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Synthesis, Structure, Electrochemistry, and Ligand Activity of the Dioxobis(μ -sulfido)bis(dithiocarbamato)dimolybdenum(V) Complex

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The synthesis and characterization of the sulfido-bridged oxomolybdenum(V) dimer of dithiocarbamate (NH_2CS_2^-), $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$, is reported. The complex crystallized in the orthorhombic space group $Pnma$, $a = 9.407$ (2) Å, $b = 20.877$ (4) Å, $c = 9.010$ (2) Å, $Z = 4$, with the neutral complex molecules hydrogen bonded to the nitrogen of the acetonitrile via the amine group of the dithiocarbamate ligand. Each molybdenum atom is centered above the base of a square-based pyramid, with the oxygen atoms coordinated on the same side of the bent MoS_2Mo bridge and a Mo-Mo distance of 2.820 (1) Å. Electrochemistry of the compound in dimethyl sulfoxide and acetonitrile was investigated by dc and ac polarography, cyclic voltammetry at Hg, Pt, and Au working electrodes, and controlled-potential electrolysis. The complex is reduced irreversibly in a two-electron process on both voltammetric and coulometric time scales, apparently with dissociation of the dithiocarbamate ligands occurring. The complex dissolves in aqueous base to produce an ESR-inactive solution that is stable at pH 12 in the absence of oxygen and whose absorption spectrum is consistent with retention of the $\text{Mo}_2\text{O}_2\text{S}_2^{2+}$ core; in air, this solution bleaches by a base-catalyzed path to a colorless solution in which the molybdenum is predominantly present as MoO_4^{2-} .

Introduction

Complexes of molybdenum with bidentate sulfur donor ligands such as dithiocarbamates, xanthates, dithiophosphinates, and dithiophosphates have been reported extensively in recent years.² The interest in the chemistry of these systems arises in part from the involvement of molybdenum associated with sulfur ligands in the redox-active molybdo enzymes.^{2,3} Although the chemistry of molybdenum complexes with N-substituted dithiocarbamic acid has been vigorously pursued,^{2,4} no complexes have yet been reported with the unsubstituted parent dithiocarbamate NH_2CS_2^- (dte^-). Although the synthesis of dte^- is well documented,⁵ it is an unstable species that decomposes at room temperature unless coordinated. It has occurred to us that the stabilizing effects of N-alkyl groups on dithiocarbamates probably reduce the level of reactivity of coordinated alkyldithiocarbamates as well. We were interested, therefore, in making molybdenum complexes with the more unstable dte^- in order to examine their properties, especially those involving ligand activity. For instance, the dte^- amine protons should be quite acidic and might bind to polymers that bind amino acids and proteins to give bound complexes from which columns of catalytic material might be prepared.

We report here the successful preparation and characterization of a dimeric Mo(V) compound containing unsubstituted dithiocarbamate, $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$ (I). The structure has been established by X-ray structure analysis, and investigations of the physical properties, electrochemistry in aprotic solutions, and reactivity of the complex in aqueous base have begun.

Experimental Section

Preparation of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$. Ammonium heptamolybdate (1.77 g, 5 mmol) was dissolved in water (50 mL), ammonium acetate (10 g) was added, and a solution of ammonium dithiocarbamate⁵ (2.20 g, 20 mmol) in water (20 mL) was added dropwise with vigorous stirring over a period of 30 min. Subsequently, 0.1 M HCl (20 mL) was added over a period of 2 h. The final

Table I. Crystallographic Summary for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$

(A) Crystal Data	
cryst syst	orthorhombic
space group	$Pnma$
a , Å	9.407 (2)
b , Å	20.877 (4)
c , Å	9.010 (2)
V , Å ³	1769.5
D_{calcd} , g cm ⁻³	2.081
empirical formula	$\text{C}_6\text{H}_{10}\text{Mo}_2\text{N}_4\text{O}_2\text{S}_6$
fw	554.4
Z	4
μ , cm ⁻¹	20.31
$F(000)$	1144
color	green
dimens	0.13 × 0.07 × 0.25
habit	needles
T , °C	23
(B) Data Collection	
diffractometer	Enraf-Nonius CAD4 four-circle
radiation	Mo K α ($\lambda = 0.7107$ Å)
monochromator	graphite
mode	ω -2 θ ; 3/scan
θ range, deg	1.2-22
ω scan angles, deg	1.0 + 0.35 tan θ
horiz counterapertures, mm	2.4 + 0.5 tan θ
reflens measd	1062 (+ h , + k , + l)
reflens employed	983 ($I > 2.5\sigma(I)$)
cor applied	absorption (Gaussian integration) ⁷ and Lorentz and polarization ⁷

