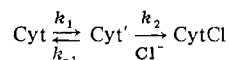


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binding was not important in her system. We would suggest that chloride binding could occur but the rate of conversion would be relatively insensitive to chloride concentration in at least two possible cases, as follow.

(a) A rate-determining dissociation step: if

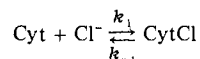


then

$$\frac{d[\text{CytCl}]}{dt} = \frac{k_2 k_1 [\text{Cl}^-]}{k_{-1} + k_2 [\text{Cl}^-]} [\text{Cyt}c]$$

assuming Cyt' to be in steady-state concentrations; if $k_2[\text{Cl}^-] \gg k_{-1}$, then the rate will be independent of chloride.

(b) A reestablishment of an equilibrium



$$\frac{d[\text{CytCl}]}{dt} = (k_1 [\text{Cl}^-] + k_{-1}) [\text{Cyt}c]$$

If $K = k_1/k_{-1} < 0.1 M^{-1}$, then changing the chloride concentration from 0.05 to 0.15 *M* will have only a small effect on the rate. Thus, a wider range of experiments must be performed before potential binding ligands such as thiocyanate or chloride can be proven not to be binding.

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Electrochemical Studies of Oxo- and Sulfido-Bridged Molybdenum(VI), -(V), and (IV) Diethyldithiocarbamate Complexes in Aprotic Solvents

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The electrochemistry of a series of *N,N*-diethyldithiocarbamate (DTC) complexes of molybdenum(VI), -(V), and -(IV) has been studied in dimethyl sulfoxide, dimethylformamide, and acetonitrile at platinum electrodes. The specific complexes that have been investigated by cyclic voltammetry and controlled-potential coulometry are $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$, $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4$, $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$, $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$, $\text{Mo}^{\text{VI}}\text{S}_2(\text{DTC})_2$, and $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ and include binuclear molybdenum groups with oxo and sulfido bridges. Oxidation-reduction mechanisms are proposed on the basis of the electrochemical data, spectroscopic measurements, and analysis of the electrolysis products. In all three solvents the monooxo-bridged molybdenum(V) complex $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_2$ disproportionates to the Mo(VI) and Mo(IV) complexes. The disulfido-bridged molybdenum(V) complex $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ undergoes a one-electron reduction at -1.00 V vs. SCE in dimethylformamide to give a product species that reacts with the parent complex to form a mixed oxidation state tetramer, $[\text{Mo}_4\text{O}_4\text{S}_4(\text{DTC})_2]^-$. The later is reduced by a second electron at -1.35 V to give the corresponding dianion.

Molybdenum is an important trace element in living organisms and is known to occur in at least five enzymes; xanthine oxidase,¹ aldehyde oxidase,² nitrate reductase,³ sulfite oxidase,⁴ and nitrogenase.⁵ All of these enzymes catalyze oxidation-reduction processes that involve two or more electrons per substrate molecule. In each case the enzyme appears to contain two atoms of molybdenum, and in the cases of xanthine oxidase, aldehyde oxidase, and possibly nitrate reductase, two molecules of flavine also are present in the enzyme.⁴

Although some Mo(V) has been detected by ESR in four of the enzymes in the presence of a substrate,^{2,3,6-8} the oxidation state(s) of the molybdenum atoms in each of the native enzymes is (are) not known; the VI, V, IV, and III states have

been postulated.⁴ Regardless of the direction of the electron flow in these systems, evidence indicates a close interaction between flavine and molybdenum in the molybdoflavoprotein enzymes.⁹

The importance of molybdenum in flavoproteins has been reviewed from the standpoint of possible coordination chemistry¹⁰ and has prompted a study of the kinetics of complex formation in aqueous solution between Mo(VI) and 8-quinolinol;¹¹ this latter complex has been proposed as a model for xanthine oxidase. A review of oxomolybdenum(VI) and -(V) and their complexes provides a useful background for electrochemical studies of Mo(VI) and -(V) model compounds.¹²

The question of the degree of interaction or association

between molybdenum and flavine, as well as an interest in the electron-transfer processes in molybdoflavoproteins, has led to several recent studies by our group of the molybdenum complexes formed with 8-quinolinol^{13,14} and with the riboflavin anion radical in aprotic solvents.¹⁵ The results of these studies indicate that the inner coordination sphere about the molybdenum has a profound effect upon both its redox chemistry and its spectroscopy. In particular, the presence of terminal and/or bridging oxo groups coordinated to the molybdenum has been shown to be a dominant feature of the chemistry of molybdenum in its higher oxidation states (IV, V, VI). This consideration combined with the extensive presence of inorganic sulfide in a number of these molybdenum-containing enzymes has led us to consider whether sulfur might not be an equally important coordinating group for biological molybdenum.

Molybdenum(V) appears to prefer to be in the form of a binuclear oxo-bridged species under conditions analogous to biological acidity. For the 8-quinolinol complexes this has led to interesting electrochemical results, including formation of transient mixed oxidation state Mo^V-Mo^{IV} and Mo^V-Mo^{VI} dimeric species.¹³ Stabilization of such mixed oxidation states would account for the observed ESR signals in xanthine oxidase, while still permitting the close association of the two molybdenum atoms.

To elucidate further the oxidation-reduction chemistry of binuclear oxo-bridged molybdenum species as well as to ascertain the effects of the introduction of sulfur into the inner coordination sphere on this redox chemistry, the present investigation of the complexes formed between molybdenum(IV)-(V), and -(VI) and the *N,N*-dialkyldithiocarbamate ligand has been undertaken. Because this ligand system provides a more electron-rich environment than 8-quinolinol, the results should further clarify the importance of flavine association with molybdenum in molybdoflavoenzymes. Specifically, the goal has been to learn the effect of substituting *N,N*-dialkyldithiocarbamate for 8-quinolinol in molybdenum complexes and the effect of substituting bridging sulfido groups for a bridging oxo group.

