the sum of van der Waals radii (3.78 Å).[11,12] No other I–S distances of any type appear to have been reported. Burow's normal-coordinate analysis for ISO_2^- assumed a much shorter I–S distance of 2.5 Å.[8] No unusual features were evident in the triphenylbenzyl cation or the crystal packing.

Conclusions

The use of large organo cations allows convenient synthesis of a series of well-defined, easily handled iodosulfinate complexes. The complexes have SO_2 dissociation pressures in the range 0.5–17 Torr at ambient temperature and SO_2 dissociation pressures in excess of 1 atm at 100 °C and higher. The geometry of the ISO_2^- anion has been shown by x-ray diffraction to be pyramidal with an I–S distance of 3.251 (3) Å.

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Registry No. [K(18-crown-6)](ISO_2), 65392-62-3; [Rb(18-crown-6)](ISO_2), 65392-61-2; [$AsPh_4$](ISO_2), 65392-60-1; [PPh_3Bz](ISO_2), 65392-59-8; [Ph_3P-N-PPh_3](ISO_2), 65392-58-7; [Na(18-crown-6)]($NCSSO_2$), 65392-57-6; [K(18-crown-6)]($NCSeSO_2$), 65392-56-5; [K(18-crown-6)]I_3, 65392-54-3.

Supplementary Material Available: A listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

Molybdenum and Rhenium Complexes of Aromatic Amine Thiolate Ligands

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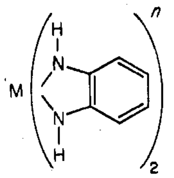
Complexes of the form $Mo(C_6H_3XSNH)_3$ (X = H, Cl) are prepared by reaction of the *o*-aminobenzenethiol ($C_6H_3XSHNH_2$) either with MoO_4^{2-} in acidic aqueous ethanol or with $MoO_2(acac)_2$ in CH_3OH. The N-deprotonation, established by analytical and spectroscopic studies, illustrates the acidity enhancement effect of metals in high formal oxidation states. The observation of ^1H and ^{14}N superhyperfine splitting in the EPR spectrum of $Mo(C_6H_4SNH)_3^-$ prepared in situ from $Mo(C_6H_4SNH)_3$ confirms the protonation state of the ligands. Reaction of ReO_4^- and $C_6H_3XSHNH_2$ under similar conditions yields complexes of tentative formulation $Re(C_6H_3XSNH)_2(C_6H_3XSN)$ from which $Re(C_6H_3XSNH)_3^n$ complexes can be prepared where n = 1–, 0, 1+. The complex with charge 1+ is only stable in acid solution. Both Mo and Re complexes show reversible electron-transfer behavior in polar aprotic solvents, and their electronic spectra indicate a close resemblance to tris(1,2-dithiolene) complexes which possess trigonal-prismatic coordination. Incorporation of the *o*-aminobenzenethiolate unit into tetradentate ligands, L = $C_6H_4(S^-)NHCHRCHRNHC_6H_4(S^-)$ (R = H, CH_3), allows preparation of Mo(VI) complexes of the form MoO_2L and $Mo_2(SC_6H_4NCH_2CH_2NC_6H_4S)_3$, the latter spectroscopically resembling the tris complexes reported above. The observed EPR properties and the ability of some of these complexes to transfer both electrons and protons are discussed in relation to the possible role of molybdenum in enzymes.

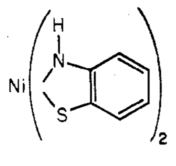
Introduction

The unsaturated 1,2-dithiolate ligands (1,2-dithiolenes[2]) have been found to form bis,[2,3] tris,[2,4–6] and tetrakis[7] complexes which display an array of interesting chemical, electrochemical, structural, and electronic structural properties. In particular, the tris complexes display reversible electron-transfer properties[4–6] and structural variation[8–13] as a function of metal, ligand, and oxidation state. For a given metal, the more highly oxidized members of an electron-transfer series display trigonal-prismatic coordination while the reduced members show structures closer to the octahedral geometry.[6,9,10] Similarly, as one moves from right to left (e.g., from Mo to Zr) in the periodic table, the tendency to adopt trigonal-prismatic coordination decreases.[11–13]

Certain unsaturated amine and amine thiol ligands[14–18] display many of the properties of the dithiolenes. For example, a series of complexes, I, has been prepared from *o*-phenylenediamine[17] for M = Co, Ni, Pd, and Pt; n = 0, 1+. In these complexes each amine group is monodeprotonated and functionally is a coordinated amido group. Additionally, the oxidized complex of nickel and *o*-aminobenzenethiol, II, $Ni(abt)_2$, has also been shown[14,15] to contain monodeprotonated amine groups and to have dithiolene character.



I



II, $Ni(abt)_2$

In contrast, this same ligand, *o*-aminobenzenethiol, also forms a series of more conventional complexes wherein the amine retains its fully protonated form. Larkworthy et al.[19]

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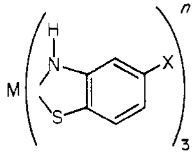
Table I. Elemental Analysis Data

