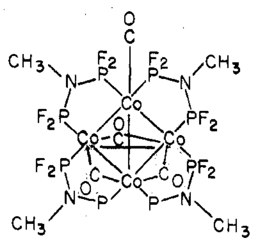
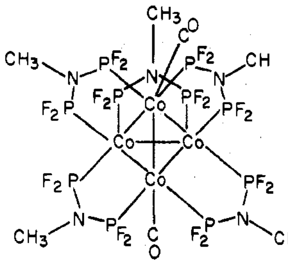


IV



V

product may be formulated as a completely substituted $Rh_4(CO)_{12}$ with $CH_3N(PF_2)_2$ bridges along each of the six edges of the Rh_4 tetrahedron (i.e., $[CH_3N(PF_2)_2]_6Rh_4$). However, the extreme insolubility of this product, which precludes, for example, its molecular weight determination in solution, suggests a polymeric structure containing Rh_4 tetrahedra bridged by intertetrahedral bidentate $CH_3N(PF_2)_2$ ligands (i.e., $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$). In any case the facile formation of a carbonyl-free complex $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$ from $Rh_4(CO)_{12}$ and $CH_3N(PF_2)_2$ under conditions milder than those where $Co_4(CO)_{12}$ forms products $[CH_3N(PF_2)_2]_nCo_4(CO)_{12-2n}$ still containing carbonyl groups is a further demonstration of the weaker metal–carbon bonds formed by 4d transition metals relative to corresponding systems involving 3d and 5d transition metals.[13]

Acknowledgment. We are indebted to the U.S. Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. J.G. is indebted to the Program of Cultural Cooperation between the U.S.A. and Spain, administered by the Fulbright Commission of Spain, for a fellowship. We are indebted to Dr. Main Chang for obtaining the mass spectra. We also acknowledge the technical assistance of Mr. Courtney Pape in running some of the carbon-13 and phosphorus-31 NMR spectra.

Registry No. $[CH_3N(PF_2)_2]_3Co_2(CO)_2$, 64799-21-9; $[CH_3N(PF_2)_2]_3Co_2(CO)(PF_2NHCH_3)$, 66674-80-4; $[CH_3N(PF_2)_2]_5Co_2$, 66632-81-3; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, 64799-20-8; $[CH_3N(PF_2)_2]_3Co_2(CO)(PF_2N(CH_3)_2)$, 66632-80-2; $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, 66674-78-0; $[CH_3N(PF_2)_2]_3Co_2(CO)(P(OC_2H_5)_3)$, 66632-79-9; $[CH_3N(PF_2)_2]_3Co_2(P(OC_2H_5)_3)_2$, 66632-78-8; $[CH_3N(PF_2)_2]_3Co_2(P(C_6H_5)_3)_2$, 66632-91-5; $[CH_3N(PF_2)_2]_3Co_2(CO)P(C_6H_5)_3$, 66632-90-4; $[CH_3N(PF_2)_2]_3Co_2(CO)[CNC(CH_3)_3]$, 66632-89-1; $[CH_3N(PF_2)_2]_3Co_2(CO)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$, 66674-77-9; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)(PF_2N(CH_3)_2)$, 66632-88-0; $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)(P(OC_2H_5)_3)$, 66632-87-9; $[CH_3N(PF_2)_2]_2Co_4(CO)_8$, 66687-70-5; $[CH_3N(PF_2)_2]_3Co_4(CO)_6$, 66687-71-6; $[CH_3N(PF_2)_2]_4Co_4(CO)_4$, 66632-86-8; $[CH_3N(PF_2)_2]_5Co_4(CO)_2$, 66702-33-8; $\{[CH_3N(PF_2)_2]_6Rh_4\}_n$, 66687-72-7; $Co_2(CO)_8$, 10210-68-1; $Co_4(CO)_{12}$, 17786-31-1; $Rh_4(CO)_{12}$, 19584-30-6; $[CH_3N(PF_2)_2]_3Co_2(CNC(CH_3)_3)_2$, 66632-85-7.