yellow-brown precipitate was filtered, washed several times with water and then ethanol and ether, and dried in vacuo. Almost identical results were obtained without ammonium acetate. The precipitate was dissolved in a minimum volume of dried, degassed acetonitrile; upon standing under vacuum in a desiccator for several days, yellow-brown crystals of the product were obtained and collected by filtration. Anal. Calcd for $\text{C}_6\text{H}_{10}\text{N}_4\text{Mo}_2\text{O}_2\text{S}_6$: C, 13.00; H, 1.81; N, 10.10; S, 34.69. Found: C, 12.84; H, 1.7; N, 9.9; S, 34.3. Absorption spectrum (λ , nm (ϵ , M⁻¹ cm⁻¹)) in acetonitrile: 370 sh (1760), 350 sh (2780), 270 (16800), 240 (31800). Infrared spectrum (KBr disk):⁶ 3270 (br, s), 3160 (br, s), 2260 (m), 1695 (m), 1630 (m), 1605 (sh, m), 1455 (s), 970 (s), 960 (s), 848 (m), 710 (br, m), 675 (br, m), 620 (m), 548 (m), 475 (m), 395 (s), 335 (m) cm⁻¹. The crystalline product slowly loses acetonitrile if left in the air but can be stored indefinitely in an acetonitrile-saturated atmosphere. The amorphous solid obtained on standing in the air can be recrystallized from acetonitrile to regenerate the original product.

- (1) (a) University of Illinois. (b) On leave at the The Australian National University, 1981-1982. (c) University of Adelaide. (d) The Australian National University.
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- (3) Steifel, E. J.; Newton, W. E.; Watt, G. D.; Hadfield, K. L.; Bulen, W. A. *Adv. Chem. Ser.* 1977, No. 162, 353.
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(6) Abbreviations: br = broad, s = strong, m = medium, sh = shoulder.

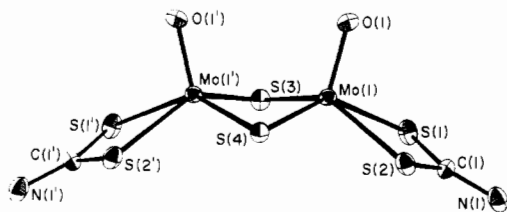


Figure 1. ORTEP diagram of the $\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2$ molecule.

Structure Solution and Refinement. A crystallographic summary is presented in Table I.⁷ The position of the molybdenum atom was determined from a three-dimensional Patterson synthesis, and all other non-hydrogen atoms were located from a difference Fourier phased on the metal atom site. Refinement of all atoms with anisotropic thermal parameters and calculation of a further difference map revealed all expected hydrogen atoms. These were subsequently included and refined.

Full-matrix least-squares refinement was used to refine all positional and thermal parameters and an overall scale factor. A weighting scheme was also applied and refined, converging at $w = 1.0/(\sigma^2(F_o) + 0.0016F_o^2)$. Overall refinement converged (all shifts less than 0.5σ) with $R = 0.030$ and $R_w = 0.035$ ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \sum(|F_o| - |F_c|)w^{1/2}/\sum|F_o|w^{1/2}$). There were no structurally significant peaks in a final difference map; the largest (ca. $0.6 \text{ e } \text{\AA}^{-3}$) are located in the vicinity of the molybdenum atom.

All calculations were performed with the SHELX⁸ system of programs, and all scattering factors (neutral Mo for Mo(V)) and anomalous dispersion terms were taken from ref 9.

Physical Measurements. Infrared spectra were recorded as KBr disks with a Perkin-Elmer 683 spectrophotometer. ESR spectra were recorded at room temperature with a Bruker ER200D spectrometer.

Electrochemical studies were performed with a conventional three-electrode configuration with *iR* compensation and a PAR Model 170 electrochemical system. For rapid-scan cyclic voltammograms (to 200 V/s), a Tektronix C-70 oscilloscope camera coupled to a Tektronix 5031 dual-beam storage oscilloscope and the PAR Model 170 were used. Working electrodes employed were a dropping-mercury-drop electrode (DME) for dc and ac techniques and a hanging-mercury-drop electrode (HMDE) or stationary platinum or gold-billet electrode for cyclic voltammetry (CV). The reference electrode was Ag/AgCl and was separated from the working and auxiliary electrodes in an electrode bridge with a fine-porosity frit. The auxiliary electrode was a platinum coil. Solutions were deoxygenated with solvent-saturated argon through a standard purge tube. Dried (molecular sieves) and distilled analytical reagent grade acetonitrile or dimethyl sulfoxide were used as solvents. Tetrabutylammonium tetrafluoroborate (0.1 M) or tetramethylammonium trifluoromethanesulfonate (0.1 M) were used as electrolytes, with complex concentrations in the millimolar range.

