)_2$ and the other sulfido-bridged dtc complexes achieves reversible behavior (Figure

3), the peak potential becomes *independent of concentration* and values of $E_p - E_{p/2}$ are only slightly larger than the 57 mV expected for a one-electron process. This result also precludes reduction by a reversible dimerization consuming one electron per Mo dimer (eq 7), since in this case, $E_p - E_{p/2}$

$$2A + 2e^- \rightleftharpoons A_2^{2-} \tag{7}$$

= 41 mV and $\Delta E_p/\Delta \log C = +30$ mV.[38-40,42,43] Saveant and co-workers[38] have calculated the shapes of cyclic voltammograms for a number of electrodimerization mechanisms. For systems with two reversible $^1/_2$-electron waves, the first wave changes from reversible to irreversible behavior as the scan rate increases (Figure 4 in ref 38). Our findings are that the first wave changes from irreversible to reversible behavior upon increasing scan rate, which is more in the manner of an irreversible chemical reaction following the electron-transfer step. We therefore conclude that the initial step in the reduction of $Mo_2O_2S_2(dtc)_2$ is a simple one-electron transfer (reaction 2) rather than a reversible $^1/_2$-electron dimerization (reaction 4). Due to the substantial difference in peak potentials, it is likely that De Hayes et al.[30] obtained results on a (possibly impure) sample of a compound other than $Mo_2O_2S_2(dtc)_2$. Inspection of peak potential data in Table II suggests that $Mo_2OS_3(dtc)_2$ may have been the compound investigated.[36]

Our results indicate that an irreversible second-order chemical reaction follows reduction of the sulfido-bridged dtc complexes. This reaction produces a material more easily reduced than the starting complex and is responsible for the transition from one-electron to two-electron behavior. The reaction could be an irreversible dimerization if the product were reduced by one electron per original Mo dimer at the potential of the first wave. However, other mechanisms exhibiting a second-order dependence on initial concentration also could explain the observed behavior.[44-46] Since spectroscopic and ESR studies of the mixed-valence Mo(V)–Mo(IV) species produced in reaction 2 would be of interest, the means by which these materials are depleted from solution is of some importance. We have not, however, established the nature of the chemical reaction following the electron-transfer step at this time. In the case of the di-μ-oxo compound, no reverse wave is observed at the potential of the first reduction. Either the following chemical reaction is very rapid or the compound is reduced directly by an irreversible two-electron transfer.

$$Mo_2O_4(dtc)_2 + 2e^- \rightarrow 2Mo^{IV}dtc \tag{8}$$

Placement of sulfido groups in bridging and terminal positions has a measurable and systematic effect on the ease of reduction of the dinuclear Mo(V)–dtc complexes and the chemical stability of their one-electron reduction products. Substitution of sulfur for bridging oxygen shifts the reduction potential of the first wave in the positive direction by ~100 mV per S atom. A similar shift is observed upon S substitution in the analogous $Mo^V{}_2$–Etcys complexes.[19] Insertion of the first sulfur atom at a terminal site causes a much larger positive shift of ~300 mV, while conversion of the second terminal group causes a change of only slightly more than 100 mV. The ease of reduction of the dinuclear Mo(V) unit therefore increases in the sequence: $Mo_2O_4 < Mo_2O_3S < Mo_2O_2S_2 < Mo_2OS_3 < Mo_2S_4$.

The regular variation of $E_1{}^f$ and $E_2{}^f$ (or E_{p2}) with the extent of sulfur substitution is an excellent qualitative indicator of the composition of the Mo_2X_4 bridge system. This regular behavior, in fact, contributed to the identification of the $Mo_2OS_3(dtc)_2$ complex which contains mixed oxo and sulfido terminal groups. Initially, difficulty was encountered in distinguishing between this formulation and one containing a persulfido group with only oxygen atoms in the terminal positions. The first sample used was impure and gave electrochemical current parameters approximately two-thirds the magnitude of the other compounds (see Table II). Comparison of voltammetric peak potentials with the other dtc complexes placed this compound between $Mo_2O_2S_2(dtc)_2$ and $Mo_2S_4(dtc)_2$. Subsequent purification and chemical and spectral characterization of this material confirmed the electrochemical parameters and assignment as $Mo_2OS_3(dtc)_2$. Difficulty in obtaining the compound in pure form[36] could account for the $^1/_2$-electron behavior reported by De Hayes et al.[30] for reduction of "$Mo_2O_2S_2(dtc)_2$", which on the basis of its E^f values appears to be $Mo_2OS_3(dtc)_2$.