In addition the present investigation has attempted to determine the effects of different aprotic solvents upon the chemistry and electrochemistry of these molybdenum *N,N*-dialkyldithiocarbamate complexes. The results of such studies may provide insight into the importance of solvation and media properties upon the oxidation-reduction chemistry of the molybdoenzyme enzymes.

During the course of the present studies, Pace and Watt presented some results concerning the electrochemistry of the oxomolybdenum *N,N*-dialkyldithiocarbamate complexes in acetonitrile.¹⁶ In several instances our results appear to conflict with their interpretations.

Experimental Section

Materials and Measurements. The cyclic voltammetric experiments were performed using a versatile instrument constructed from Philbrick operational amplifiers.¹⁷ The controlled-potential electrolysis experiments were performed using a Wenking Model 61RH potentiostat. Coulometry was accomplished by integrating the current-time curve using a K&E Model 62005 compensating polar planimeter. For cyclic voltammetry, a Beckman platinum-inlay electrode was used as the working electrode; a platinum gauze electrode was employed as the working electrode in the coulometric experiments. The reference electrode was comprised of an Ag-AgCl electrode in aqueous tetramethylammonium chloride solution (0.000 V vs. SCE) contacted in a tube having a cracked glass bead junction.

All electrochemical experiments and transfers to airtight spectrometer cells were carried out in a Vacuum Atmospheres Corp. Dry-Lab glove box because of the oxygen-sensitive nature of the reduced species.

The electronic spectra were recorded using quartz cells with path lengths ranging from 0.01 to 10 cm in a Cary Model 14 spectro-

photometer. The ESR spectra were recorded with a Varian 4500 X-band spectrometer using a Varian V-4548 solution cell.

Dimethyl sulfoxide (DMSO) (J. T. Baker Analyzed reagent grade) was obtained in pint bottles to minimize water contamination; the water content, as specified by the source, varied from 0.02 to 0.05%. DMSO was degassed with argon or nitrogen and stored over activated (200–250° for 48 hr) Linde 5-Å molecular sieve. Acetonitrile (MC/B Spectroquality) was degassed and stored over activated molecular sieves. Dimethylformamide (DMF) (MC/B ACS reagent grade) was purified using the procedure of Ritchie and Mergerle.¹⁸ Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte for all electrochemical studies and was used in 50–100-fold excess over the electroactive material. TEAP was prepared according to the procedure of House et al.¹⁹ Molybdenum(V) oxytrichloride and molybdenum(V) pentachloride were donated by the Climax Molybdenum Co. Sodium molybdate(VI) was obtained from the Mallinckrodt Chemical Works. Sodium diethyldithiocarbamate (DTC) was obtained from the Sigma Chemical Co. and sodium dithionite was obtained from MC/B.

Preparation of the Complexes. 1. **Bis(*N,N*-diethyldithiocarbamato)dioxomolybdenum(VI).** The MoO₂(DTC)₂ complex was synthesized according to the procedure of Jowitt and Mitchell.²⁰

2. **μ -Oxo-bis[bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(V)].** The Mo₂O₃(DTC)₄ complex was prepared from molybdenum pentachloride as described by Newton et al.²¹ or from molybdenum oxytrichloride by an analogous procedure.

3. **Bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(IV).** The complex was prepared according to the procedure of Jowitt and Mitchell.²²

4. **Di- μ -oxo-bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(V).** The Mo₂O₄(DTC)₂ complex was prepared using a modification of the procedure of Newton et al.²¹ A typical synthesis consisted of dissolving MoCl₅ (0.01 mol) in an oxygen-free solution of NaOH (0.04 mol) in distilled water. Sodium diethyldithiocarbamate (0.01 mol) was added and the solution was refluxed until the initial purple precipitate had been discharged. The reactions were carried out under a purified nitrogen atmosphere. The solid was washed with water, ethanol, and diethyl ether and dried in vacuo.

5. **Bis(*N,N*-diethyldithiocarbamato)disulfidomolybdenum(VI).** Ammonium thiomolybdate(VI), (NH₄)₂MoS₄, prepared according to Kruss²³ was used to synthesize the MoS₂(DTC)₂ complex according to the procedure given above for the oxo analog (compound 1).

6. **Di- μ -sulfido-bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(V).** The Mo₂O₂S₂(DTC)₂ complex was prepared by treating Mo₂O₃(DTC)₂ with H₂S in dichloromethane. The yellow crystals, which formed in 10 min, were collected by filtration and were recrystallized from dichloromethane-methanol. Analysis indicates that the compound isolated is Mo₂O₂S₂(DTC)₂. Anal. Calcd for Mo₂C₁₀H₂₀O₂S₆N₂: C, 20.55; H, 3.45; S, 32.91. Found: C, 20.93; H, 3.71; S, 34.23.

Results

The oxomolybdenum(VI), -(V), and -(IV) *N,N*-diethyldithiocarbamate (DTC) complexes have been studied in dimethylformamide, acetonitrile, and dimethyl sulfoxide. Although there are similarities in the results for the three different solvents, each has special noteworthy features.

Dimethylformamide. Figure 1a illustrates the cyclic voltammogram for Mo^{VI}O₂(DTC)₂. Controlled-potential electrolysis at a point just cathodic of either the first peak or the second peak (–0.76 and –0.93 V vs. SCE) indicates a 1-electron-per-molybdenum reduction and eliminates both of the first two peaks as demonstrated by subsequent cyclic voltammetry. The same occurs in the case of the second pair of peaks at –1.68 and –1.90 V vs. SCE. A cyclic voltammogram recorded immediately after the preparation of a sample solution indicates that the peaks at –0.93 and –1.90 V dominate initially and that with time the –0.76- and –1.68-V peaks increase in height. A series of controlled-potential coulometric electrolyses that have been monitored by cyclic voltammetry confirms that the –0.76-V species is coupled with the –1.68-V species and that the –0.93-V peak is coupled with the –1.90-V peak. Apparently, the first two peaks are due to a slow equilibrium between two forms of a molybdenum(VI)