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Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309

Synthesis and Characterization of a Series of Thiobenzoate Complexes of Molybdenum(V)

M. RAKOWSKI DuBOIS

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New dimeric molybdenum(V) complexes of formulas $Mo_2O_4L_2(py)_2$, $Na_2Mo_2O_4L_4$, $Mo_2O_3SL_2(py)_2$, and $Na_2Mo_2O_3SL_4$, where L = monothiobenzoate, have been synthesized. The complexes have been characterized by analytical, spectral, conductivity, and electrochemical measurements. The five-coordinate neutral dimers, $Mo_2O_3XL_2$ (where X = O or S), show a high affinity for electron donors. Strong intermolecular associations occur through terminal oxygen–metal interactions unless a good donor ligand is added. The neutral dimers react with excess sodium thiobenzoate to form molybdenum(V) dimeric anions. Infrared studies indicate that the Mo_2O_3X units of the dimers remain intact in this reaction. The neutral complexes can be regenerated by the addition of 2 equiv of acid. The dissociation behavior of the complexes $Na_2Mo_2O_3XL_4$ in solution is discussed.

Introduction

The coordination chemistry of molybdenum(V) is dominated by the formation of dimeric species with metal ions bridged by one or two oxygen or, in some cases, sulfur atoms. A number of such dimeric units are stabilized by bidentate ligands with oxygen, nitrogen, or sulfur donors.[1] Studies have shown that when di-μ-oxo-molybdenum(V) dimers are converted to monooxo-bridged complexes,[2] cleaved to form molybdenum(V) monomers,[3] or reduced to form lower valent monomeric complexes[4] very reactive molybdenum species may be produced. Such reactions have led, for example, to the formation of catalytically active species for acetylene,[4] nitrogen,[4] and nitrate[3a] reductions. However, relatively few studies of reactions of molybdenum(V) dimers have been reported in which the di-μ-oxo (or μ-oxo, μ-sulfido, or di-μ-sulfido) bridge remains intact.[5] Electrochemical[6] and other characterization studies[7] of molybdenum(V) compounds suggest that the tendency of dimeric complexes to undergo or to resist bridge cleavage reactions can be significantly affected by the nature of the chelating ligand as well as by reaction conditions and the nature of the added reagents.

In order to extend the understanding of the scope of molybdenum coordination chemistry, we are interested in the study of dimeric molybdenum(V) complexes which, because

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of their structural and electronic properties, have a potential for reactivity while retaining their dimeric nature. We report in this paper the synthesis and characterization of a new series of such dimeric molybdenum(V) complexes which are stabilized by thiobenzoate ligands. Few molybdenum complexes with bidentate ligands with both sulfur and oxygen donors have been characterized previously[7a,8] despite their possible relevance to coordination spheres of molybdenum in biological systems.[9] Studies have indicated that, compared to its dithio analogue, a mixed oxygen–sulfur donor ligand can display significantly different donor properties for metal ions.[10] These differences may be significant in molybdenum coordination chemistry. For example, despite the ready preparation of dithiocarbamate complexes of molybdenum(IV), -(V), and -(VI),[11] recent attempts to isolate the analogous monothiocarbamate complexes were unsuccessful.[12]

The new neutral thiobenzoate complexes of molybdenum are initially of the form $Mo_2O_4(OSCC_6H_5)_2$ and $Mo_2O_3S(OSCC_6H_5)_2$. These complexes, which (excepting the Mo–Mo bond) are five-coordinate at each metal ion, show a particularly strong affinity for electron donors. In terms of reactivity characteristics, the five-coordinate dimers may be considered to be coordinatively unsaturated. The reactions of these dimers with excess ligand produce two examples of a new type of molybdenum(V) dimeric complex with potentially bidentate uninegative ligands: $Na_2Mo_2O_4(OSCC_6H_5)_4$ and $Na_2Mo_2O_3S(OSCC_6H_5)_4$. Crystals suitable for an X-ray diffraction study have not yet been obtained. However, spectral and analytical data indicate that in the new dimers the two-atom bridges remain intact while the additional ligands coordinate to each metal ion.

Results and Discussion

Preparation and Characterization of Di-μ-oxo Complexes. A 2:1 molar ratio of sodium thiobenzoate and dichlorodioxomolybdenum(VI) reacted in ether to form a di-μ-oxo-bridged dimer of molybdenum(V) (reaction 1a). Dibenzoyl

$$2MoO_2Cl_2 + 4NaOSCC_6H_5 \rightarrow Mo_2O_4(OSCC_6H_5)_2 + C_6H_5C(=O)SSC(=O)C_6H_5 + 4NaCl \quad (1a)$$