The chemical stability of the one-electron reduction products of the $Mo_2X_4(dtc)_2$ complexes in Me_2SO clearly is enhanced by placement of sulfur in the bridging and terminal positions. This behavior can be seen most clearly by examining the reverse-to-forward peak current ratio of the first reduction wave for the entire series of complexes at constant scan rate and concentration. The magnitude of the reverse wave increases systematically as sulfur is substituted for oxygen in coordination positions around Mo. Although the mechanism of the decomposition step has not been determined, it is evident that the stability of the products of reaction 2 increases in the sequence: $Mo_2O_4 < Mo_2O_3S < Mo_2O_2S_2 < Mo_2OS_3 < Mo_2S_4$. Such stabilization of the Mo(V)–Mo(IV) mixed-valence oxidation state by sulfido bridging atoms has been observed previously in dinuclear complexes with Etcys[19] and dtc[30,47] ligands.

A basis for understanding the effects of sulfur atom substitution on redox potentials and electrode product stability may be gained from recent electronic-state calculations (SCF–MO methods) of $Mo_2O_4^{2+}$ and $Mo_2O_2S_2^{2+}$ centers.[48,49] These calculations show that the five virtual orbitals of lowest energy are either Mo–Mo bonding or antibonding in nature and contain substantial contributions from bridging and terminal atoms. Significantly, inclusion of formally empty sulfur atom d orbitals in calculations for the $Mo_2O_2S_2^{2+}$ center[49] leads to significant bonding interactions between bridging S atoms, between bridging S and terminal O, and between bridging S and a coordinated S atom on the ligand (cysteine). Calculation of formal atomic charges shows that charge is more evenly distributed throughout the di-μ-sulfido center than the di-μ-oxo center. Presence of sulfur atoms with their diffuse d orbitals apparently promotes electron delocalization over the framework of the dinuclear unit. This delocalization may be expected to provide (i) orbitals of lower energy for occupancy of an additional electron and (ii) stabilization of reduced species by more effective charge distribution, making them potentially less reactive in possible decomposition reactions. These effects of sulfur substitution on redox potentials and product stability were noted previously[19] for a series of $Mo_2O_2X_2(Etcys)_2$ complexes and now have been established over the entire range of $Mo_2O_4(dtc)_2$ through $Mo_2S_4(dtc)_2$ complexes.

A study of the effects of ligand on electrochemical behavior also would be desirable, but a full comparison is made difficult by the fact that no single type of dinuclear structural unit has been studied over the entire range of ligands considered. The most meaningful comparison is to contrast potentials for the reduction steps of the di-μ-sulfido complexes with Etcys ($E_1{}^f = -1.44$ V, $E_{p2} = -1.66$ V),[19] dtc ($E_1{}^f = -1.30$ V, $E_{p2} = -1.61$ V), and *i*-mnt ($E_1{}^f = -1.42$ V, $E_{p2} = -1.7$ V) ligands. Although the ease of reduction follows the sequence Etcys ~ *i*-mnt < dtc, there is not much difference between the reduction potentials of these compounds. The nature of the lowest energy unfilled molecular orbitals[48,49] suggests that reduction of these compounds involves electron transfer into orbitals distributed principally over the Mo atoms and atoms at the bridging and terminal sites. It therefore stands to reason that the redox potential of the dinuclear $Mo_2X_4^{2+}$ unit will be influenced more directly by the nature of atoms at the bridging and terminal positions than by the ligand. This conclusion appears to be confirmed by the similarity of E_1^f values for the dtc, *i*-mnt, and Etcys complexes.

Results for the dithiophosphinate complexes are difficult to interpret because of poor electrochemical behavior. The di-μ-O and μ-O-μ-S species are reduced at less negative potentials than comparable complexes with the other ligands, and these are the only compounds to exhibit an oxidation wave in Me_2SO. Reasons for the uncharacteristic behavior of the dtp complexes are unknown.