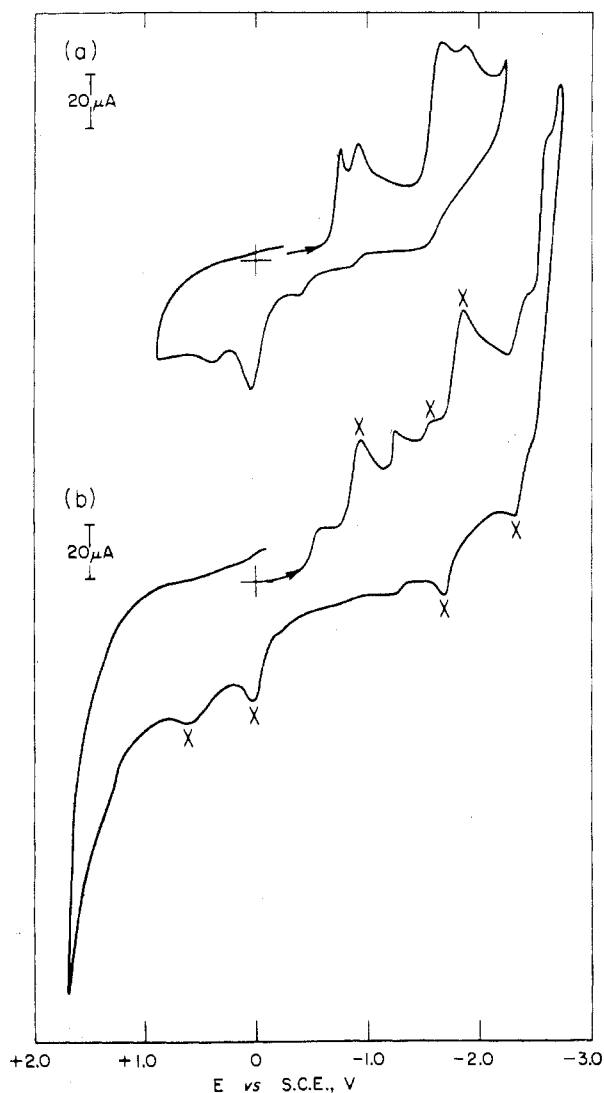


Figure 1. Cyclic voltammograms of (a) 1 mM $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ and (b) 1 mM $\text{Mo}^{\text{VI}}\text{S}_2(\text{DTC})_2$ (peaks due to contamination by oxo species and DTC^- indicated by X) in 0.1 F TEAP in DMF at a platinum electrode; scan rate 0.2 V/sec. (See Table I for values of peak potentials.)

complex²⁴ and the second pair of peaks is due to a pair of Mo(V) species.

In contrast, the thio derivative of this complex, $\text{Mo}^{\text{VI}}\text{S}_2(\text{DTC})_2$, gives the cyclic voltammogram illustrated in Figure 1b. Controlled-potential electrolysis just cathodic to the peak at -0.60 V indicates that this is a 1-electron-per-molybdenum process as does reduction after the reversible -1.29 -V couple. The reversibility of the latter has been established on the basis of peak separation and the independence of peak potentials with scan rate.

Dimethylformamide solutions of $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4$ initially are purple but quickly change to yellow-brown. Cyclic voltammograms of these solutions are analogous to that of Figure 1a. In addition, there is an enhanced anodic peak at $+0.40$ V vs. SCE. These data confirm that the μ -oxo-dimolybdenum(V) complex disproportionates to the Mo(VI) complex and a Mo(IV) species.²¹ In contrast, the di- μ -oxo-molybdenum(V) species $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$ gives a well-defined reduction peak at -1.49 V vs. SCE. Controlled-potential coulometry establishes that this reduction process involves 1 electron per molybdenum and results in a Mo(IV) species.

The $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$ complex has an anodic peak at $+0.4$

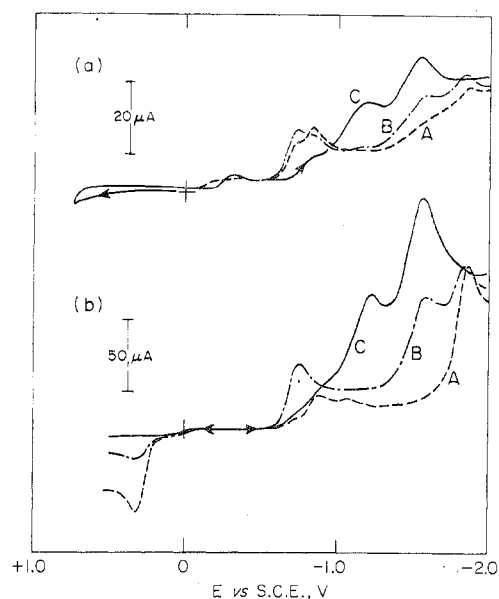


Figure 2. Cyclic voltammograms of (a) 1 mM $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ (time after mixing: A, 10 min; B, 25 min; C, 210 min) and of (b) 1 mM $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$ (time after mixing: A, 5 min; B, 17 min; C, 46 min) in 0.1 F TEAP in DMSO; scan rate 0.1 V/sec.

V vs. SCE. and a cathodic peak at -2.03 V. Controlled-potential electrolysis establishes that the anodic process yields a Mo(VI) species with a reduction peak at -0.88 V; the cathodic peak at -2.03 V is a 1-electron process, leading to a Mo(III) species.

Acetonitrile. Cyclic voltammetry of $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ gives an initial pair of cathodic peaks (-0.73 and -0.93 V) similar to those observed in dimethylformamide (Figure 1a). Again, controlled-potential electrolysis negative of either of these peaks results in the elimination of both peaks and gives a stoichiometry of 1 electron per molybdenum. In contrast to the dimethylformamide data, however, only a single additional cathodic peak is observed at -2.00 V. Controlled-potential electrolysis at this potential indicates a stoichiometry of 2 additional electrons per molybdenum. As in the case of dimethylformamide, preparation of a solution of $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4$ in acetonitrile results in a disproportionation to give the $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$ and $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ complexes. The di- μ -oxo-dimolybdenum complex $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$ has a reduction peak at -1.42 V. This species is reduced by 2 electrons to a Mo(IV) species.