$$Mo_2O_4(OSCC_6H_5)_2 \rightarrow [Mo_2O_4(OSCC_6H_5)_2]_n \quad (1b)$$

disulfide was the oxidized product in this redox-coordination reaction. Although the ethereal solution of the product was bright orange, concentration of the solution produced a brown molybdenum complex which was insoluble in almost all common organic solvents (eq 1b). The infrared spectrum of the compound had a strong broad band at 830 cm^{-1} which was attributed to intermolecular metal–oxygen interactions (Mo=O···Mo=O···). Similar bands have been observed in solid-state spectra of molybdenum(V) xanthate dimers.[13] The polymeric thiobenzoate complex was soluble in the strong donor solvent pyridine which filled the sixth coordination site at each molybdenum ion. The crystals which formed from the pyridine solution (reaction 2) were soluble in chloroform

$$[Mo_2O_4(OSCC_6H_5)_2]_n + py \rightarrow Mo_2O_4(OSCC_6H_5)_2(py)_2 \quad (2)$$

and other organic solvents and gave no spectral evidence for intermolecular associations. The presence of terminal oxo ligands in $Mo_2O_4(OSCC_6H_5)_2(py)_2$ was confirmed by a strong characteristic absorption in the infrared spectrum at 980 cm^{-1}. Bands at 737 and 476 cm^{-1} were assigned to vibrations of the bridging oxo ligands. The $\nu_{C—S}$ of the thiobenzoate ligand was observed at 960 cm^{-1} [14] and $\nu_{C—O}$ was tentatively assigned to a band at 1470 cm^{-1}. Several absorptions of the phenyl groups and pyridine ligands were also observed in the region between 1450 and 1600 cm^{-1} as well as between 700 and 800 cm^{-1}.

Other spectral data provided only minimal information on the structure of the compound. The NMR spectrum confirmed the presence of two pyridine molecules per dimer. The visible spectrum of the complex was characterized by an absorption at 490 nm (ϵ_M = 340) which occurred as a shoulder on a strong ultraviolet absorption. The visible absorption obeyed Beer's law through 1 × 10^{-4} M concentrations when measured in pyridine solutions. The extinction coefficient varied with concentration in chloroform solution, and this was probably due to some dissociation of the neutral ligand.

Table I. Infrared Data for Metal Thiobenzoate Complexes[a]

complex	$\nu_{C\underset{\cdot\cdot}{-}O}$, cm^{-1}	$\nu_{C\underset{\cdot\cdot}{-}S}$, cm^{-1}
$Na(OSCC_6H_5)$	1500	960
$Cr(OSCC_6H_5)_3$	1465	982
$Ni(OSCC_6H_5)_2$	1508	958
$Zn(OSCC_6H_5)_2$	1545	955, 928
$Hg(OSCC_6H_5)_2$	1640	912

[a] Data taken from ref 14.

The dimeric complex reacted with 2 equiv of sodium thiobenzoate (reaction 3). The displacement of pyridine

$$Mo_2O_4(OSCC_6H_5)_2(py)_2 + 2NaOSCC_6H_5 \xrightarrow{THF} Na_2[Mo_2O_4(OSCC_6H_5)_4] + 2py \quad (3)$$

molecules by the thiobenzoate ligands to form an anionic molybdenum dimer was confirmed by analytical and spectral data. There was no evidence for the reaction path observed for the analogous molybdenum complex with dithiocarbamate ligands in which an oxygen bridge was cleaved (reaction 4).[11a]

$$Mo_2O_4(S_2CNR_2)_2 + 2NaS_2CNR_2 \rightarrow Mo_2O_3(S_2CNR_2)_4 \quad (4)$$

The Mo_2O_4 unit in the product of reaction 3 did not appear to be significantly altered. Infrared stretches assigned to the terminal and bridging oxo ligands were observed at 980, 970, 730 and 463 cm^{-1}, respectively.

Infrared studies of thiobenzoate complexes with other metal ions have been reported.[14,15] A trend of $C\underset{\cdot\cdot}{-}O$ and $C\underset{\cdot\cdot}{-}S$ stretching frequencies was observed for different metal complexes as the nature of bonding interactions with the thiobenzoate ligand changed. Infrared data for several of the complexes are listed in Table I. The ligand in the Cr(III) complex was assigned a bidentate bridging mode with the stronger interaction between the oxygen donor and the chromium ion. The ligands in the nickel complex had spectral characteristics similar to those of sodium thiobenzoate, and this type of metal ligand interaction was termed a symmetrical chelating bonding mode. For the zinc complex the IR stretches indicated an increased strength in the metal–sulfur bond, while the mercuric complex was proposed to have a monodentate S-bonded ligand. Crystallographic studies of two of the complexes have subsequently confirmed the correlations between IR shifts and types of bonding interactions between metal ions and the thiobenzoate ligand.[16]