Coulometric analysis were performed with a PAR Model 377A coulometry cell system using a platinum-basket working electrode and an Amel Model 551 potentiostat and Model 731 digital integrator.

Results

A facile synthesis of the $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$ dimer of the unsubstituted dithiocarbamate has been developed and the structure confirmed by X-ray crystal analysis. The structure consists of neutral complex molecules and acetonitrile molecules of crystallization. There are hydrogen bonds between the nitrogen of the acetonitrile molecules and the $-\text{NH}_2$ groups of the dte^- ligand. Close-contact dimensions are as follows: for $\text{N}(1)-\text{H}(2) \cdots \text{N}(2)$, $\text{N} \cdots \text{N} = 3.142 \text{ \AA}$ and $\text{N} \cdots \text{H} = 2.21 \text{ \AA}$; for $\text{N}(1)-\text{H}(1) \cdots \text{N}(2)$, $\text{N} \cdots \text{N} = 3.023 \text{ \AA}$ and $\text{N} \cdots \text{H} = 2.19 \text{ \AA}$. Attempts to obtain crystals from dichloromethane, chloroform, and acetone solutions, where such strong hydrogen-bonding interactions with solvents of crystallization are

Table II. Positional Parameters ($\times 10^3$) for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$

	x	y	z
Mo(1)	5116 (1)	1825 (1)	4903 (1)
S(1)	3209 (1)	1018 (1)	4912 (1)
S(2)	5669 (1)	1001 (1)	6770 (1)
S(3)	3330 (1)	$1/4$	4052 (2)
S(4)	6328 (1)	$1/4$	6518 (2)
O(1)	6171 (3)	1632 (1)	3470 (3)
C(1)	4167 (4)	605 (2)	6224 (4)
N(1)	3767 (5)	67 (2)	6785 (5)
C(2)	4548 (7)	1699 (2)	267 (6)
C(3)	4281 (4)	1045 (2)	637 (5)
N(2)	4052 (4)	532 (2)	968 (5)
H(1)	298 (6)	-9 (2)	658 (5)
H(2)	448 (7)	-14 (3)	735 (7)
H(3)	597 (6)	-199 (2)	904 (6)
H(4)	620 (11)	-186 (3)	61 (11)
H(5)	76 (9)	188 (3)	422 (11)

Table III. Bond Lengths (\AA) and Valence Angles (deg) for $[\text{Mo}_2\text{O}_2\text{S}_2(\text{dte})_2] \cdot 2\text{CH}_3\text{CN}$

Bond Lengths			
S(1)-Mo(1)	2.460 (1)	S(2)-Mo(1)	2.461 (1)
S(3)-Mo(1)	2.324 (1)	S(4)-Mo(1)	2.325 (1)
O(1)-Mo(1)	1.677 (3)	Mo(1)-Mo(1)	2.820 (1)
C(1)-S(1)	1.718 (4)	C(1)-S(2)	1.711 (4)
N(1)-C(1)	1.287 (5)	C(3)-C(2)	1.426 (7)
N(2)-C(3)	1.134 (5)		
Valence Angles			
S(2)-Mo(1)-S(1)	71.0	S(3)-Mo(1)-S(1)	83.6
S(3)-Mo(1)-S(2)	143.3	S(4)-Mo(1)-S(1)	140.4
S(4)-Mo(1)-S(2)	83.8	S(4)-Mo(1)-S(3)	101.1
O(1)-Mo(1)-S(1)	105.7 (1)	O(1)-Mo(1)-S(2)	103.5 (1)
O(1)-Mo(1)-S(3)	108.6 (1)	O(1)-Mo(1)-S(4)	109.7 (1)
Mo(1)-S(3)-Mo(1)	74.7	Mo(1)-S(4)-Mo(1)	74.7
C(1)-S(1)-Mo(1)	87.9 (1)	C(1)-S(2)-Mo(1)	88.1 (1)
S(2)-C(1)-S(1)	112.8 (2)	N(1)-C(1)-S(1)	123.7 (4)
N(1)-C(1)-S(2)	123.4 (4)	N(2)-C(3)-C(2)	178.0 (5)