The $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$ complex has a voltammetric oxidation peak at $+0.52$ V vs. SCE and a reverse peak at -0.26 V. On the basis of the peak height, the apparent product is $\text{Mo}^{\text{VO}}(\text{DTC})_2^+$ which subsequently disproportionates to a Mo(VI) complex and a Mo(IV) complex.

Dimethyl Sulfoxide. A freshly prepared DMSO solution of $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ has a broad peak or pair of peaks between -0.8 and -1.0 V. However, as illustrated by Figure 2a, with time the species responsible for this peak disappears to give a species with a reduction peak at -1.20 V. Controlled-potential electrolysis of the latter peak indicates that the new species is reduced by 1 electron per molybdenum. A second cathodic peak appears at -1.58 V and has coulometry equivalent to 1 electron per molybdenum.

As with other solvents studied, the $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4$ complex is unstable in DMSO and rapidly disproportionates to $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ and $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$. After several hours of aging, the solutions of this complex yield a cyclic voltammogram analogous to that of the aged solution of Figure 2a.

The $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$ complex (synthesized and isolated from an aqueous solution) initially has a reduction peak in DMSO

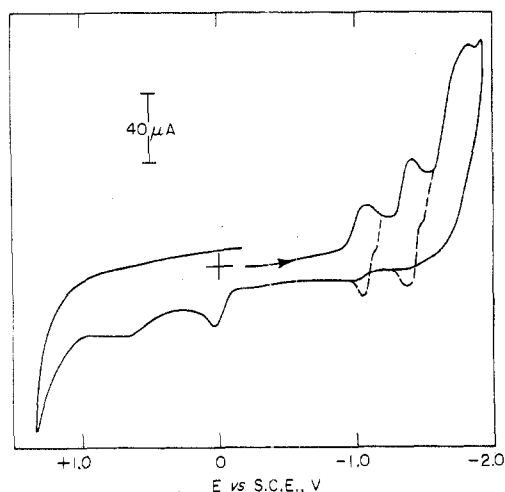


Figure 3. Cyclic voltammograms of 1 mM $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ in 0.1 F TEAP in DMF; scan rate 0.2 V/sec.

at -1.50 V. After 20 hr of equilibration, the peak height is reduced by more than half and a new well-defined reduction peak at -1.23 V becomes the dominant cathodic process. The coulometry for this peak indicates a 1-electron-per-molybdenum reduction. Apparently the solid complex includes an H_2O group in the sixth coordination site which is slowly displaced by a DMSO ligand.

Initially, DMSO solutions of $\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$ yield cyclic voltammograms similar to those for the complex in dimethylformamide with an anodic peak at approximately $+0.4$ V. However, as illustrated by Figure 2b, with time the solution yields reduction peaks characteristic of $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$. At a still later time the solution finally stabilizes to give a reduction peak at -1.20 V which is characteristic of the $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$ species in DMSO and a second peak at -1.58 V.

Independent experiments in all of the solvents have established that the dithiocarbamate anion (DTC^-) is oxidized at $+0.06$ V and reduced at -2.1 V. The product of the oxidation of the DTC^- is a dimeric species, $(\text{DTC})_2$, with a reduction potential at -1.58 V vs. SCE and reduction coulometry of one electron per DTC or 2 electrons per dimer.²⁵ The -1.59 -V peak observed with time in Figure 2 probably is due to $(\text{DTC})_2$. Thus, in DMSO the electrochemical results indicate that regardless of which of the molybdenum-dithiocarbamate complexes one has initially, with time the species react with the solvent and/or the ligand to yield the stable $\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2$ complex and $(\text{DTC})_2$ plus solvent decomposition products.

Di- μ -sulfido-bis(*N,N*-diethyldithiocarbamateoxomolybdenum(V)) in Dimethylformamide. Figure 3 illustrates the cyclic voltammograms for the $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ complex; reverse scans are illustrated for various cathodic peaks. On the basis of the cyclic voltammetry, reversible couples occur at -1.00 and -1.35 V. Controlled-potential electrolysis at a potential just negative of the first cathodic peak gives an electron stoichiometry of 0.25 electron per molybdenum. Likewise, a controlled-potential electrolysis of this product at a potential just negative of the second reduction peak also gives a reduction stoichiometry of 0.25 electron per molybdenum. The reduction of this second product at a potential just negative of the third peak gives a stoichiometry of 0.50 electron per molybdenum. The product from this controlled-potential electrolysis at -1.83 V exhibits an anodic cyclic voltammetric peak at $+0.54$ V. Electrochemical analyses of the electrolysis solutions during the course of these reductions confirm that the stoichiometry for each of these processes is constant throughout the electrolysis.

Elemental analysis of the starting complex (C, H, S) gives

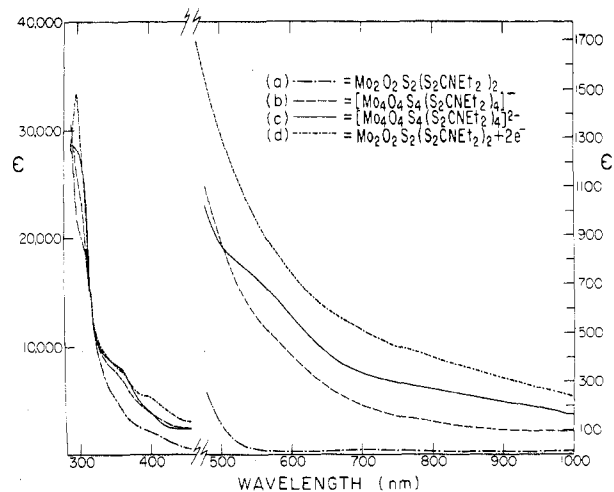


Figure 4. Absorption spectra of 1 mM $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ in DMF: (a) for unreduced complex; (b) after reduction at -1.08 V; (c) after reduction at -1.42 V; (d) after reduction at -1.80 V.

a good fit for the empirical formula $\text{MoOS}(\text{DTC})$. Molecular weight determinations have been run in dichloromethane and chloroform by osmometry; the results of these studies confirm that the predominant species in solution is a dimer, $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$.