When the infrared spectrum of $Na_2Mo_2O_4(OSCC_6H_5)_4$ was compared to that of $Mo_2O_4(OSCC_6H_5)_2(py)_2$, three new bands of roughly equal intensity appeared between 1550 and 1600 cm^{-1}. These were attributed to the $C\underset{\cdot\cdot}{-}O$ and phenyl ring vibrations of the added ligands. Absorptions at 935 and 920 cm^{-1} were assigned to $\nu_{C—S}$. The relatively high energy region for the carbon–oxygen stretch(es) and the low energy carbon–sulfur stretches indicated that the added ligands in $Na_2Mo_2O_4(OSCC_6H_5)_4$ were asymmetrically bonded with strong metal–sulfur interactions. The spectral data did not establish whether the two added ligands each bonded to a single metal ion or acted as bridging ligands between two metals. Molybdenum(V) complexes in which the two metal ions of an intact Mo_2O_4 unit were bridged by a single carboxylate anion have been reported.[5b,c] The visible spectrum of $Na_2Mo_2O_4(OSCC_6H_5)_4$ had the same poorly resolved

Table II. Visible Electronic Absorption Data[a]

compound	$\lambda_{\max}$, nm	ϵ, L/(m cm)
$Mo_2O_4(OSCC_6H_5)_2(py)_2$	~480 sh	~300
$Na_2Mo_2O_4(OSCC_6H_5)_4$	~480 sh	~300
	~490 sh[b]	~400[b]
$Mo_2O_3S(OSCC_6H_5)_2(py)_2$	480	520
$Na_2Mo_2O_3S(OSCC_6H_5)_4$	480	460
	490[b]	760[b]

[a] Pyridine solutions, 1×10^{-4}-4×10^{-3} M. [b] Acetonitrile solutions, 4×10^{-5}-4×10^{-3} M.

absorption features as that of the neutral pyridine adduct. Variations of the spectra in different solvents or in the presence of excess ligand were not detected. The data are summarized in Table II.

$Na_2Mo_2O_4(OSCC_6H_5)_4$ could be recrystallized from pyridine without change. However, the anionic dimer was converted to the neutral derivative by the addition of 2 equiv of acid (reaction 5). The complex $Na_2Mo_2O_4(OSCC_6H_5)_4$

$$\begin{array}{l} Na_2Mo_2O_4(OSCC_6H_5)_4 + 2HCl \rightarrow \\ \qquad 2NaCl + 2C_6H_5COSH + Mo_2O_4(OSCC_6H_5)_2 \\ \qquad\qquad\qquad\qquad \big\downarrow \text{py} \\ \qquad\qquad\qquad\qquad Mo_2O_4(OSCC_6H_5)_2(py)_2 \end{array} \qquad (5)$$

reacted rapidly with 2 equiv of sodium dialkyldithiocarbamate in THF solution to form the neutral dithiocarbamate dimer (reaction 6). The infrared spectrum of the product confirmed

$$Na_2Mo_2O_4(OSCC_6H_5)_4 + 2NaS_2CN(Et)_2 \rightarrow Mo_2O_4(S_2CNEt_2)_2 + 4NaOSCC_6H_5 \qquad (6)$$

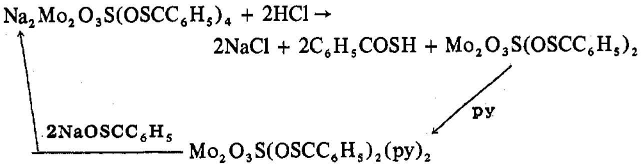
that complete displacement of the thiobenzoate ligands had occurred.

Preparation and Characterization of μ-Oxo, μ-Sulfido Complexes. Excess thiobenzoic acid reacted with sodium molybdate in ethanol to form an anionic molybdenum(V) complex formulated as $Na_2Mo_2O_3S(OSCC_6H_5)_4$ (reaction 7).

$$Na_2MoO_4 + C_6H_5COSH \xrightarrow{EtOH} Na_2Mo_2O_3S(OSCC_6H_5)_4 + C_6H_5C(=O)SSC(=O)C_6H_5 + C_6H_5CO_2C_2H_5 + H_2S + H_2O \qquad (7)$$