Complex		% C	% H	% N	% S
$Mo(NHSC_6H_4)_3$	Calcd	46.45	3.22	9.03	20.64
	Found	45.82	3.29	8.84	19.48
		(46.36)	(3.56)	(9.30)[a]	
$Mo(NHSC_6H_3Cl)_3$	Calcd	37.99	2.11	7.39	
	Found	37.05	1.85	7.38	
$Re(NSC_6H_4)(NHSC_6H_4)_2$	Calcd	38.99	2.53	7.58	17.63
	Found	39.28	2.92	7.03	16.68
$Re(NHSC_6H_4)_3$	Calcd	38.94	2.70	7.57	17.30
	Found	40.01	3.08	7.19	16.45
$[(C_6H_5)_4As^+][Re(NHSC_6H_4)_3^-]$	Calcd	53.70	3.55	4.26	9.75
	Found	54.22	3.92	4.61	9.08
$[Re(NHSC_6H_4)_3^+][C_7H_7SO_3^-]$	Calcd	41.32	3.03	5.78	17.33
	Found	41.37	3.05	5.68	16.18
$Re(NSC_6H_3Cl)(NHSC_6H_3Cl)_2{\cdot}C_2H_5OH$	Calcd	34.12	2.42	5.97	
	Found	35.05	2.34	6.55	
$[(C_6H_5)_4As^+][Re(NHSC_6H_3Cl)_3^-]$	Calcd	48.20	3.07	4.05	
	Found	48.18	2.99	3.93	
$[Re(NHSC_6H_3Cl)_3^+][C_7H_7SO_3^-]$	Calcd	36.70	2.32	5.14	
	Found	37.20	2.26	5.68	
$Mo(NHSC_6H_4)_3{\cdot}0.5[(C_4H_9)_4N^+Br^-]{\cdot}CH_2Cl_2$	Calcd	45.50	4.92	6.88	13.50
	Found	45.23	5.07	6.75	13.06
$Re(NHSC_6H_4)_3{\cdot}0.5[(C_4H_9)_4N^+Br^-]$	Calcd	43.60	4.61	6.64	13.40
	Found	44.45	4.86	6.64	12.13
$MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$	Calcd	41.79	3.60	8.33	
	Found	41.04	3.79	8.29	
$MoO_2(C_6H_4SNHCHCH_3CHCH_3NHSC_6H_4)$	Calcd	44.65	4.21	6.51	
	Found	44.72	4.45	6.69	
$Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3$	Calcd	49.99	3.60	8.33	
	Found	49.84	3.79	8.29	

[a] Prepared by method b.

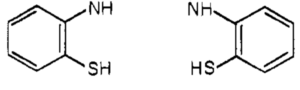
have prepared such complexes for most of the first-row transition metals. Pt(II) and Pd(II) complexes of this ligand were prepared by Livingstone,[20] and Hodge et al.[21] studied complexes of VO^{2+}. These complexes do not behave similarly to dithiolenes and when considered together with complexes such as II illustrate the dual capability of the *o*-aminobenzenethiol ligand.

In this paper we report the investigation of complexes of $C_6H_4SHNH_2$ and related ligands with Mo and Re. The isolation and characterization of tris(*o*-aminobenzenethiolato) complexes (III, M = Mo, Re, X = H, Cl) reveals their distinct



III
X = H, $M(abt)_3^n$
X = Cl, $M(abtCl)_3^n$

similarities to the previously studied[2,8] tris(1,2-dithiolene) complexes and illustrates the capacity of the amine thiol complexes to transfer or exchange protons as well as electrons. The observable proton and nitrogen superhyperfine splitting in the EPR spectrum of $Mo(C_6H_4SNH)_3^-$ is discussed in this regard. For comparative purposes, complexes of the tetradentate ligand IV were also prepared.



IV (R = H, CH_3)

The experimental observations are discussed in relation to transition-metal dithiolene chemistry,[2,8] molybdenum coordination chemistry,[22-24] and the role Mo plays in enzymes.[23-25]

Experimental Section

Chemicals and Equipment. *o*-Aminobenzenethiol and 4-chloro-2-aminobenzenethiol hydrochloride were purchased from Eastman Organic Chemicals and used as received. Na_2MoO_4 was obtained from J. T. Baker Chemical Co. and $KReO_4$ from Alfa Inorganics. $MoO_2(acac)_2$ was a generous gift of Climax Molybdenum Corp. Tetrahydrofuran was treated with $LiAlH_4$ and distilled prior to use. DMF was distilled from and stored over Linde 4A molecular sieves. Other solvents were spectroscopic grade and used as received.

Elemental analyses were carried out by Galbraith Labs., Inc., Knoxville, Tenn., Chemalytics Inc., Tempe, Ariz., and PCR, Inc., Gainesville, Fla., or were done on a PE 240 elemental analyzer equipped with an MC 240 microejector from Control Equipment Corp. (at CFKRL). Elemental analyses are presented in Table I.

Infrared spectra were obtained on a Perkin-Elmer 257, Perkin-Elmer 437, or Beckman IR 20 spectrometer. Spectra were run in KBr pellets. Electronic spectra were obtained on a Cary 14 or 118C spectrophotometer. Polarography and cyclic voltammetry were run on a Chemtrix SSP-3 or a Princeton Applied Research Model 170 Electrochemistry System using a dropping-mercury or stationary-platinum electrode. Conductivity values were obtained on a Serfass bridge using shiny platinum electrodes.

Preparation of Complexes. $Mo(abt)_3$. Method a. To a solution of 1.1 mL (10 mmol) of *o*-aminobenzenethiol dissolved in 5 mL of 5% H_2SO_4 and 45 mL of 95% ethanol is added a solution of 0.81 g (3.3 mmol) of sodium molybdate in 50 mL of water. The solution turns deep brown and then dark green with the formation of a dark green precipitate which is collected by filtration. The complex is recrystallized from *dry* tetrahydrofuran (THF) and *dry* 2-propanol to give the microcrystalline product (henceforth designated $Mo(abt)_3$): yield 90% based on MoO_4^{2-}; mp 175 °C dec.