The uv-visible absorption spectra for $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$, its reduction product from controlled-potential electrolysis at -1.1 V, its reduction product from controlled-potential electrolysis at -1.45 V, and its reduction product from controlled-potential electrolysis at -1.83 V consist of broad, featureless absorptions that are illustrated by Figure 4.

Infrared measurements indicate that the starting complex does not have any bridging oxo groups and that it does have bridging sulfido^{21,26} groups as well as terminal oxo groups.

Room-temperature ESR measurements of the $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$ complex in DMF indicate the absence of any unpaired electron spin. However, both the reduction product from controlled-potential electrolysis at -1.1 V and the product from electrolysis at -1.45 V exhibit a broadened ESR line with a g value of 2.00. Such a signal is not atypical of $\text{Mo}(\text{V})$ complexes with polarizable ligands.²⁷ The reduction product from controlled potential-electrolysis at -1.83 V does not exhibit an ESR signal.

X-Ray data have been collected for the sulfido-bridged complex $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$. Preliminary analysis indicates that the crystalline species is a binuclear complex. The crystals are monoclinic, space group $P2_1/c$ with unit cell parameters $a = 17.70$ Å, $b = 6.87$ Å, $c = 17.65$ Å, $\beta = 104.8^\circ$.²⁸ Isolation and X-ray structural characterization of the products from the electrolysis at both the first and second reduction peaks is in progress and will be reported in a subsequent publication.

Discussion and Conclusions

On the basis of the electrochemical and associated studies the oxidation-reduction chemistry and reaction chemistry of this group of molybdenum-dithiocarbamate complexes are summarized in Table I. This summary in particular illustrates the effect of the solvent systems upon the electrochemistry and solution chemistry.

In general the electrochemical results in acetonitrile closely parallel those in dimethylformamide. However, in the case of DMF the $\text{Mo}(\text{VI})$ complex is reduced to a $\text{Mo}(\text{V})$ species, which in turn is reduced to $\text{Mo}(\text{IV})$, while in acetonitrile the same complex is reduced first to $\text{Mo}(\text{V})$ and then ultimately to a $\text{Mo}(\text{III})$ product. The behavior of the molybdenum-dithiocarbamate complexes in dimethyl sulfoxide is surprisingly different and unique among this group of solvents. Apparently,