The acid served as both a protonating and a reducing agent for the molybdate ion. Dibenzoyl disulfide was also isolated as a product from reaction 7 and identified by its mass spectrum and melting point. The thiol acid also served as the ultimate source of a bridging sulfido ligand in the product. Esterification of thiobenzoic acid is known to form the sulfur-free ester and hydrogen sulfide.[18] The esterification of thiobenzoic acid appeared to be catalyzed in the reaction with molybdate since the reaction of thiol acids with primary alcohols is normally slow relative to the time required for reaction 7.[19] Ethyl benzoate was distilled from the reaction and identified by its mass spectrum. The hydrogen sulfide which was produced in the esterification process was the probable source of the bridging sulfido ligand in the dimeric molybdenum product. Sulfur substitution of bridging oxo ligands has been effected in several molybdenum(V) dimers by hydrogen sulfide.[6c,6e,7a,8,13,20]

Scheme I



The addition of 2 equiv of 1 M HCl to a THF solution of $Na_2Mo_2O_3S(OSCC_6H_5)_4$ produced the neutral dimeric complex with bridging oxygen and sulfur ligands. Intermolecular associations could be prevented by recrystallization from pyridine. The addition of sodium thiobenzoate to the bis(pyridine) adducts produced the original anionic dimer (Scheme I).

The infrared spectra of the new complexes provided evidence for the μ-oxo μ-sulfido bridging unit.[6c] In the infrared spectrum of $Mo_2O_3S(OSCC_6H_5)_2(py)_2$ vibrations of the bridging oxo ligand occurred at 720 and 500 cm^{-1}, shifts to respectively lower and higher frequencies than those observed for the analogous di-μ-oxo complex. A new band at 460 cm^{-1} was assigned to a Mo–S_b vibration. The other bands in the spectrum were assentially identical with those observed for $Mo_2O_4(OSCC_6H_5)_2(py)_2$. The spectrum of the anionic molybdenum dimer with a sulfido bridge showed similar shifts in the low-energy region of the spectrum. The IR data for all of the complexes are summarized in Table III.

The visible spectrum of $Na_2Mo_2O_3S(OSCC_6H_5)_4$ varied in pyridine and acetonitrile solvents (Table II). The pyridine spectrum was very similar to that of $Mo_2O_3S(OSCC_6H_5)_2(py)_2$, and this suggested that the dissociation of the sodium molybdenum salt occurred in pyridine according to eq 8.

$$Na_2Mo_2O_3S(OSCC_6H_5)_4 \rightarrow 2Na^+ + 2C_6H_5COS^- + Mo_2O_3S(OSCC_6H_5)_2(solv)_2 \qquad (8)$$

However, it has been proposed that the electronic absorptions of molybdenum(V) dimers represent transitions between molecular orbitals with contributions primarily from metal and ligand orbitals of the Mo_2O_4 or $Mo_2O_{4-x}S_x$ unit.[17,6c] In this case similar spectral features might be expected for the neutral and anionic dimers even in the absence of the dissociation process. It was not possible to carry out further spectral studies of the possible equilibrium of eq 8 since no change was observed in the spectrum of $Na_2Mo_2O_3S(OSCC_6H_5)_4$ upon the addition of excess ligand (2 equiv). Additional data supporting the occurrence of eq 8 in pyridine were obtained in electrochemical studies (vide infra).

Conductivity Studies. Equivalent conductivities of acetonitrile solutions of $Na_2Mo_2O_3S(OSCC_6H_5)_4$ and Na_2Mo_2-

Table III. Infrared Data

compound	$\nu_{Mo=O}$, cm^{-1}	ν_{Mo-O_b}, cm^{-1}	ν_{Mo-S_b}, cm^{-1}	$\nu_{C\dot{-}S}$, cm^{-1}	$\nu_{C\dot{-}O}$, cm^{-1}
$Mo_2O_4(OSCC_6H_5)_2(py)_2$	980	737		960	1470
		476		940	
$Na_2Mo_2O_4(OSCC_6H_5)_4$	980	730		935	1470
	970	463		910	~1590[a]
$Mo_2O_3S(OSCC_6H_5)_2(py)_2$	980	720	460	960	1460
		500		940	
$Na_2Mo_2O_3S(OSCC_6H_5)_4$	985	720	448	955	1470
		508		925	1475
					~1590[a]
$NaOSCC_6H_5$[14]				960	1500

[a] Both phenyl and $C\dot{-}O$ vibrations appear in the region 1550–1600 cm^{-1}. The strongest band was tentatively assigned to $V_{C\dot{-}O}$ and is listed in this table.

Table IV. Cyclic Voltammetric Reductions[a]

compound	E_{pc}, V, vs. SCE
$Mo_2O_4(OSCC_6H_5)_2(py)_2$	−1.52
$Na_2Mo_2O_4(OSCC_6H_5)_4$	−1.53 −2.04
$Mo_2O_3S(OSCC_6H_5)_2(py)_2$	−1.31
$Na_2Mo_2O_3S(OSCC_6H_5)_4$	−1.31 −1.88

[a] ~1 mM complexes in pyridine, 0.1 M n-Bu_4NClO_4.