less likely, were not successful. An ORTEP plot of the complex molecule with the atom-numbering scheme employed is shown in Figure 1. The Mo atom lies on a general site (multiplicity 8), while S(3) and S(4) lie in the mirror plane at $y = 1/4$, giving four dimeric molecules per unit cell. Mo(1) and Mo(1') are related by this mirror, and the symmetry of the molecule is crystallographically maintained at C_2 . Overall, molecule symmetry approximates C_{2v} . Positional parameters are collected in Table II, while bond lengths and bond angles are collected in Table III. Observed and calculated structure factors for the compound have been deposited as supplementary material.

The infrared spectrum is fully consistent with the structure. A sharp band at 2260 cm^{-1} due to $\text{C}\equiv\text{N}$ of the hydrogen-bonded acetonitrile of crystallization was observed. Amine stretching vibrations ($3270, 3160 \text{ cm}^{-1}$) and bending modes ($1630, 1605 \text{ cm}^{-1}$) can be assigned. The C-N stretch occurs at 1455 cm^{-1} , with the C-S (dte^-) and Mo-S (dte^-) stretches possibly at 620 and 395 cm^{-1} , respectively. The terminal molybdenyl moieties are characterized¹⁰ by the strong $\nu(\text{Mo}-\text{O}_t)$ bands at 970 and 960 cm^{-1} , while the characteristic modes for the bis(μ -sulfido) bridge⁴ are observed at 475 and 355 cm^{-1} . The molybdenyl and bis(μ -sulfido) resonances have been assigned at similar positions in the $\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2\text{CNET}_2)_2$ analogue although the C-N stretching vibration in alkylidithiocarbamates is usually in the range $1480\text{--}1550 \text{ cm}^{-1}$.¹¹ A normal-coordinate analysis of $\text{Pt}(\text{dte})_2$ has been reported,¹²

(7) "SUSCAD, Data Reduction Program for the CAD4 Diffractometer" and "ABSORD, Absorption Correction Program for the CAD4 Diffractometer"; University of Sydney: Sydney, Australia, 1976.

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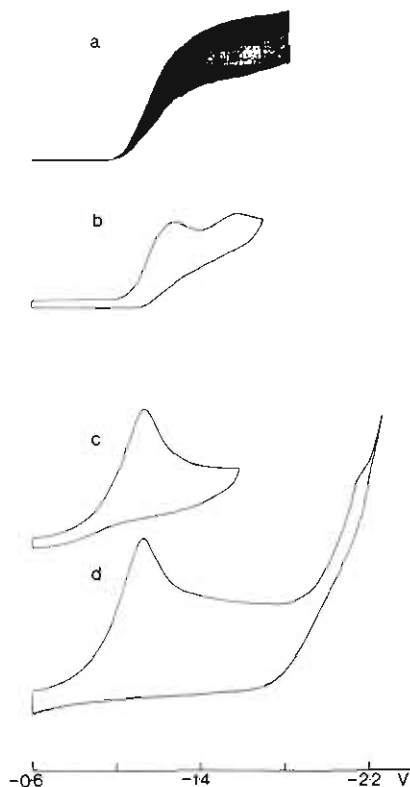


Figure 2. Representative voltammetric results for Mo₂O₂S₂(dte)₂ in Me₂SO: (a) dc polarogram; (b) CV at the HMDE (scan rate 20 V/s); (c) CV at stationary Pt (scan rate 200 mV/s, switching potential at -1.6 V); (d) CV at stationary Pt (scan rate 200 mV/s, switching potential at solvent limit).

and most of the vibrations assigned to chelated dtc⁻ closely approximate bands observed in the present complex.

The electrochemistry was investigated in both dimethyl sulfoxide (Me₂SO) and acetonitrile (ACN) with (Bu₄N)(BF₄) or (Me₄N)(CF₃SO₃) electrolytes; results in each solvent were essentially the same. The complex displays a single irreversible wave near -1.1 V in both solvents at Pt and Au electrodes. Coulometry at a potential 200 mV more negative than the reduction potential in Me₂SO and ACN at a Pt electrode yielded *n* = 2; further, application of the Ilkovic equation (dc at the DME)¹³ or the appropriate and approximate equation for CV at a stationary electrode¹⁴ employing *n* = 2 to data at all working electrodes yielded a diffusion coefficient of ~2.5 × 10⁻⁶ cm², similar to the diffusion coefficient obtained for Mo₂O₃Q₄ (Q = 8-quinolinol)¹⁵ and Mo₂X₄(Etdtc)₂ (X₄ = O₃S, O₂S₂, OS₃, S₄; Etdtc⁻ = ⁻S₂CN(C₂H₅)₂). Selection of other values of *n* yielded values of *D* that are unreasonable for molecules of the size, and hence the reduction appears to be two-electron in nature on both the voltammetric and coulometric time scales.