Table I. Summary of Electrochemical Data for Molybdenum Complexes

		V vs. SCE			
		E'	E_{pc}	E_{pa}	e/Mo
I. Mo-DTC Complexes					
A. DMF (Oxidation State)					
(VI)	$2\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 \leftrightarrow \text{Mo}^{\text{VI}}_2\text{O}_4(\text{DTC})_4^a$				
	$\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{V}}\text{O}_2(\text{DTC})_2^-$		-0.93		1
	$\text{Mo}^{\text{VI}}_2\text{O}_4(\text{DTC})_4 + 2e^- \rightarrow \text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-}$		-0.76		1
	$\text{Mo}^{\text{V}}\text{O}_2(\text{DTC})_2^- + e^- \rightarrow \text{Mo}^{\text{IV}}\text{O}_2(\text{DTC})_2^{2-}$		-1.90		1
	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-} + 2e^- \rightarrow 2\text{Mo}^{\text{IV}}\text{O}_2(\text{DTC})_2^{2-}$		-1.68		1
(VI, S)	$\text{Mo}^{\text{VI}}\text{S}_2(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{V}}\text{S}_2(\text{DTC})_2^-$		-0.60		
	$\text{Mo}^{\text{V}}\text{S}_2(\text{DTC})_2^- + e^- \leftrightarrow \text{Mo}^{\text{IV}}\text{S}_2(\text{DTC})_2^{2-}$	-1.29	-1.32	-1.26	1
(V)	$\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4 \leftrightarrow \text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 + \text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2^a$				
	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4 + 2e^- \rightarrow 2\text{Mo}^{\text{IV}}\text{O}_2(\text{DTC})_2^-$		-1.49		1
(IV)	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 \rightarrow \text{Mo}^{\text{VI}}\text{O}(\text{DTC})_2^{2+} + 2e^-$			+0.40	2
	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{III}}\text{O}(\text{DTC})_2^-$		-2.03		1
	$2\text{DTC}^- \rightarrow (\text{DTC})_2 + 2e^-$			+0.06	
	$(\text{DTC})_2 + 2e^- \rightarrow 2\text{DTC}^-$		-1.58		
	$\text{DTC}^- + e^- \rightarrow \text{DTC}^{2-}$		-2.1		
B. AN					
(VI)	$\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{V}}\text{O}_2(\text{DTC})_2^-$		-0.93		1
	$\text{Mo}^{\text{VI}}_2\text{O}_4(\text{DTC})_4 + e^- \rightarrow \text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-}$		-0.82		1
	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-} + 4e^- \rightarrow 2\text{Mo}^{\text{III}}\text{O}_2(\text{DTC})_2^{3-}$		-2.00		2
(V)	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4 + 2e^- \rightarrow 2\text{Mo}^{\text{IV}}\text{O}_2(\text{DTC})_2^{2-}$		-1.42		1
(IV)	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 \rightarrow \text{Mo}^{\text{V}}\text{O}(\text{DTC})_2^+ + e^-$			+0.52	
	$\text{Mo}^{\text{V}}\text{O}(\text{DTC})_2^+ + e^- \rightarrow \text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2$		-0.26		
	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{III}}\text{O}(\text{DTC})_2^-$		-1.93		
C. DMSO					
(VI)	$\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{V}}\text{O}_2(\text{DTC})_2^-$		-0.83	-1.10	
	$\text{Mo}^{\text{VI}}_2\text{O}_4(\text{DTC})_4 + 2e^- \rightarrow \text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-}$		-0.76		
	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4^{2-} \rightarrow \text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2 + 2\text{DTC}^-$				
	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_4 \rightarrow \text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2 + (\text{DTC})_2$				
	$(\text{DTC})_2 + 2e^- \rightarrow 2\text{DTC}^-$		-1.58		
(V)	$\text{Mo}^{\text{V}}_2\text{O}_4(\text{DTC})_2 + 2e^- \rightarrow 2\text{Mo}^{\text{IV}}\text{O}_2(\text{DTC})_2^-$		-1.23		1
			(-1.50)		
(IV)	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 + \text{DMSO} \rightarrow \text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2 + \text{DMS}$				
	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 \rightarrow \text{Mo}^{\text{V}}\text{O}(\text{DTC})_2^+ + e^-$			+0.32	
	$\text{Mo}^{\text{IV}}\text{O}(\text{DTC})_2 + e^- \rightarrow \text{Mo}^{\text{III}}\text{O}(\text{DTC})_2^-$		-1.85		
D. DMF; Mo ^V -S-DTC					
	$2\text{Mo}^{\text{V}}_2\text{O}_3\text{S}_2(\text{DTC})_2 + e^- \leftrightarrow \text{Mo}^{\text{V}}_3\text{Mo}^{\text{IV}}\text{O}_4\text{S}_4(\text{DTC})_4^-$	-1.00	-1.05	-0.95	0.25
	$\text{Mo}^{\text{V}}_3\text{Mo}^{\text{IV}}\text{O}_4\text{S}_4(\text{DTC})_4^- + e^- \leftrightarrow \text{Mo}^{\text{V}}_2\text{Mo}^{\text{IV}}\text{O}_3\text{S}_4(\text{DTC})_4^{2-}$				
	$\text{Mo}^{\text{V}}_2\text{Mo}^{\text{IV}}\text{O}_3\text{S}_4(\text{DTC})_4^{2-} + 2e^- \rightarrow 4\text{Mo}^{\text{IV}}\text{OS}(\text{DTC})^-$	-1.35	-1.40	-1.30	0.25
	$\text{Mo}^{\text{IV}}\text{OS}(\text{DTC})^- \rightarrow \text{Mo}^{\text{V}}\text{OS}(\text{DTC}) + e^-$		-1.77		0.50
				+0.54	
II. Other Complexes					
A. DMSO; Mo ^V -OH ⁻ -Cl ⁻					
	$\text{Mo}^{\text{V}}_2\text{O}_3\text{Cl}_4(\text{OH})_2^{2-} + e^- \rightarrow \text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Cl}_4(\text{OH})_2^{3-}$		-0.73		
	$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Cl}_4(\text{OH})_2^{3-} + e^- \rightarrow \text{Mo}^{\text{IV}}_2\text{O}_3\text{Cl}_4(\text{OH})_2^{4-}$		-1.03		
	$\text{Mo}^{\text{V}}_2\text{O}_3\text{Cl}_4(\text{OH})_2^{2-} + 4e^- \rightarrow 2[\text{Mo}^{\text{III}}\text{-Cl}^-\text{-OH}^-]$		-1.80		
B. DMSO; Molybdenum-8-Quinolinol (Q)					
(VI)	$\text{Mo}^{\text{VI}}\text{O}_2\text{Q}_2 + e^- \leftrightarrow \text{Mo}^{\text{V}}\text{O}_2\text{Q}_2^-$	-1.07			
	$\text{Mo}^{\text{V}}\text{O}_2\text{Q}_2^- + e^- \rightarrow [\text{Mo}^{\text{IV}}\text{-Q}]$		-1.12		
	$[\text{Mo}^{\text{IV}}\text{-Q}] + e^- \rightarrow [\text{Mo}^{\text{III}}\text{-Q}]$		-1.85		
(V)	$\text{Mo}^{\text{V}}_2\text{O}_3\text{Q}_4 + e^- \leftrightarrow \text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Q}_4^-$	-1.19			
	$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Q}_4^- \leftrightarrow \text{Mo}^{\text{IV}}_2\text{O}_3\text{Q}_4^{2-}$		-1.56		
	$\text{Mo}^{\text{V}}_2\text{O}_3\text{Q}_4 \rightarrow \text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}\text{O}_3\text{Q}_4^+ + e^-$			+0.6	

^a Reaction also occurs in AN and DMSO.

the Mo(VI) complex oxidizes its coordinated dithiocarbamate by an intramolecular process to yield the dimeric di- μ -oxo-molybdenum(V) dithiocarbamate complex and (DTC)₂. The former has a reduction peak of -1.20 V and gives a 2-electron reduction to a Mo(IV) species, and the latter is reduced at -1.58 V to give a dithiocarbamate anion. The molybdenum(IV) dithiocarbamate complex apparently reacts with dimethyl sulfoxide by an oxygen-transfer process to give Mo^{VI}O₂(DTC)₂ and dimethyl sulfide. This type of process is particularly intriguing and relevant to the enzyme chemistry characteristic of molybdenum-containing enzymes; xanthine oxidase, nitrate reductase, aldehyde oxidase, and sulfite oxidase all could be characterized as oxygen-transfer catalysts rather than 2-electron oxidation-reduction catalysts.

The electrochemical data, as well as the report by Colton and Rose,²⁴ indicate that Mo^{VI}O₂(DTC)₂ undergoes a dimerization reaction in these solvents to give Mo^{VI}₂O₄(DTC)₄, probably in the form of a di- μ -oxo-bridged arrangement with one terminal oxygen from each monomeric unit serving as a bridging group. Such a configuration would provide a convenient means for the intramolecular oxidation-reduction process that is observed in DMSO for this species. Because of the nominal seven-coordinate bonding of the Mo(VI) dimer, conversion to the dimeric di- μ -oxo-dimolybdenum(V) complex and (DTC)₂ is a reasonable proposition. Formation of Mo^{VI}₂O₄(DTC)₄ would undoubtedly give a species that would be more easily reduced to give reduction products that also would be more easily reduced than the monomeric products.