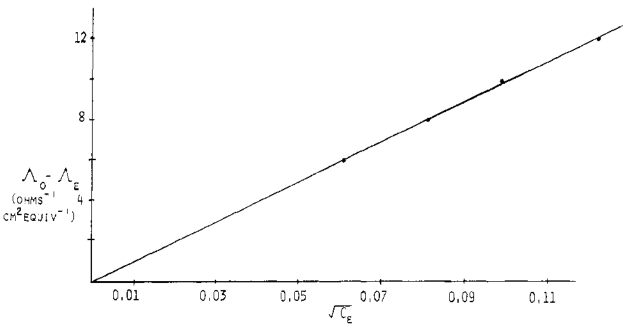


Figure 1. Onsager plot for $Na_2Mo_2O_3S(OSCC_6H_5)_4$ for concentrations $>2.5 \times 10^{-3}$ N. The slope of the plot is 100. The calculated slope for 1:1 electrolytes in acetonitrile is in the range 306–376; for 2:1 electrolytes the calculated slope is in the range 892–1038.[22]

$O_4(OSCC_6H_5)_4$ were plotted as a function of concentration over a range of $\sim 1 \times 10^{-2}$–1×10^{-4} N. The equivalent conductivity Λ_ϵ (which equals $^1/_2\Lambda_{molar}$ for a 2:1 electrolyte) approached the value expected for a 2:1 electrolyte[21] only in the region of very dilute solutions. The plot indicated that a single process involving complete dissociation of the sodium ion according to eq 9 did not occur at concentrations $>10^{-4}$

$$Na_2Mo_2O_3X(OSCC_6H_5)_4 \rightarrow 2Na^+ + [Mo_2O_3X(OSCC_6H_5)_4]^{2-} \quad (9)$$
$$X = O \text{ or } S$$

N. In the second possible equilibrium involving the dissociation of sodium thiobenzoate (eq 8), the equivalent conductivity of sodium and thiobenzoate ions would equal the conductivity based on the molar concentration of sodium thiobenzoate. Observed values approached those expected for a 1:1 electrolyte[21] only at very low concentrations. In addition, an Onsager plot for $Na_2Mo_2O_3S(OSCC_6H_5)_4$ in the concentration region of linear dependence had a slope much lower than that expected for either a 2:1 or 1:1 electrolyte in acetonitrile[22] (Figure 1). Conductivity data for solutions of sodium thiobenzoate in acetonitrile were recorded over the same concentration range for comparison. The extent of ion pairing for the free ligand salt was very similar to that observed for the solutions of $Na_2Mo_2O_3X(OSCC_6H_5)_4$. On the basis of these data, the extensive ion pairing which occurs in acetonitrile solutions of $Na_2Mo_2O_3X(OSCC_6H_5)_4$ may involve sodium and thiobenzoate ions produced according to eq 8 and/or sodium and dimeric molybdenum ions produced according to eq 9.

Cyclic Voltammetry. Electrochemical studies of the complexes were carried out in pyridine to eliminate complications from pyridine ligand dissociation. In the available cathodic potential range (up to ~−2.0 V vs. SCE) the complexes $Mo_2O_3S(OSCC_6H_5)_2(py)_2$ and $Mo_2O_4(OSCC_6H_5)_2(py)_2$ each displayed one reduction curve which was irreversible at scan rates of 100–500 mV/s.[23] Peak potentials were observed at −1.31 and −1.52 V, respectively. It has been noted previously that the substitution of sulfur for a bridging oxygen ligand in molybdenum(V) dimers results in less cathodic reduction potentials.[6c,f]

It has also been observed that the nature of the chelating ligand did not greatly alter the reduction potentials of neutral oxo- and sulfido-bridged molybdenum(V) dimers.[6c] However, in this system the reduction potential of an anionic dimer in pyridine solution might be expected to show some cathodic shift relative to that of a corresponding neutral dimer. Two irreversible processes were observed for each anionic molybdenum complex. However, the peak potential for the first curve in each case was identical with that of the corresponding neutral dimer (Figure 2). The second curve in each system may be associated, at least in part, with the reduction of sodium thiobenzoate. These latter curves increased in current amplitude (and shifted to slightly more cathodic potentials) as additional ligand salt was added to the solutions[24] (Figure 3). These data suggested that in pyridine solution, some dissociation of the complexes $Na_2Mo_2O_3S(OSCC_6H_5)_4$ and $Na_2Mo_2O_4(OSCC_6H_5)_4$ occurred to form neutral dimers and sodium thiobenzoate according to eq 8.