Ligands do exert a significant effect on the chemical behavior of the one-electron reduction products in nonaqueous media. The most striking contrast is that between the behavior of the Etcys and dtc complexes. Reduction of $Mo_2O_2X_2$-$(Etcys)_2$ complexes produces Mo(V)–Mo(IV) species which, although unstable on the voltammetric time scale, decay to nonelectroactive products. Consequently, current parameters representative of a one-electron transfer are observed over the entire range of measurement times. Products from reduction of $Mo_2X_4(dtc)_2$ complexes, however, undergo a second-order chemical reaction to yield species which are reduced further at the potential of the first voltammetric wave. A transition from one-electron to two-electron behavior therefore is observed with the $Mo_2X_4(dtc)_2$ complexes although the rate of this process decreases with increasing S substitution. A quantitative comparison of reactivity cannot be made because the mechanism of the decomposition reactions has not been identified. However, a qualitative comparison of reverse-to-forward peak current ratios under approximately equivalent experimental conditions suggests that electrode product stability may follow the sequence: dtp < Etcys < dtc < *i*-mnt. It is interesting to note that among the compounds investigated to date the most stable Mo(V)–Mo(IV) mixed-valence species we have encountered is that generated by the one-electron reduction of the di-μ-sulfido complex $Mo_2O_2S_2(i\text{-mnt})_2^{2-}$.

The effects of terminal and/or bridging sulfide ligands in the $Mo_2X_4^{2+}$ core that we have observed may provide insight into a role for sulfide coordination at molybdenum in the sulfur-rich molybdo enzymes.[50] The presence of sulfide ligands in these enzymes might allow molybdenum to be more easily reduced by both one- and two-electron processes compared with a similar core ligated by oxo groups. Thus, reduction of an enzyme-bound molybdenum core (to the Mo(IV) or possibly the Mo(III) level) would be aided by sulfide as would the dissociation of dinuclear cores into mononuclear species[51] which are the likely catalytically active entities in these enzymes.[2a,52] Experiments are in progress to characterize the mixed-valent species produced, the nature of the chemical reaction following the initial reduction, and the highly electroactive species produced subsequently and to elucidate possible functional relationships of molybdenum and sulfur in enzymes.

Acknowledgment. Research at Florida Atlantic University was supported by the National Science Foundation through Grants GP-38442X and CHE 76-18703. We wish to thank Professor J. M. Saveant for providing us with a copy of Dr. Andrieux's thesis and for helpful discussions regarding electrodimerization mechanisms.

Registry No. $Mo_2O_4(S_2P\text{-}i\text{-}Pr_2)_2$, 63912-56-1; $Mo_2O_3S(S_2P\text{-}i\text{-}Pr_2)_2$, 63912-57-2; $Mo_2O_3S(S_2CNEt_2)_2$, 63912-48-1; $Mo_2O_2S_2(S_2CNEt_2)_2$, 55723-33-6; $Mo_2OS_3(S_2CNEt_2)_2$, 66290-40-2; $Mo_2S_4(S_2CNEt_2)_2$, 36539-27-2; $K_2[Mo_2O_2S_2(i\text{-mnt})_2]$, 66322-51-8; $[(n\text{-Bu})_4N]_2$-$[Mo_2O_2S_2(i\text{-mnt})_2]$, 59389-04-7; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; μ-oxo-di-μ-thiophenolato-bis[oxo(S_2CNEt_2)molybdenum(V)], 63016-34-2; μ-oxo-di-μ-thiophenolato-bis[oxo($S_2P\text{-}i\text{-}Pr_2$)molybdenum(V)], 66290-39-9; P_4S_{10}, 12066-62-5; $H_6Mo_7O_{24}$, 12027-67-7.

References and Notes

(1) (a) Florida Atlantic University. (b) Charles F. Kettering Research Laboratory.

(2) (a) E. I. Stiefel, W. E. Newton, G. D. Watt, K. L. Hadfield, and W. A. Bulen, *Adv. Chem. Ser.*, **No. 162**, 353 (1977); (b) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1976).

(3) W. E. Newton, J. L. Corbin, and J. W. McDonald in "Proceedings of First International Symposium on N_2 Fixation", W. E. Newton and C. J. Nyman, Ed., Washington State University Press, Pullman, Wash., 1976, pp 53–74.

(4) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 8640 (1972).