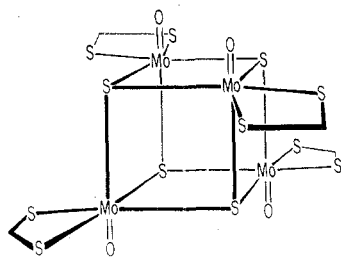


Figure 5. Possible structure of the anion and dianion formed by reduction of $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$.

This is consistent with the electrochemical data of Table I and Figure 1.

The μ -oxo-bridged complex $\text{Mo}^{\text{V}}_2\text{O}_3(\text{DTC})_4$ is unstable in all three solvents and disproportionates to the Mo(VI) and Mo(IV) complexes. That this occurs is clearly evident both from the electrochemical data and from the rapid loss of the compound's purple coloration upon solution in each of the solvents. However, the combination of this disproportionation reaction plus the monomer-dimer equilibrium for the $\text{Mo}^{\text{VI}}\text{O}_2(\text{DTC})_2$ complex caused a great deal of confusion during the initial stages of this research. It also appears to have led to some different electrochemical interpretations by Pace and Watt¹⁶ relative to those presented here. On the basis of an extended series of electrochemical studies, particularly in the context of controlled-potential electrolysis and time-dependent studies of the cyclic voltammetry of the Mo(VI) complex, the equilibrium reactions and reduction steps outlined in Table I are believed to be self-consistent and an accurate representation of the many processes occurring in these solutions.

Reference to section IA of Table I provides a concise comparison of the oxo and sulfido versions of the molybdenum(VI)-dithiocarbamate complexes. The oxo species appear to exist in solution in a monomer-dimer equilibrium with the monomers being reduced at -0.93 and -1.90 V while the dimers are reduced at -0.76 and -1.68 V. In the case of the sulfido complex, only a single reduction peak is observed for the Mo(VI) species at -0.6 V and a second reduction peak is seen at -1.32 V, which is a reversible couple in contrast to the oxo complex. Whether the sulfido complex is monomeric or dimeric is not clear from the electrochemical data. However, the data allow the generalization that terminal sulfido groups cause a complex to be more easily reduced and cause the corresponding reduction products to be more difficult to oxidize.

Whereas the dimeric molybdenum(V) di- μ -oxo-dithiocarbamate complex is reduced by a 2-electron process at -1.49 V to give a Mo(IV) complex, the di- μ -sulfido version of this complex is reduced by a reversible dimerization process at -1.00 V on the basis of the electron stoichiometry and the ESR resonance for the product species. The product species appears to be the tetramer $\text{Mo}_4\text{O}_4\text{S}_4(\text{DTC})_4^{4-}$ with the formal redox stoichiometry of one Mo(IV) species and three Mo(V) species. This species is further reduced by a reversible 1-electron process at -1.35 V to give an entity that formally includes two Mo(V) species and two Mo(IV) species. A third reduction step occurs at -1.77 V to give a Mo(IV) product which is reoxidized at $+0.54$ V. These oxidation-reduction propositions are summarized in section ID of Table I. Figure 5 illustrates a proposed structure for the product species that results from the first and second electrolysis steps. Such a configuration is closely analogous to those that have been established for the iron cubane models of ferredoxin.²⁹ The latter also involve the formal combination of oxidation states in a given complex molecule. The proposition of a molybdenum-sulfur-bridged array is consistent with the known association of iron-sulfur

systems with most of the molybdenum enzymes. Work is in progress to isolate the reduction products represented by Figure 5 with the goal of determining their molecular structures by crystallographic methods.

The observation of a Mo(V) ESR spectrum for the 1-electron and 2-electron product species is noteworthy, especially in view of the fact that the parent complex, $\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2(\text{DTC})_2$, is ESR inactive. That is, spin pairing in the dimeric Mo(V) complex gives a diamagnetic species, but addition of an electron promotes the formation of a tetramer with at least one of the three remaining Mo(V) ions unpaired such that an ESR signal is observed. Addition of a second electron results in two Mo(V) species in the proposed tetrameric molecule that are unpaired and give an ESR signal. This is especially noteworthy because Bray and coworkers have claimed that the two molybdenums in xanthine oxidase are separated from each other because an ESR signal for Mo(V) is observed in the enzyme. Their argument has been that if the two molybdenum atoms were associated, then spin pairing of the Mo(V) oxidation state would preclude observation of an ESR signal. The present results indicate that structurally associated molybdenums can occur in mixed oxidation states such that one or more Mo(V) ions are not spin paired and yield ESR signals. It seems reasonable that a similar situation may prevail in the dimolybdoenzymes, particularly xanthine oxidase.

The proposed tetramer that is illustrated in Figure 5 may provide a versatile reducing agent that can serve as a multi-electron manifold. In addition, such a system may be relevant to the kind of chemistry that is essential in nitrogenase to bring about the 6-electron reduction of molecular nitrogen. This system also illustrates the probable importance of the Mo(IV) oxidation state in molybdenum-containing enzymes, as well as the probable importance of molybdenum-sulfur bonding in such systems.

Additional electrochemical and spectroscopic studies of other oxo- and sulfido-bridged molybdenum complexes are in progress and will be reported in subsequent communications. Particular attention is being directed to the Mo(IV)-Mo(V) couple, especially in the context of dimeric and tetrameric bridged molecules.

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Registry No. $\text{MoO}_2(\text{DTC})_2$, 19680-83-2; $\text{Mo}_2\text{O}_3(\text{DTC})_4$, 20023-86-3; $\text{MoO}(\text{DTC})_2$, 25395-92-0; $\text{Mo}_2\text{O}_4(\text{DTC})_2$, 50860-31-6; $\text{MoS}_2(\text{DTC})_2$, 55723-32-5; $\text{Mo}_2\text{O}_2\text{S}_2(\text{DTC})_2$, 55723-33-6; DMSO, 67-68-5; DMF, 68-12-2; TEAP, 2567-83-1.