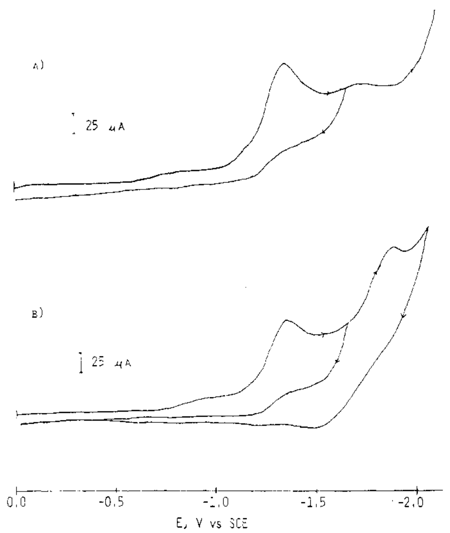


Figure 2. Cyclic voltammetric reductions in pyridine/0.1 M n-Bu_4NClO_4, scan rate 0.1 V/s: (A) $Mo_2O_3S(OSCC_6H_5)_2(py)_2$ (~10^{-3}) M); (B) $Na_2Mo_2O_3S(OSCC_6H_5)_4$ (~10^{-3} M).

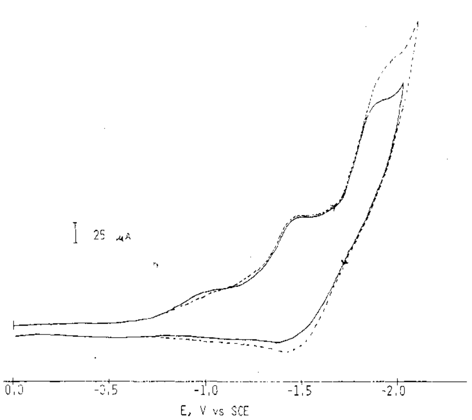


Figure 3. (—) Cyclic voltammetric reduction of $Na_2Mo_2O_4(OSCC_6H_5)_4$ in pyridine/0.1 M n-Bu_4NClO_4; (---) cyclic voltammogram of same solution to which $NaOSCC_6H_5$ has been added. The small peak at −1.0 V may be due to an impurity.

Experimental Section

Materials. Thiobenzoic acid (95%) from Aldrich and dichlorodioxomolybdenum(VI) from Alfa were used without further purification. Reagent grade solvents used in synthetic procedures with MoO_2Cl_2 and in physical measurements were dried: tetrahydrofuran was distilled from lithium aluminum hydride, diethyl ether was distilled from sodium, and toluene was distilled from calcium hydride. Pyridine was stored over potassium hydroxide and then distilled from barium oxide before use. Acetonitrile was refluxed over P_2O_5 for 24 h, distilled onto calcium hydride, refluxed and distilled a second time. Only the middle fractions of the distillates were used.

Preparation of Compounds. Sodium thiobenzoate was prepared by the stoichiometric addition of an aqueous sodium hydroxide solution to an ethanolic solution of thiobenzoic acid or by the reported neutralization procedure with sodium carbonate.[14] The product was dried in a vacuum desiccator over P_2O_5.

Unless otherwise noted, the syntheses of the molybdenum complexes were carried out in a Vacuum Atmospheres Model HE-94-2 glovebox containing a nitrogen atmosphere.

$Mo_2O_4(OSCC_6H_5)_2(py)_2$ (1). Dichlorodioxomolybdenum(VI) (0.64 g, 3.2 mmol) and sodium thiobenzoate (1.02 g, 6.4 mmol) were dissolved in diethyl ether/tetrahydrofuran (40 mL/10 mL), and the reaction was stirred for 12–16 h. The orange solution was filtered to remove NaCl and evaporated to dryness. The resulting brown solid was washed with several 10-mL portions of ether to remove dibenzoyl disulfide and then dissolved in ~15 mL of pyridine to which approximately 5 mL of ether was added. The red-orange crystals which formed after several hours were filtered, washed with ether, and dried in vacuo; mp ~200 °C dec. Anal. Calcd for $C_{24}H_{20}O_6S_2N_2Mo_2$: C, 41.86; H, 2.91; S, 9.30. Found: C, 41.71; H, 2.89; S, 9.27. Yield 60–70%.