(5) W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, **13**, 1100 (1974).

(6) J. W. McDonald, W. E. Newton, C. T. C. Creedy, and J. L. Corbin, *J. Organomet. Chem.*, **92**, C25 (1975).

(7) W. E. Newton, D. C. Bravard, and J. W. McDonald, *Inorg. Nucl. Chem. Lett.*, **11**, 553 (1975).

(8) W. E. Newton, G. J-J. Chen, and J. W. McDonald, *J. Am. Chem. Soc.*, **98**, 5387 (1976).

(9) J. W. McDonald, J. L. Corbin, and W. E. Newton, *Inorg. Chem.*, **15**, 2056 (1976).

(10) G. J-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).

(11) K. Yamanouchi, J. H. Enemark, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **99**, 3529 (1977).

(12) W. E. Newton, J. L. Corbin, and J. W. McDonald, *J. Chem. Soc., Dalton Trans.*, 1044 (1974).

(13) J. W. McDonald, J. L. Corbin, and W. E. Newton, *J. Am. Chem. Soc.*, **97**, 1970 (1975).

(14) J. L. Corbin, W. E. Newton, and J. W. McDonald, *Org. Prep. Proced. Int.*, **7**, 309 (1975).

(15) G. J-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Nucl. Chem. Lett.*, **12**, 697 (1976).

(16) G. J-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chim. Acta*, **19**, L67 (1976).

(17) V. R. Ott and F. A. Schultz, *J. Electroanal. Chem.*, **59**, 47 (1975).

(18) V. R. Ott and F. A. Schultz, *J. Electroanal. Chem.*, **61**, 81 (1975).

(19) V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, **16**, 2538 (1977).

(20) R. Gompper and W. Topfl, *Chem. Ber.*, **95**, 2851 (1962).

(21) K. Yamanouchi, J. H. Enemark, and W. E. Newton, publication in preparation.

(22) T. Sakurai, H. Okabe, and H. I. Soyama, *Bull. Jpn. Pet. Inst.*, **13**, 243 (1971).

(23) W. E. Newton and J. W. McDonald in "Proceedings of the Second Climax Symposium on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell and A. Seaman, Ed., Climax Molybdenum Co., London, 1976, p 25; *J. Less-Common Met.*, **54**, 51 (1977).

(24) L. Meites in "Physical Methods of Chemistry", Part IIA, Vol. 1, A. Weissberger and B. W. Rossiter, Ed., Wiley, New York, N.Y., 1971, Chapter 9.

(25) P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience, New York, N.Y., 1954, Chapter 3.

(26) A. F. Isbell, Jr., and D. T. Sawyer, *Inorg. Chem.*, **10**, 2449 (1971).

(27) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(28) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965).

(29) G. S. Alberts and I. Shain, *Anal. Chem.*, **35**, 1859 (1963).

(30) L. J. De Hayes, H. C. Faulkner, W. H. Doub, Jr., and D. T. Sawyer, *Inorg. Chem.*, **14**, 2110 (1975).

(31) B. Spivack, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975).

(32) L. Ricard, C. Martin, R. Wiest, and R. Weiss, *Inorg. Chem.*, **14**, 2300 (1975).

(33) J. Dirand-Colin, L. Ricard, and R. Weiss, *Inorg. Chim. Acta*, **18**, L21 (1976).

(34) R. Winograd, B. Spivack, and Z. Dori, *Cryst. Struct. Commun.*, **5**, 373 (1976).

(35) J. Dirand, L. Ricard, and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **11**, 661 (1975).

(36) It is unclear which oxo-bridged molybdenum(V) species was reacted with H_2S in ref 30. We have found that treatment of $Mo_2O_3(dtc)_4$ with H_2S anaerobically yields $Mo_2OS_3(dtc)_2$.[21] In contrast, treatment of $Mo_2O_4(dtc)_2$ with H_2S anaerobically at room temperature yields mixtures mainly of $Mo_2O_2S_2(dtc)_2$ and $Mo_2O_3S(dtc)_2$ with some other compounds. Similarly, H_2S and $MoO_2(dtc)_2$ in acetone under air also give product mixtures.[35]

(37) M. S. Shuman, *Anal. Chem.*, **41**, 142 (1969).