Method b. Addition of 3 mmol (0.37 g) of ligand in 15 mL of methanol to a filtered solution of 1 mmol (0.33 g) of $MoO_2(acac)_2$ in 10 mL of methanol gives dark green crystals of the compound in nearly 100% yield. These are filtered, washed with methanol and ether, and dried under vacuum. Recrystallization is effected from THF and 2-propanol. In the absence of oxygen, solutions of the compound in *dry* THF or *dry* dimethylformamide (DMF) are stable for at least 2 days.

$Mo(abt)_3{\cdot}0.5[(C_4H_9)_4N^+Br^-]{\cdot}CH_2Cl_2$. Tetrabutylammonium bromide (0.5 g; 1.5 mmol) and $Mo(abt)_3$ (0.5 g; 1 mmol) are dissolved in methylene chloride and the solution is filtered. An equal volume of dry 2-propanol is added and the solution is reduced in volume until precipitation is complete: yield 75% based on $Mo(abt)_3$; mp 169 °C.

$Mo(abtCl)_3$. 4-Chloro-2-aminobenzenethiol hydrochloride (1.0 g; 5 mmol) is dissolved in 50 mL of 95% ethanol, and 5 mL of 5% H_2SO_4

is added. To this, a solution of sodium molybdate (0.40 g; 1.65 mmol) in 40 mL of water is added. To the resulting green solution, water is slowly added until precipitation is complete. The complex is recrystallized from hot methylene chloride and carbon tetrachloride: yield 30% based on MoO_4^{2-}; mp 204 °C.

$Re(C_6H_4NS)(C_6H_4NHS)_2$. To a solution of 0.60 mL (5 mmol) of *o*-aminobenzenethiol and 5 mL of 5% H_2SO_4 in 50 mL of 95% ethanol is added potassium perrhenate (0.50 g; 1.7 mmol) in 80 mL of hot water. The resulting solution slowly turns deep brown. It is heated on a steam bath for 1 h, during which time a brown crystalline product precipitates: yield 100% based on ReO_4^-; mp 201 °C.

$Re(abt)_3$. $Re(C_6H_4NS)(C_6H_4NHS)_2$ (0.60 g; 1 mmol) is dissolved in 75 mL of acetone and filtered. To this is added 40 mL of water, and the solution is allowed to stand for several days. The solution turns blue green, and dark needles precipitate: yield 55%; mp >250 °C.

$[(C_6H_5)_4As^+][Re(abt)_3^-]$. To a solution of $Re(abt)_3$ (0.25 g; 0.42 mmol) in 75 mL of THF under nitrogen, N_2H_4 (95%) is added dropwise until a deep blue solution is obtained. To this is added $(C_6H_5)_4As^+Cl^-$ (0.20 g; 0.47 mmol) in 50 mL of 2-propanol. The solution is allowed to stand under nitrogen for about 2 h during which time the blue product precipitates. It can be recrystallized from hot methylene chloride and 2-propanol: yield 90% based on $Re(abt)_3$; mp 150 °C.

$[Re(abt)_3^+][C_7H_7SO_3^-]$. A solution of $Re(abt)_3$ (0.25 g; 0.42 mmol) and *p*-toluenesulfonic acid (1.5 g; 8 mmol) in 75 mL of THF is bubbled with O_2 for 1 h and allowed to stir overnight. 2-Propanol (50 mL) is then added and the solution is reduced in volume until the dark green complex just begins to precipitate. The initial precipitate is filtered off and discarded. To the supernatant solution water is added until the green complex precipitates: yield 20% based on $Re(abt)_3$; mp 185 °C dec.

$Re(abt)_3{\cdot}0.5[(C_4H_9)_4N^+Br^-]$. This complex is made by the same procedure as is $Mo(abt)_3{\cdot}0.5(C_4H_9)N^+Br^-{\cdot}CH_2Cl_2$: yield 60% based on $Re(C_6H_4NHS)_3$; mp 195–197 °C.

$Re(C_6H_3ClNS)(C_6H_3ClNHS)_2{\cdot}C_2H_5OH$. This compound is made by the procedure used for $Re(C_6H_4NS)(C_6H_4NHS)_2^0$: yield 50% based on ReO_4^-; mp 210 °C.

$Re(abtCl)_3$. The crude product is prepared in the same manner as $Re(abt)_3$. Further purification can be achieved by dissolving the crude product in THF and chromatographing on a silica gel column. The complex is eluted with anhydrous ether as a blue-green band which is collected. The eluate is diluted with hexane (in equal volume) and the solution concentrated until precipitation is complete: yield 25% based on $Re(C_6H_3ClSN)(C_6H_3ClSNH)_2$; mp 220 °C. Although this complex does not analyze satisfactorily, it is sufficiently pure for use in the preparations described below.

$[(C_6H_5)_4As^+][Re(abtCl)_3^-]$. This compound is prepared from $Re(abtCl)_3$ using the same procedure as for $[(C_6H_5)_4As^+][Re(C_6H_4NHS)_3^-]$. Reduction in volume is necessary to aid in the precipitation of the complex: yield 50%; mp 253 °C.

$[Re(abtCl)_3^+][C_7H_7SO_3^-]$. To a solution of $Re(abtCl)_3^0$ (0.25 g; 0.38 mmol) and excess *p*-toluenesulfonic acid (1 g; 5 mmol) in 50 mL of THF, H_2O_2 (30%) is added dropwise until a deep green color is obtained. An equal volume of 2-propanol is added, and the solution is reduced to about half the original volume. Water is then added until precipitation is complete. Recrystallization can be effected from THF, 2-propanol, and hexane: yield 50% based on $Re(C_6H_3SNHCl)_3$; mp 210 °C.

$MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$. Ligand IV (R = H)[26] (1.93 g; 7 mmol) in 30 mL of hot methanol is added to a filtered solution of $MoO_2(acac)_2$ (2.28 g) in 50 mL of warm methanol. The dark brown mixture deposits dark brown crystals which are filtered after 30 min of stirring; these are washed with about 80 mL of CH_2Cl_2 and the intense green washings collected. On further washing with CH_2Cl_2 the green color of the washings diminishes and eventually disappears leaving behind red-brown crystals. These are washed with methanol and ether and dried under vacuum (yield 54%, 1.5 g). The compound is soluble in DMF and to a lesser extent in CH_2Cl_2 and $C_2H_4Cl_2$; mp 218–220 °C dec.

$Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3$. Evaporation of the green washings from the preparation of $MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$ above gives a green solid which on recrystallization from CH_2Cl_2 gives green crystals of the compound (yield 20% based on total $MoO_2(acac)_2$).

Table II. Susceptibility and Conductivity Data

Complex	Conductivity,[a] Λ^{-1} M^{-1} cm^2	μ_{eff},[b] μ_B
$Mo(abt)_3$	Nonelectrolyte	Diam
$Mo(abtCl)_3$	Nonelectrolyte	Diam
$Re(abt)_3$	Nonelectrolyte	1.47
$[(C_6H_5)_4As^+][Re(abt)_3^-]$	50.0	0.6
$[Re(abt)_3^+][C_7H_7SO_3^-]$	40.6	0.4
$Re(NSC_6H_4)(NHSC_6H_4)_2$	Nonelectrolyte	0.6
$Re(abtCl)_3$	Nonelectrolyte	1.45
$[(C_6H_5)_4As^+][Re(abtCl)_3^-]$	45.6	Diam
$[Re(abtCl)_3^+][C_7H_7SO_3^-]$	39.5	0.6
$Re(abtCl)(NHSC_6H_3Cl)_2$	Nonelectrolyte	0.6
$Mo(abt)_3{\cdot}0.5[(C_4H_9)_4N^+Br^-]{\cdot}CH_2Cl_2$	41.5	Diam
$MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$	Nonelectrolyte	Diam[c]
$MoO_2(C_6H_4SNHCHCH_3CHCH_3NHSC_6H_4)$	Nonelectrolyte	Diam[c]
$Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3$	Nonelectrolyte	Diam[c]

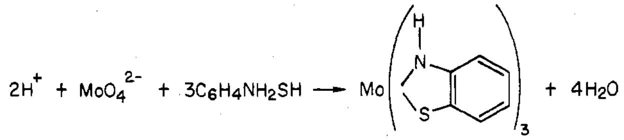
[a] Complexes are 10^{-3} M in DMF; $T = 22$ °C. [b] Measured as solids by the Gouy method at room temperature 21–23 °C. [c] Diamagnetism assigned by NMR spectroscopy.

$MoO_2(C_6H_4SNHCHCH_3CHCH_3NHSC_6H_4)$. Dark red-brown crystals of this compound are isolated in 65–70% yield using ligand IV (R = CH_3),[26] $MoO_2(acac)_2$, and the procedure described above for $MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$. The CH_2Cl_2 washings are green here too, but the green complex analogous to that obtained for IV (R = H) could not be obtained in analytically pure form; mp 197–199 °C dec.

Titrations of supernatant solutions were accomplished in the following manner. The titration curves of both the 5% H_2SO_4 and *o*-aminobenzenethiol (in ethanol, water) were recorded using a Beckman SS2 pH meter, a combination calomel, glass electrode, and standardized sodium hydroxide. Reactants were then carefully mixed in the concentrations listed above. The precipitate was filtered off and washed several times with distilled water. The filtrate and washing liquid were collected and brought to 250 mL. Aliquots were then withdrawn, and the titration curve was recorded. The experiments above showed that phenolphthalein was a suitable indicator, and further runs were done to the phenolphthalein end point.

Tris Complexes of Molybdenum and Rhenium

Synthesis and Characterization of Molybdenum Complexes. The reaction of sodium molybdate with *o*-aminobenzenethiol goes to completion in acidified aqueous ethanol. Titration of the supernatant solution and the analytical data (Table I) agree with the reaction formulated as



The analogous reaction for 4-chloro-2-aminobenzenethiol does not go to completion under these conditions. The crude product is contaminated with what seems to be an oxo species. Infrared bands at 890 and 900 cm^{-1} as well as several additional bands in the N–H region disappear upon recrystallization.

An alternative method of preparation involves the reaction

$$3C_6H_4NH_2SH + MoO_2(acac)_2 \rightarrow Mo(abt)_3 + 2H_2O + 2acacH$$

where the yield is again virtually 100% and the product is in all respects identical with that prepared from molybdate. Addition of less than the 3:1 stoichiometric amount of ligand still results in the preparation of the tris complex albeit in lower yields.