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Reaction of Dinitratobis(pyridine)cobalt(II) with Dihalobis(pyridine)cobalt(II) Complexes. Preparation and Characterization of Dinitratobis(pyridine)cobalt(II) and Chloronitratobis(pyridine)cobalt(II)

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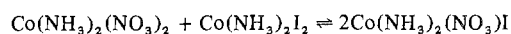
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The spectroscopic and magnetic properties of dinitratobis(pyridine)cobalt(II) are very similar to those of analogous cobalt complexes such as dinitratobis(trimethylphosphine oxide)cobalt(II) which has been shown to contain bidentate nitrate ions. In solution dinitratobis(pyridine)cobalt(II) reacts with the dihalobis(pyridine) complexes of cobalt(II) to establish what appears to be an equilibrium of the type $\text{Co}(\text{py})_2(\text{NO}_3)_2 + \text{Co}(\text{py})_2\text{X}_2 \rightleftharpoons 2\text{Co}(\text{py})_2(\text{NO}_3)\text{X}$ (where $\text{X}^- = \text{Cl}^-$, Br^- , or I^-). The equilibrium constants for these reactions exhibit little temperature or solvent dependence. The numerical values of K_{eq} range from approximately 0.3 to 1.5. A mixed-anion complex having the stoichiometry $\text{Co}(\text{py})_2(\text{NO}_3)\text{Cl}$ can be isolated from solutions containing $\text{Co}(\text{py})_2(\text{NO}_3)_2$ and $\text{Co}(\text{py})_2\text{Cl}_2$. Although this mixed-anion complex appears to be monomeric in solution, it is a chlorine-bridged dimer in the solid state. The magnetic susceptibility of the material in the 297–77°K range obeys the Curie–Weiss law with a Weiss constant of -10° . These data indicate that the exchange coupling between the two cobalt atoms in the dimer is fairly small.

Introduction

A recent study has suggested that dinitratodiamminecobalt(II) reacts with diiododiamminecobalt(II) in acetonitrile solution to establish the equilibrium¹



The mixed-anion complex $\text{Co}(\text{NH}_3)_2(\text{NO}_3)\text{I}$ can actually be isolated from solutions containing equimolar quantities of $\text{Co}(\text{NH}_3)_2(\text{NO}_3)_2$ and $\text{Co}(\text{NH}_3)_2\text{I}_2$. The spectroscopic and magnetic properties of $\text{Co}(\text{NH}_3)_2(\text{NO}_3)_2$ indicate that the dinitratodiammine complex is structurally similar to dinitratobis(trimethylphosphine oxide)cobalt(II) which has been shown by X-ray diffraction to adopt a distorted six-coordinate structure where the nitrate ions coordinate in bidentate fashion.² The diiododiammine complex has been determined to be tetrahedral by infrared studies,³ while the mixed-anion species $\text{Co}(\text{NH}_3)_2(\text{NO}_3)\text{I}$ has not been completely characterized. A number of other dinitratobis(ligand)cobalt(II) complexes have been prepared and appear to have structures which resemble that of the trimethylphosphine oxide complex. Numerous tetrahedral dihalo species of the type $\text{Co}(\text{L})_2\text{X}_2$ have been made and characterized. It seems reasonable to assume that dinitrato and dihalo complexes containing a variety of ligands might react in the same manner as the diammine complexes. This paper presents a study of the reaction between dinitratobis(pyridine)cobalt(II) and dichloro-, dibromo-, and diiodobis(pyridine)cobalt(II). The pyridine complexes were chosen because they are soluble in a variety of organic solvents and are relatively easy to prepare and handle. The objectives of this investigation were, first, to establish that the anion-exchange equilibrium takes place with complexes containing ligands other than ammonia and, second, to isolate and elucidate the solution and solid-state structure of a mixed-anion complex of the type $\text{Co}(\text{L})_2(\text{NO}_3)\text{X}$.

Experimental Section

Solvents. The solvents used in this study were all carefully dried. Reagent grade acetonitrile, methylene chloride, and chloroform were distilled from P_2O_5 under nitrogen and stored over molecular sieves. Petroleum ether and ligroin were allowed to stand over anhydrous calcium sulfate for at least 24 hr.

Dinitratobis(pyridine)cobalt(II). The $\text{Co}(\text{py})_2(\text{NO}_3)_2$ complex was prepared by a number of procedures. The method described below is considered to be the most convenient. Reagent grade cobalt(II) nitrate hexahydrate was dried at room temperature under vacuum for 36 hr. This partially dehydrated material was determined from a cobalt analysis to be $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Approximately 10 g of this trihydrate was added to a 250-ml round-bottom flask containing 100 ml of benzene and 20 ml of acetonitrile. A stoichiometric amount of pyridine (~6.6 g) was added and the flask was stoppered. The mixture was stirred overnight at room temperature with a magnetic stirrer. The solvent was then distilled from the mixture under a stream of dry nitrogen. The cobalt salt was dehydrated by the formation of the benzene–water azeotrope which was distilled from the mixture. During the distillation all the solid material dissolved forming a maroon solution. When only 50 ml of solution remained, an additional 50 ml of benzene was added and the distillation was continued. When the total volume was again reduced to 50 ml, the solution was allowed to cool to room temperature. The remaining solvent was removed by evaporation under vacuum at room temperature. The evacuated flask was transferred to a nitrogen-filled glove bag and the residue was dissolved in 70 ml of dry methylene chloride. The solution was filtered and added to a 250-ml erlenmeyer flask with a ground-glass stopper. Approximately 50 ml of dry petroleum ether was added to the methylene chloride solution and the flask was stoppered. The flask was placed in a freezer taking care not to mix the contents any more than necessary. After 1 or 2 days the petroleum ether diffused into the methylene chloride solution and the $\text{Co}(\text{py})_2(\text{NO}_3)_2$ crystallized out of solution. The flask was then transferred to the glove bag and the solution was decanted. The red-violet crystalline solid was washed first with a mixture of petroleum ether and methylene chloride and finally with pure petroleum ether. The product (~7.5 g) was dried under vacuum. The material is quite stable but rapidly picks up water