Cyclic voltammetry at each electrode at scan rates of up to 200 V/s showed no reverse wave, with the current at the foot of the wave independent of sweep rate. This could indicate that the forward electron transfer is totally irreversible, which would result if any follow-up chemical process leading to an electroinactive species were faster than the reverse electron transfer to regenerate the precursor.¹⁶ Further, the peak

Table IV. Electrochemical Data for the Two-Electron Reduction of Mo₂O₂S₂(LL)₂^a

LL	solvent	elec-trode	<i>E</i> _{1/2} (dc), V	<i>E</i> _p (ac) ^b , V	<i>E</i> _p (CV) ^c , V	<i>n</i> ^d
dte	CH ₃ CN	Hg	-1.10	-1.02, -1.28	-1.23	2.1
		Au	-1.28	
		Pt	-1.20	
	Me ₂ SO	Hg	-1.15 ^e	-1.20, -1.37	-1.20, -1.40 ^f	2.2
		Au	-1.18	
		Pt	-1.14	
Etdtc ^g	Me ₂ SO	Pt	-1.30, -1.61 ^h	~2

^a Potentials vs. Ag/AgCl unless otherwise stated. A determination vs. calomel in one case gave differences of <0.05 V. ^b ω = 40 Hz; Δ*E*_{pp} = 10 mV. ^c *v* = 200 mV/s unless otherwise stated. ^d From controlled-potential electrolysis 200 mV more negative than *E*_{1/2}. ^e *E*_{1/4} - *E*_{3/4} = 140 mV; *D* = 2.6 × 10⁻⁶ cm² s⁻¹; *n* = 2. ^f *v* = 20 V/s. ^h Vs. saturated calomel.

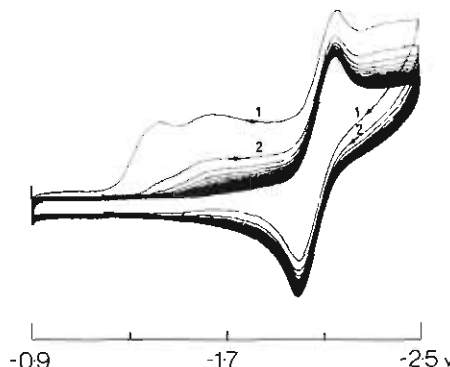


Figure 3. Repeat-scan CV at the HMDE for Mo₂O₂S₂(dte)₂ in Me₂SO (scan rate 10 V/s).

potential shifts in the positive direction with decreasing scan rate and with increasing concentrations of complex, while the voltammetric current parameter (*i*_p/*v*^{1/2}AC) was constant over the range of scan rates at Pt.

Results at the Hg electrode are complicated by adsorption processes, which were identified from ac polarography and comparative cycle voltammetry at several different electrodes. The dc polarogram exhibited a single relatively broad wave centered at -1.15 V; the wave shape is concentration dependent and solvent dependent, but the limiting current is fully consistent in all cases with a two-electron reduction. From ac polarography, waves were observed at -1.20 V (with a clear shoulder at -1.12 V) and -1.37 V. Phase-sensitive and concentration-dependent ac polarography indicated that the first wave involves adsorption as well as electron-transfer character, since the wave shape is concentration dependent, and a significant quadrature ac signal was observed.¹⁷ The ac wave heights were essentially first order in complex concentration and were, apart from adsorption effects, frequency independent, which is consistent with the operation of a rapid following chemical reaction.¹⁷ The cyclic dc at the HMDE is not a simple wave (Figure 2b): At fast scan rates in Me₂SO, a small wave at ~-1.4 V follows the initial reduction wave at ~-1.2 V, while in ACN the second wave is not observed, although the single wave is broad. The peak maxima are scan rate dependent and shift to more negative potentials at higher scan rates (Δ*E*/Δ(log *v*) ~30 mV per decade). However, cyclics at Pt or Au exhibit only a single simple reduction wave