(38) C. P. Andrieux, L. Nadjo, and J. M. Saveant, *J. Electroanal. Chem.*, **26**, 147 (1970).

(39) C. P. Andrieux, Doctoral Thesis, University of Paris.

(40) J. M. Saveant, private communication.

(41) Under conditions of complete thermodynamic equilibrium (zone DE in ref 38), either of two mechanisms, radical–radical coupling

$$A + e^- \rightleftarrows A^{-\cdot} \qquad E_i^f$$

$$2A^{-\cdot} \rightleftarrows A_2^{\ 2-}$$

$$A_2^{\ 2-} \rightleftarrows A_2^{-\cdot} + e^- \qquad E_{ii}^f\ (<E_i^f)$$

or parent–radical coupling

$$A + e^- \rightleftarrows A^{-\cdot} \qquad E_i^f$$

$$A^{-\cdot} + A \rightleftarrows A_2^{-\cdot}$$

would give the net reaction in eq 6, but would be indistinguishable from one another.

(42) J. M. Saveant and E. Vianello, *Electrochim. Acta*, **12**, 1545 (1967).
(43) M. S. Shuman, *Anal. Chem.*, **42**, 521 (1970).
(44) M. Mastragostino, L. Nadjo, and J. M. Saveant, *Electrochim. Acta*, **13**, 721 (1968).
(45) M. L. Olmstead and R. S. Nicholson, *Anal. Chem.*, **41**, 862 (1969).
(46) L. Nadjo and J. M. Saveant, *J. Electroanal. Chem.*, **33**, 419 (1971).
(47) J. K. Howie and D. T. Sawyer, *Inorg. Chem.*, **15**, 1892 (1976).
(48) D. H. Brown, P. G. Perkins, and J. J. Stewart, *J. Chem. Soc., Dalton Trans.*, 1105 (1972).
(49) D. H. Brown and P. G. Perkins, *Rev. Roum. Chim.*, **20**, 515 (1975).
(50) R. C. Bray in "Proceedings of Climax Second International Conference on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell and A. Seaman, Ed., Climax Molybdenum Co., London, 1976, p 271.
(51) F. A. Schultz, D. A. Ledwith, and L. O. Leazenbee, *ACS Symp. Ser.*, No. **38**, 78 (1977).
(52) R. C. Bray in "Proceedings of Climax First International Conference on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co., London, 1973, p 216.

Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver V6T 1W5, Canada

Synthesis and Structural Characterization of Fluorosulfate Derivatives of Silver(II)

P. C. LEUNG and F. AUBKE*

Received November 11, 1977

The synthesis of silver(II) fluorosulfate, $Ag(SO_3F)_2$, by a variety of routes is described. The preparations of a mixed-valency compound of the composition $Ag_3(SO_3F)_4$ and its potassium analogue $K_2Ag^{II}(SO_3F)_4$, the compounds $Ag^{II}Pt^{IV}(SO_3F)_6$ and $Ag^{II}Sn^{IV}(SO_3F)_6$, and the complex $[Ag(bpy)_2](SO_3F)_2$ are also reported. Structural studies are based on vibrational, electronic mull and diffuse reflectance, and ESR spectra as well as magnetic susceptibility measurements in the temperature range of 80 to about 300 K. Both $Ag_3(SO_3F)_4$ and $K_2Ag(SO_3F)_4$ show antiferromagnetic coupling. All other divalent silver compounds synthesized here are magnetically dilute with the Ag^{2+} ion in a square-planar or tetragonally distorted (elongated) octahedral environment.

(A) Introduction

Even though many divalent silver compounds have been reported over the years,[1-3] the fluoride AgF_2[4] has remained the only simple, binary silver(II) compound which is stable at room temperature. All other Ag(II) compounds are either derivatives of silver(II) fluoride, ternary fluorides like $K[Ag^{II}F_3]$[5] or $Ag^{II}[SnF_6]$,[6] or coordination complexes, where divalent silver is stabilized by mono- or polydentate donor ligands.

Only recently[7a] have we reported on another binary silver(II) compound, $Ag(SO_3F)_2$, in a preliminary communication. Earlier unsuccessful attempts to obtain pure $Ag(SO_3F)_2$ have been summarized.[7b] We now describe in detail the synthesis and the structural characterization of $Ag(SO_3F)_2$ and of a number of new silver(II) fluorosulfate derivatives.