The MoL_3 compounds are diamagnetic in the solid state and in solution and are nonelectrolytes in DMF (Table II). Infrared spectra of the purified complexes show a lack of oxo bands in the 850–970-cm^{-1} region. $Mo(abt)_3$ shows a set of three sharp peaks with ν(N–H) at 3190, 3250, and 3300 cm^{-1}

Table III. Electronic Spectral Properties of Tris(*o*-aminobenzenethiolato) Complexes

Complex	ν_1, cm^{-1} (ϵ, ×10^4)	ν_2, cm^{-1} (ϵ, ×10^4)	ν_3,^{b} cm^{-1} (ϵ, ×10^4)	ν_4, cm^{-1} (ϵ, ×10^4)	ν_5, cm^{-1} (ϵ, ×10^4)
$Mo(abt)_3$	14 400 (1.4)			24 600 (1.7)	
$Mo(abtCl)_3$	14 200 (1.1)			24 400 (1.2)	
$[Re(abt)_3^+](C_7H_7SO_3^-)$	14 600 (2.0)		22 700 (1.0)	25 600 (1.35)	
$[Re(abtCl)_3^+](C_7H_7SO_3^-)$	14 500 (2.0)		22 200 (0.90)	26 500 (1.5)	
$Re(abt)_3$	14 900 (1.3)	16 800 (1.4)	22 100	27 300 (1.75)	32 300 (1.0)
$Re(abtCl)_3$	14 700 (1.2)	16 500 (1.1)	22 700	27 100 (1.76)	33 100 (2.1)
$[(C_6H_5)As^+][Re(abt)_3^-]$	14 600 (0.48)	16 900 (0.78)		29 500 (1.5)	32 900 (1.7)
$[(C_6H_5)_4As^+][Re(abtCl)_3]$	13 700 (0.43)	16 900 (1.2)		28 200 (2.0)	30 500 (1.5)

[a] Complexes dissolved in CH_2Cl_2. [b] Shoulder.

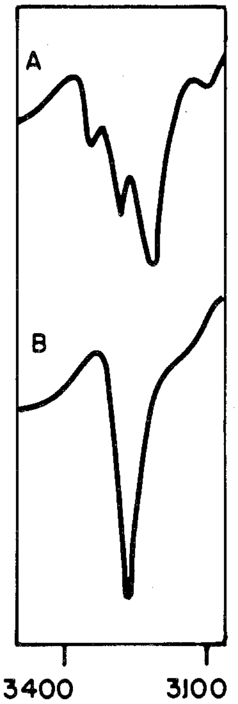


Figure 1. Infrared absorption spectrum in the N–H stretching region of (A) $Mo(abt)_3$ and (B) $Mo(abtCl)_3$.

as shown in Figure 1. Preparation of the complex using deuterated solvents (or exchange with CH_3OD in $C_2H_4Cl_2$) leads to the expected spectral shift (ν(N–D) observed at 2370, 2410, 2445 cm^{-1}). $Mo(abtCl)_3$, on the other hand, displays a sharp single peak at 3300 cm^{-1}. In both complexes the sharpness of the peaks is reminiscent of the infrared spectrum of $Ni(abt)_2$, II.[15]

The electronic absorption spectra of the tris Mo complexes (Table III) strongly resemble that of $Mo(S_2C_6H_4)_3{}^0$[27,28] (vide infra). The combined evidence leads us to formulate these complexes as six-coordinate tris(*o*-aminobenzenethiolato)-molybdenum complexes. A key feature of these complexes is the presence of deprotonated amine nitrogens in a complex prepared in acid solution. This formulation of the Mo coordination sphere is confirmed by the EPR studies of its one-electron reduction product.

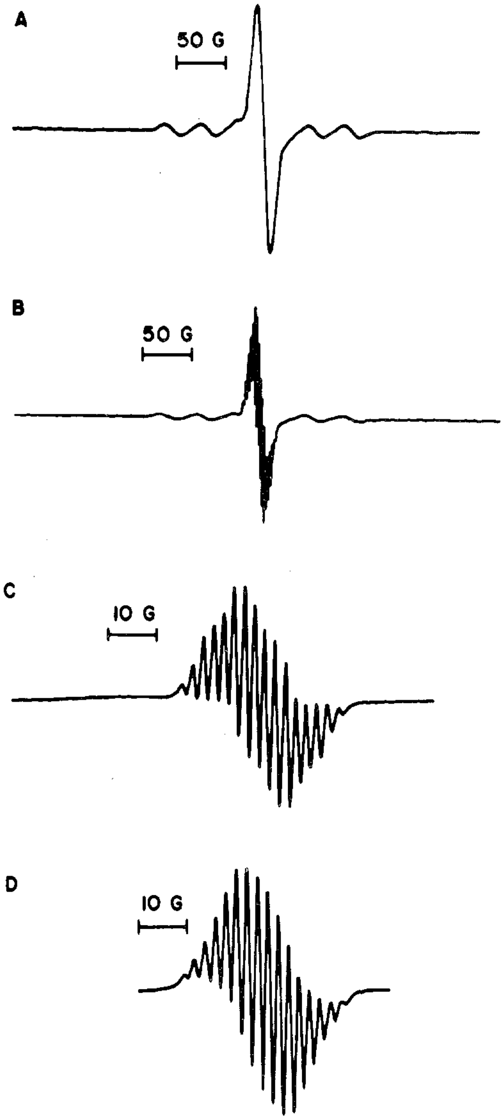


Figure 2. Electron paramagnetic resonance spectrum of $Mo(NHSC_6H_4)_3^-$ generated by reduction with Na(Hg) in THF (A) at 23 °C, (B) at −65 °C, and (C) at −85 °C, expanded scale. D is a computer simulation of C.