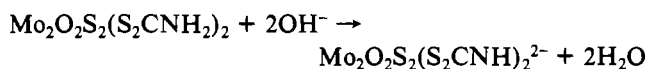
(13) *i*_d = 706*nCD*^{1/2}*m*^{2/3}*t*^{1/6}; see, for example: Crow, D. R. "Polarography of Metal Complexes"; Academic Press: London, 1969; Chapter 2.
 (14) For an irreversible process, *i*_p = 602(*an*)^{1/2}*AD*^{1/2}*v*^{1/2}*C**χ*⁰ (Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 723); with the maximum value of *χ*⁰ (0.4958) and α = 0.5, this reduces to the approximation *i*_p = 211*n*^{1/2}*ACD*^{1/2}*v*^{1/2}, which is sufficiently accurate to determine *D* for various *n* values for this exercise.
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($E_p = -1.14$ V, 200 mV/s CV; stationary Pt in Me_2SO). Therefore, the assignment of the complicated waves observed at Hg to two sequential one-electron processes is not compelling, and the behavior at Hg arises from adsorption/desorption phenomena. Representative scans are collected in Figure 2, and reduction potentials are included in Table IV.

Apart from the wave near -1.2 V, no further reductions are observed before -2 V and no oxidations up to $+1$ V. An apparently irreversible wave is observed at the Pt electrode in Me_2SO with $E_p = -2.2$ V, but the process is very near the solvent limit for that system (Figure 2). At the HMDE, a quasi-reversible couple is established at -2.05 V in Me_2SO ($\Delta E_p = 70$ mV, 200 mV/s CV); this behavior is illustrated in Figure 3. This wave corresponds in position to the wave at Pt and is assigned to the reversible one-electron couple for free $\text{dtc}^- + e^- = \text{dtc}^{2-}$ reported to occur near -2 V.¹⁸ The well-defined reversible couple at the HMDE is related to adduct formation at that electrode surface. The implication of this observation is that reduction of the Mo^V dimer involves dissociation of dtc^- in a rapid chemical step following electron transfer. This is supported by voltammetric analysis of the product of the controlled-potential reduction of the complex. The polarogram of the reduction product in Me_2SO showed a wave at -2.0 V and a double wave associated with oxidation to $(\text{dtc})_2$ at -0.45 and -0.15 V, identical with waves for an authentic sample of free dtc^- in Me_2SO . Addition of dtc^- enhanced those waves observed in the reduction product. Apart from free dtc^- , the coulometrically reduced product exhibited an irreversible wave near the solvent limit at -2.4 V, which is not coupled with the dtc^- reduction wave, since addition of dtc^- does not alter the size of the wave, and is apparently a metal-centered electron transfer. The absorption spectrum of the reduction product of I in Me_2SO exhibited shoulders at 350 nm (ϵ 5900) and 295 nm (ϵ 14 600), and was ESR inactive. No oxidation waves (apart from dtc^-) were observed below $+0.7$ V. The Mo^{IV} product is not similar to species such as $\text{Mo}^{IV}\text{O}(\text{Etdtc})_2$ in absorption spectrum¹⁹ or electrochemical behavior,¹⁸ which is consistent with the absence of coordinated dtc^- in the product.

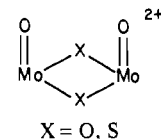
The neutral dimer I dissolves in aqueous base to produce a yellow solution that is ESR inactive. Potentiometric titration of the solid dimer I with aqueous sodium hydroxide gives a shallow break at a mole ratio of 2 OH^- per dimer at which dissolution of I was complete:



At pH 12 in the absence of oxygen, the complex is stable for appreciable periods, with absorption maxima at 295 nm (ϵ 680), 325 nm (sh, ϵ 1200), and 395 nm (ϵ 2200). This intermediate fades in air at a rate that is first order in complex to produce a colorless solution of MoO_4^{2-} . (Related species such as $\text{MoO}_3\text{S}^{2-}$ and $\text{MoO}_2\text{S}_2^{2-}$ exhibit absorption bands in the visible region.) Rough preliminary experiments indicate $t_{1/2} \sim 20$ min and 40 min in 6 and 3 M NaOH, respectively. The absorption spectrum of the intermediate is not markedly different from that of the $\text{Mo}_2\text{O}_2\text{S}_2^{2+}(\text{aq})$ core (maxima at 370, 310 sh, and 290 nm),²⁰ and it is likely that the integrity of the dimer is preserved upon initial dissolution. Studies of the reactivity of the complex, especially ligated dtc , will continue.