(B) Experimental Section

(I) Chemicals. All chemicals obtained from commercial sources were of reagent grade or of the highest purity obtainable. All silver(I) salts were used without further purification. Metallic silver powder, 100 mesh, of 99.999% purity was obtained from the Ventron Corp.

Dichloromethane and acetonitrile were dried using standard methods, degassed in vacuo, and stored over Linde 4A molecular sieves. Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) was distilled at reduced pressure (100 mmHg) from concentrated H_2SO_4 before use. Fluorosulfuric acid (Allied Chemicals) of technical grade was doubly distilled at atmospheric pressure as described.[8] Bromine(I) fluorosulfate,[9] $BrOSO_2F$, chloryl fluorosulfate,[10] ClO_2SO_3F, bis(fluorosulfuryl) peroxide,[11] $S_2O_6F_2$, silver(II) bis(α,α'-bipyridyl) bis(trifluoromethyl sulfate),[12] and KSO_3F[8] were synthesized according to literature methods. The solvolysis of silver trifluoroacetate, AgO_2CCF_3, in HSO_3F was found to be the simplest and most convenient route to silver(I) fluorosulfate, $AgSO_3F$.

(II) Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 457 or a Unicam SP1100 grating spectrophotometer. Depending on reactivity, thin films or Nujol mulls were used with BaF_2, AgCl, AgBr, KRS-5, or CsI as window materials (all obtained from Harshaw Chemicals). Spectra of gaseous materials were recorded using a Monel cell of 7-cm path length, fitted with AgCl windows and a Whitey valve.

IR spectra of liquid N_2 temperature were obtained on a Perkin-Elmer 225 grating spectrophotometer. A cell fitted with CsI windows and a "spray on" technique as described[13] previously were used. Raman spectra were obtained with a Spex Ramalog 5 spectrometer equipped with an argon ion laser using the line at 514.5 nm for excitation. The samples were contained in melting point capillaries. ESR spectra were recorded on a Varian Associates E-3 spectrometer equipped with 100-kHz field modulation at room temperature and at liquid nitrogen temperature. Powdered solids or solutions were contained in 4-mm o.d. quartz tubes.

Magnetic susceptibilities were determined using a Gouy apparatus described before.[14] Measurements were made at constant field strengths of approximately 4500 and 8000 G. All susceptibilities measured were found to be independent of field strength. Calibrations were carried out using $HgCo(CNS)_4$.[15] Diamagnetic corrections were obtained from the literature.[16] The diamagnetic correction for SO_3F^- was assumed to be identical with the value of SO_4^{2-} (40.1×10^{-6} cgsu). Electronic spectra were recorded on either a Cary 14 or a Perkin-Elmer Model 124 spectrophotometer. Diffuse reflectance spectra were recorded on a modified Bausch and Lomb Spectronic 600 spectrometer in the region of 350–740 nm.

The Mössbauer spectrometer has been described elsewhere.[17] Measurement was made at 80 K and the $Ba^{119m}SnO_3$ source at 298 K. The isomer shift is reported relative to SnO_2 absorber at 80 K. The accuracy for both isomer shift and quadrupole splitting is judged to be ±0.03 mm/s.

All moisture-sensitive solids and nonvolatile ligands were handled in a Vacuum Atmospheres Corp. "Dri-Lab", Model HE-43-2, filled with purified dry nitrogen and equipped with a "Dri-Train", Model HE-93B.

Volatile materials were distilled using vacuum-line techniques. The manifold was equipped with Kontes Teflon stem stopcocks.

Reactions involving fluorine were performed in Monel metal cans of about 150-mL contents fitted with a screw-on top and a Whitey valve. All other reactions were carried out in glass reaction vials of an approximate volume of 50 mL and fitted with Kontes Teflon stem stopcocks and equipped with Teflon-coated stirring bars. Where large amounts of highly volatile materials (O_2, CO_2) evolved, the reactions were carried out in thick-wall reaction vials. All reactions were monitored by weighing.

(III) Synthetic Reactions. (a) Silver(II) Fluorosulfate. All reactions leading to $Ag(SO_3F)_2$ together with their reaction times and tem-

0020-1669/78/1317-1765 01.00/0