EPR of $Mo(C_6H_4SNH)_3^-$ and $Mo(C_6H_4SND)_3^-$. The monoanionic one-electron reduction product of $Mo(abt)_3$ can be generated in THF using Na(Hg) or Li(Hg) as reductant. At room temperature the EPR signal of Figure 2A is obtained from which $g = 1.988$ G and $A(^{95,97}Mo) = 38$ G are calculated. While superhyperfine splitting from ^1H or ^{14}N is not observed at room temperature, lowering the temperature reveals the patterns of Figure 2B and C where splitting from both nuclei are clearly resolved. It should be noted that the temperature at which highest resolution (lowest line width) is obtained is *above* the freezing point of the solvent.[29,30] Spectral simulation (Figure 2D) of the 16-line pattern in Figure 2C reveals that the values of $A_{^{14}N} = 2.1$ and $A_{^1H} = 6.3$ G adequately simulate the spectrum. However, the values of $A_{^{14}N} = 4.8$ and $A_{^1H} = 2.4$ G also lead to the same spectral pattern. These latter values have been assigned by other workers[30] for $Mo(C_6H_4SNH)_3^-$ prepared in solution in DMF from $MoCl_5$ and $C_6H_4SHNH_2$.[30] To unequivocally establish the assignment, we reduced $Mo(C_6H_4SND)_3$ prepared in a manner analogous to the protio complex. The complex spectrum appearing in Figure 3 is found for which simulation reveals $A_{^{14}N} = 2.1$ and $A_{^2H} = 1.1$ G. Since it is not reasonable to expect $A_{^{14}N}$ to change by a substantial amount upon deuterio substitution,

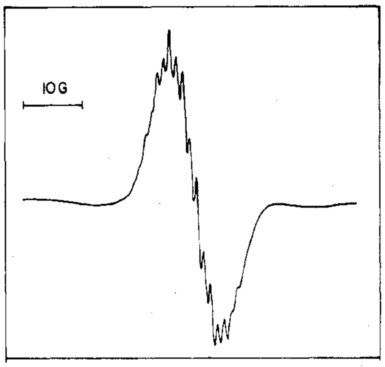


Figure 3. Electron paramagnetic resonance spectrum of $Mo(ND\text{-}SC_6H_4)_3^-$ in THF at -86 °C.

the spectrum of the deuterio complex is inconsistent with the assignment of $A_{^{14}N}$ as 4.8 G and the assignments of $A_{^{14}N}$ = 2.1 and $A_{^1H}$ = 6.3 G are confirmed for the protio complex.

The observed superhyperfine splitting in the Mo complex clearly establishes the presence of three $C_6H_4SNH^{2-}$ ligands in the Mo coordination sphere. Insofar as these splittings are concerned, the three ligands appear equivalent.

Rhenium Complexes. Reaction of $KReO_4$ with *o*-aminobenzenethiol results in apparent 100% yield of a brown complex which we formulate as $Re(C_6H_4SN)(C_6H_4SNH)_2^0$. Titration of the supernatant and analytical data agree with the formulated reaction

$$H^+ + ReO_4^- + 3C_6H_4SHNH_2 \rightarrow Re(C_6H_4SN)(C_6H_4SNH)_2 + 4H_2O$$

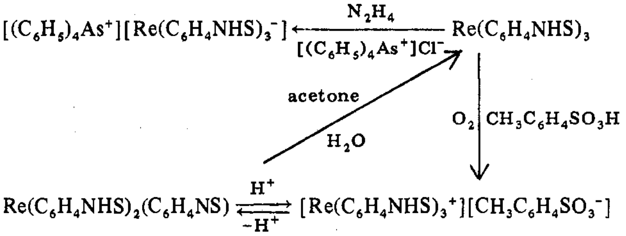
Two sharp bands are observed in the N–H region of the infrared spectrum with ν(N–H) at 3234 and 3255 cm^{-1}. The absence of metal–oxo bands in the infrared region makes formulations containing oxygen unlikely.

The analogous (4-chloro-2-aminobenzenethiol)rhenium complex is made by the same procedure. It displays three sharp bands in the N–H region at 3280, 3250, and 3205 cm^{-1}. Analysis as well as IR spectral data [ν(O–H) 3410 cm^{-1} and ν(C–H) 2910 cm^{-1}] indicates the presence of a stoichiometric amount of ethanol in the crystalline complex. The Re complexes each show a small magnetic moment of 0.6 μ_B (Table II) which we attribute to temperature-independent paramagnetism commonly found in Re(VII) compounds.[31,32] Both complexes are nonelectrolytes in DMF. For these formally Re(VII) complexes, the data require one doubly deprotonated and two singly deprotonated coordinated amines. Recalling that the complexes are prepared in acid solutions, this result illustrates the extreme acidity of ligands in complexes with high formal oxidation states.

The blue-green $Re(abt)_3$ and $Re(abtCl)_3$ complexes can be prepared by prolonged treatment of $Re(C_6H_4SN)(C_6H_4SNH)_2^0$ or $Re(C_6H_3ClSN)(C_6H_3ClSNH)_2^0$ with aqueous acetone. The $Re(abt)_3^0$ complex shows a single ν(N–H) peak at 3200 cm^{-1} in its infrared spectrum. The complex can be prepared in its *N*-deuterio form by reaction of the parent Re(VII) compound with D_2O/acetone. The *N*-deuterio complex shows ν(N–D) at 2400 cm^{-1}. The compounds are nonelectrolytes in DMF and are paramagnetic with $Re(abt)_3^0$ showing a magnetic moment of 1.47 μ_B while $Re(abtCl)_3^0$ shows a moment of 1.45 μ_B at 22 °C. The moments are corrected for diamagnetism. Incorporation of a correction for the temperature-independent paramagnetism found in the Re(VII) systems in the calculation would give a moment of about 1 μ_B. Electrochemical studies (Table IV, vide infra) reveal that the ReL_3 complexes undergo reversible one-electron oxidation and reduction processes at potentials which indicate the existence of chemically accessible species.