Discussion

The $\text{Mo}_2\text{X}_4^{2+}$ core (X = O, S) is commonly encountered in molybdenum(V) chemistry



and examples of the single family from $\text{Mo}_2\text{O}_4\text{L}_2$ to $\text{Mo}_2\text{S}_4\text{L}_2$ have been reported recently for the L = Etdtc^- chelate.⁴ While such complexes of *N,N*-dialkyl-substituted dithiocarbamate have been widely reported, no analogues of the parent dithiocarbamate have been published prior to this study.

Under experimental conditions similar to those described in the synthesis of I, substituted dithiocarbamates yield MoO_2L_2 .²¹ It is conceivable that $\text{MoO}_2(\text{dtc})_2$ formed initially is unstable and decomposes to produce $\text{Mo}_2\text{O}_4(\text{dtc})_2$, SCN^- , and H_2S . The H_2S produced in situ may account for the ultimate formation of $\text{Mo}_2\text{O}_2\text{S}_2(\text{dtc})_2$, with the change from Mo(VI) to Mo(V) being accommodated via a $-\text{S}^- \rightarrow (-\text{S}-\text{S}-) + e^-$ reaction such as $\text{SCN}^- \rightarrow (\text{SCN})_2 + e^-$. It is notable that release of S^{2-} from R_2NCS_2^- to form a bis(μ -sulfido) dimolybdenum complex with a chelated R_2NCS_2^- ligand has been observed and established by a crystal structure analysis,²² and various routes to the product may be available. Certainly, all our attempts to produce $\text{Mo}^{VI}\text{O}_2(\text{dtc})_2$ by a variety of routes were unsuccessful. $\text{Mo}^{VI}\text{O}_2(\text{S}_2\text{CNR}_2)_2$ is usually the initial product when our procedures are used with *N*-alkyl dtc ligands.

I has been characterized by an X-ray structural investigation (Figure 1) and is structurally similar to the previously reported compounds $\text{Mo}_2\text{S}_4(\text{Etdtc})_2$,^{23,24} $\text{Mo}_2\text{S}_4(\text{Budtc})_2$,²⁵ ($\text{Budtc} = \text{N,N}$ -di-*n*-butyldithiocarbamate), and $\text{Mo}_2\text{O}_2\text{S}_2(\text{Cyst})_2$,²⁶ ($\text{Cyst} = \text{L-cysteine}$). The diamagnetism of all these complexes suggests a strong metal-metal interaction, which is apparent from the structural analysis. The Mo-Mo distances are 2.820 (1), 2.817 (2), 2.801 (2), and 2.804 (4) Å for $\text{Mo}_2\text{O}_2\text{S}_2(\text{dtc})_2$, $\text{Mo}_2\text{S}_4(\text{Etdtc})_2$, $\text{Mo}_2\text{S}_4(\text{Budtc})_2$, and $\text{Mo}_2\text{O}_2\text{S}_2(\text{Cyst})_2$, respectively. All structures exhibit the characteristic bent MoX_2Mo bridge with cis terminal $\text{Mo}=\text{X}$ groups, and each metal is centered above the base of a square-based pyramid. To date, complexes with the $\text{Mo}_2\text{X}_4^{2+}$ core exhibit a planar bridge and trans terminal $\text{Mo}=\text{X}$ groups only with cyclopentadienyl ligands.^{27,28} Crystal structures of analogues of I often fail to report bond angles and distances within the ligands. The C-N bond distance in I is 1.287 Å vs. 1.303 Å in $\text{Mo}_2\text{S}_4(\text{Etdtc})_2$;²⁴ MoSC, S MoS , and SCS bond angles and C-S bond lengths are not sensibly different among the structural analogues.

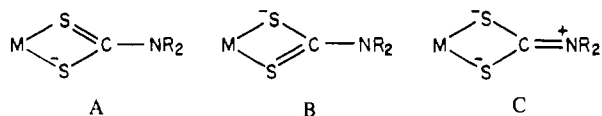
Earlier, the electrochemical reduction of $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etdtc})_2$ in dimethylformamide was studied by DeHayes and co-workers,¹⁸ who suggested the bis(μ -sulfido) complex was reduced in two reversible $1/2$ -electron steps at -1.0 and -1.35 V. A more recent study of Schultz and co-workers⁴ for the series $\text{Mo}_2\text{X}_4(\text{Etdtc})_2$ (X = O_3S through to S_4) established the process to involve two sequential one-electron steps observed at -1.3 and -1.6 V for $\text{Mo}_2\text{O}_2\text{S}_2(\text{Etdtc})_2$ in Me_2SO , with the first process reversible at fast scan rates. On the coulometric time scale, they observed a two-electron irreversible reduction. We observed a two-electron irreversible reduction on both the