$Na_2Mo_2O_4(OSCC_6H_5)_4$ (2). Compound **1** (0.24 g, 0.36 mmol) was slurried in 30 mL of tetrahydrofuran and sodium thiobenzoate (0.11 g, 0.7 mmol) was added. After stirring for an hour, all solids had dissolved. Approximately 20 mL of toluene was added, and the solution was evaporated to ~25 mL. Bright orange crystals precipitated after ~2 h. The product was filtered, washed with ether, and dried in vacuo; mp 180–184 °C dec. Anal. Calcd for $C_{28}H_{20}O_8S_4Mo_2Na_2$: C, 39.53; H, 2.35; S, 15.06. Found: C, 39.38; H, 2.49; S, 15.12. Yield ~80%.

$Na_2Mo_2O_3S(OSCC_6H_5)_4$ (3). Thiobenzoic acid (8.7 g, 63 mmol) was dissolved in 75 mL of absolute ethanol in air and sodium molybdate dihydrate (5.25 g, 21 mmol) was added with stirring. The reaction mixture changed to a deep red and after ~30 min an orange solid precipitated. This contained both the product compound and dibenzoyl disulfide. The molybdenum complex was dissolved in ~40 mL of acetone and filtered to remove the disulfide (mp 132 °C). The filtrate was reduced in volume to ~10 mL and filtered again. Addition of 20 mL of absolute ethanol and reduction in volume produced an orange solid. This was recrystallized from 30 mL of tetrahydrofuran to which 15 mL of toluene had been added. The product can also be prepared by the addition of sodium thiobenzoate (2 equiv) to $Mo_2O_3S(OSCC_6H_5)_2(py)_2$ (vide infra) in a procedure analogous to that described for the preparation of compound 2; mp 207–209 °C dec. Anal. Calcd for $C_{28}H_{20}O_7S_5Mo_2Na_2$: C, 38.80; H, 2.31; S, 18.47. Found: C, 38.87; H, 2.44; S, 18.35. Yield 35–40%.

$Mo_2O_3S(OSCC_6H_5)_2(py)_2$ (4). Compound **3** (0.31 g, 0.36 mmol) was dissolved in 20 mL of tetrahydrofuran in air and 1.0 M HCl (0.72 mL, 0.72 mmol) was added dropwise with stirring. Sodium chloride (identified by its powder pattern) precipitated immediately and was filtered. The filtrate was evaporated to form an oil and then crystallized from ~15 mL of dichloromethane. This crude orange product was dried in vacuo and then recrystallized under nitrogen from 15 mL of pyridine/5 mL of ether. Deep red crystals formed after ~1 h; mp ~200 °C dec. Anal. Calcd for $C_{24}H_{20}O_5N_2S_3Mo_2$: C, 40.91; H, 2.84; S, 13.64. Found: C, 40.86; H, 2.88; S, 13.53. Yield 70%.

Physical Measurements. Infrared spectra of Nujol and hexachlorobutadiene mulls were recorded on a Perkin-Elmer 337 grating spectrophotometer. Visible spectra were recorded on a Cary Model 17 recording spectrophotometer. NMR spectra were obtained at 90 MHz using a Varian 390 spectrometer. Conductivities were measured using a Serfass bridge from Industrial Instruments. Elemental analyses were performed by Spang Laboratories. Electrochemical studies were carried out under a nitrogen atmosphere at ambient temperatures. A Princeton Applied Research Model 174 A polarographic analyzer was used to obtain the cyclic voltammograms. Working and counter platinum wire electrodes were treated prior to electrochemical measurements by oxidation with concentrated $H_2SO_4/K_2Cr_2O_7$ and subsequent reduction with ferrous ammonium sulfate. The saturated calomel reference electrode was separated from the test solution by a bridge tube (from PAR) equipped with a Vycor disk at the tip.

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Registry No. **1**, 66940-46-3; **2**, 66940-47-4; **3**, 66940-48-5; **4**, 66940-49-6; MoO_2Cl_2, 13637-68-8.

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(23) At faster scan rates, two one-electron reductions have been observed for many molybdenum(V) dimers in nonaqueous solvents, particularly for those dimers with bridging sulfur ligands.[6c]
(24) The peak potentials of sodium thiobenzoate were sensitive to the condition of the electrode surface, and initial scans with chemically pretreated electrodes often were not reproduced after scanning through other waves. It is therefore difficult with solutions containing several species to associate waves with the redox processes of sodium thiobenzoate solely on the basis of observed peak potentials.