The chemical reduction of the Re(VI) complexes can be effected by hydrazine and leads to the deep blue Re(V) anions.

Scheme I



Addition of tetraphenylarsonium chloride in 2-propanol causes precipitation of $[(C_6H_5)_4As][Re(abt)_3]$. The $[(C_6H_5)_4As][Re(abtCl)_3]$ salt is considerably more soluble as is generally true for all of the 4-chloro complexes. The complexes are 1:1 electrolytes in DMF.

The deep green Re(VII) cation results from O_2 oxidation of $Re(abt)_3$ in acidic media. The 4-chloro analogue is not oxidized at any appreciable rate by O_2 but is easily formed by addition of 30% H_2O_2. Both are isolated from *p*-toluenesulfonic acid media as the tosylate salts. [Peroxide oxidation of $Re(abt)_3^0$ does not lead to the tosylate salt but to an insoluble green complex, the nature of which is at present unknown.] The complexes are 1:1 electrolytes in DMF and show small paramagnetism ($[Re(abt)_3^+][CH_3C_6H_4SO_3^-]$, 0.4 μ_B; $[Re(abtCl)_3^+][CH_3C_6H_4SO_3^-]$, 0.6 μ_B) which again can be attributed to temperature-independent paramagnetism.[31,32]

Significantly, we note that acid solution is necessary to isolate the cation $Re(C_6H_4NHS)_3^+$ which is formally in the Re(VII) state. In the absence of strong acid, the green Re(VII) complex is not stable and yields a brown solution presumably containing $Re(C_6H_4NHS)_2(C_6H_4NS)$. The process is reversible insofar as addition of strong acid to $Re(C_6H_4NHS)_2(C_6H_4NS)$ generates the green $Re(abt)_3^+$ complex. The interconversion of the Re complexes is displayed in Scheme I.

The combined analytical, infrared, magnetic, conductivity, polarographic, and electronic spectra data confirm the existence of the series $Re(C_6H_3XSNH)_3^{1-,0,1+}$. This series resembles the corresponding tris(dithiolene) set in attaining formal oxidation numbers V, VI, and VII, respectively.[28,33]

Solubility Enhancement–Adduct Formation. The neutral tris complexes $Mo(abt)_3$ and $Re(abtCl)_3$ are slightly soluble in methylene chloride. However, addition of tetrabutylammonium bromide causes a remarkable solubility enhancement. Subsequent addition of 2-propanol precipitates a compound which can be formulated as (complex)·$0.5Bu_4N^+Br^-$. These are termed adducts although there is clearly no indication of covalent bond formation.

The electronic spectra of the adducts are identical with those of the corresponding neutral complex indicating that the ML_3 fragment remains intact in the "adducts". Cyclic voltammetric patterns of the adducts are identical with those displayed by the parent complexes. The infrared spectra confirm the presence of the *n*-butyl groups, and the conductivity of the adducts in DMF is as expected for tetrabutylammonium bromide at the same concentration.

Adduct formation by tetraalkylammonium salts has some precedent in aromatic ring systems.[35] However, the 1:2 ratio found in isolated samples in the present case is somewhat unusual. It may result from "linear" stacking in the crystal lattice of the form shown below

Br^- complex NR_4^+ complex Br^-

giving a unit cell with the required 1:2 mole ratio. As the complexes must have a dipolar structure (vide infra), this stacking could involve the negative end of the complex interacting with NR_4^+ and the positive end interacting with Br^-.

The lack of spectral shift indicates the interaction to be weak and probably to be due to electrostatic or van der Waals forces.

Related Molybdenum Complexes. An interesting feature of the preparative reactions discussed above is the ability of the $C_6H_4SHNH_2$ ligand to effect removal of all oxo groups from the Mo coordination sphere while maintaining the Mo (at least formally) in the VI oxidation state. A second feature of interest is the N-deprotonation of the complexes which also occurs during the preparation. It is likely that these two processes, oxo removal and N-deprotonation, are related. We therefore sought to prepare $MoO_2(C_6H_4SNH_2)_2$ for comparative purposes, but all attempts led either to $Mo(C_6H_4SNH)_3$ or to the ligand disulfide (when preparations were attempted in air). However, while this direct comparison was not possible, we have found that the tetradentate ligands IV formed complexes of the type MoO_2L with the ligand present in the dianionic form (L^{2-}).

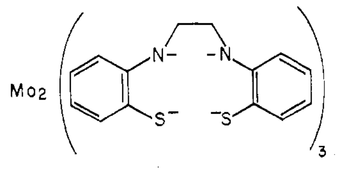
The complexes are prepared by reaction of ligand with $MoO_2(acac)_2$ presumably (but *not* quantitatively) according to

$$MoO_2(acac)_2 + IV \rightarrow MoO_2L + 2acacH$$

The species with R = H and R = CH_3 are very similar in properties and the data discussed below are for the R = H complex. Here, the N–H vibration at 3160 cm^{-1} and the Mo–O vibrational bands at 886 and 855 cm^{-1} are in agreement with the N-protonated formulation of the ligand and with the presence of the *cis*-dioxo grouping in the coordination sphere.[25] Unlike the tris complexes which are intensely green, the MoO_2L complex displays a red-brown solution with the lowest absorption maxima at 22 600 cm^{-1} (ϵ 3310) and 25 300 cm^{-1} (ϵ 10 200). The complex shows a quasi-reversible voltammetric wave at −1.0 V vs. SCE.

In these complexes where the two oxo groups remain coordinated to the Mo there is clearly no deprotonation of the coordinated amine ligands. In this case the deprotonated donors in the Mo(VI) complex are the more acidic aquo ligands which are present in their doubly deprotonated oxo form.