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voltammetric and coulometric time scales for I, analogous to the behavior of the Mo₂O₄(Etdtc)₂ complex.^{4,18} Apparently, the substitution of Etdtc⁻ by dtc⁻ alters the stability of the intermediate sufficiently to limit the observation of two sequential steps, or the reductions are sufficiently close to appear as a composite step. Certainly, the ac polarography could be interpreted as two sequential processes separated by ~200 mV, although adsorption phenomena complicate such a description. Overall, the electrochemistry is fully consistent with a two-electron process analogous to the behavior described for the Etdtc⁻ analogue by Schultz and co-workers.⁴

It is apparent that the C–N stretch in the IR spectrum of the dtc⁻ complex (1455 cm⁻¹) differs from the usual position of the vibration in alkyldithiocarbamates (1480–1550 cm⁻¹),¹¹ implying differing contributions in each case from the canonical forms



The shift in the C–N stretching frequency toward the C–N single-bond region (1250–1350 cm⁻¹) rather than the C=N region (1640–1690 cm⁻¹)²⁹ in I implies canonical form C is less represented, i.e., less electron density at the metal center that might promote reduction. The cathodic peak potential at Pt for reduction of I in Me₂SO of –1.14 V is ~150 mV less negative than the first reduction of the Etdtc⁻ analogue. The effect of hydrogen bonding on the IR stretch in the dtc⁻ complex (I) cannot be easily assessed, but the difference between dtc⁻ and Rdtc⁻ complexes appears to be fairly general. Since SCF–MO calculations of Mo₂O₄²⁺ and Mo₂O₂S₂²⁺ centers show that the orbitals of lowest energy are either Mo–Mo bonding or antibonding in nature and contain substantial contributions from terminal and bridging atoms,³⁰ it is likely that reduction involves electron transfer into orbitals distributed over the core. The way in which the dithiolate ligands affect the redox potential will then most likely be related to their contribution to the electron density of the core.

The nature of the Mo^{IV} product of reduction has not been established, although there is good evidence that dtc⁻ is released on reduction in Me₂SO. The irreversible two-electron reduction of the thioxanthate complex Mo₂O₄(S₂CSC₃H₇)₂

likewise leads to release of thioxanthate ligand.³¹ The molybdenum product is not spectroscopically similar to species such as Mo^{IV}O(Etdtc)₂; no metal-centered redox processes are observed between +0.7 and –2 V, with only one reduction wave at –2.4 V. The prospect of some stable polymeric solvento oxomolybdenum(IV) species being formed exists, and attempts to identify the product will be pursued.

Unlike the *N,N*-dialkyldithiocarbamates, the parent dithiocarbamate can in principle be deprotonated at the amine to yield an anionic and therefore water-soluble species. Dissolution of I in aqueous base (pH 12) in the absence of oxygen produces a stable yellow solution that retains the Mo₂O₂S₂²⁺ core, since it is spectroscopically similar to Mo₂O₂S₂^{2+(aq)}. In the presence of oxygen, this solution bleaches to a colorless solution of MoO₄²⁻, the dominant form of Mo(VI) in aqueous base. The latter process is catalyzed by base, and it is possible that base-catalyzed decomposition of the dimer precedes a rapid oxidation to the Mo(VI) state. Similar behavior has been observed for Mo₂O₄²⁺ complexes with pyrophosphate and triphosphate ions,³² and base-catalyzed disproportionation of Mo₂O₄²⁺ complexes has been studied.³³

It is clear that dtc⁻ does provide greater reactivity than its alkyl analogues. Complex I forms hydrogen bonds and reacts with strong base. There is some evidence that the amine of dtc⁻ will bind to appropriate groups on agarose.³⁴ Analysis of an amorphous mass obtained from the action of water on I gave N:C:S of 1:2:4, consistent with two ligands condensing with each other to give (S₂C=N=CS₂)³⁻ and NH₄⁺ or (S₂C=NHCS₂)²⁻ and NH₃. Such condensed ligand could each bind to two Mo atoms, possibly forming higher polymers with Mo₂O₂S₂²⁺ cores. These and other aspects of the reactivity of I will be further investigated.

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Registry No. I, 90065-77-3.

Supplementary Material Available: Listings of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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