Although the preparation of MoO_2L is accomplished in reasonably good yield, there is an interesting side product which is a nonoxo complex. Thus, a green crystalline complex of formulation V, can be isolated from the reaction solution.



V

This complex displays no infrared absorption in either the N–H or Mo–O stretching regions of the infrared spectrum. Its electronic absorption spectrum strongly resembles that of $Mo(abt)_3$ containing bands at 14 900 cm^{-1} (ϵ/dimer 13 400) and 23 100 cm^{-1} (ϵ 19 800). Additionally, it displays reduction waves at −0.14 and −0.88 V vs. SCE which are similar to those of $Mo(abt)_3$.

A most interesting aspect of this diamagnetic dimeric complex involves its behavior in preliminary EPR experiments upon reduction with Na(Hg) in THF. Thus, two apparently independent signals sequentially appear and Figure 4a shows both of these. One is a five-line pattern due to superhyperfine splitting of 2.2 ± 0.2 G from two equivalent N atoms, and the other is a broader signal displaying no superhyperfine splitting. We assume that these signals are due to the one- and two-electron reduction products of the neutral dinuclear species, respectively. Support for this assumption derives from the addition of excess neutral complex (Figure 4b) which enhances the amplitude of the sharp signal while decreasing the amplitude of the broad signal. The reactions

$$Mo_2L'_3 \xrightarrow{1e^-} Mo_2L'_3{}^- \xrightarrow{1e^-} Mo_2L'_3{}^{2-}$$

and

$$Mo_2L'_3{}^{2-} + Mo_2L'_3 \rightarrow 2Mo_2L'_3{}^-$$

(where L′ is the N-deprotonated form of ligand IV) are consistent with the observations. The broadness of the signal assigned to $Mo_2L_3{}^{2-}$ is attributed to spin–spin interactions between unpaired electrons on the two Mo centers. Attempts are under way to quantitate the reduction process coulometrically, to investigate the EPR of the reduced species at lower temperature, and to prepare crystals suitable for crystallography.

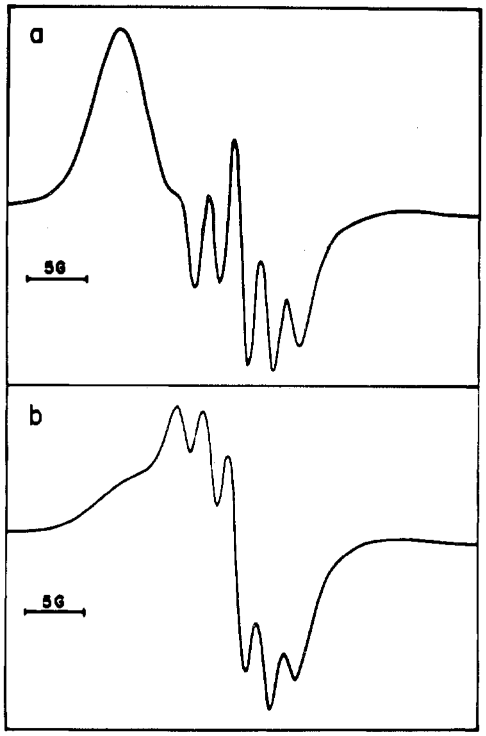
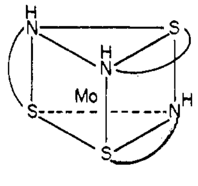


Figure 4. Electron paramagnetic resonance spectrum of $Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3{}^n$ formed by Na(Hg) reduction of the neutral molecule at −55 °C: (a) reduction allowed to proceed to color change; (b) excess $Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3$ added.

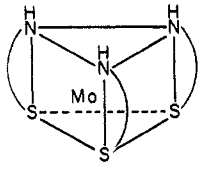
Spectral and Structural Considerations. The electronic spectra of $Mo(abt)_3$ and $Mo(abtCl)_3$ as well as the isoelectronic $[Re(abt)_3{}^+][C_7H_8SO_3{}^-]$ and $[Re(abtCl)_3{}^+][C_7H_8SO_3{}^-]$ show two intense bands in the visible region (Table III) with extinction coefficients in the 10 000–20 000 M^{-1} cm^{-1} range. These bands are similar to those of $Mo(S_2C_6H_3CH_3)_3{}^0$ and $Mo(S_2C_2[C_6H_5]_2)_3$ which are trigonal-prismatic dithiolene complexes.[2,8,24,28] The similarity suggests that the $(abt)_3$ and $(abtCl)_3$ complexes of molybdenum and rhenium may also approach trigonal-prismatic geometry.

If these compounds can indeed attain prismatic coordination, then several isomers are possible. Type A (two enantiomeric pairs of structural isomers possible), in which bridging of the

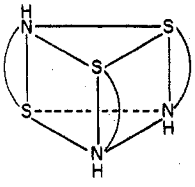


A

triangular edge occurs, is theoretically possible but has never been observed in trigonal-prismatic complexes[8] and is considered unlikely on this basis. Types B and C are considered more probable and are designated the cis and trans isomers, respectively. Although attempts have been made to distinguish between these by analysis of the infrared stretching frequencies in the ν(N–H) region, there are several possibilities and an unambiguous conclusion has not been reached.[36] The EPR spectrum of $Mo(C_6H_4SNH)_3^-$ showing three equivalent N and three equivalent H atoms would appear to favor structure B. However, the difference in coupling constants theoretically expected for structure C may not be sufficiently large to be observable.



B



C

Two potentially interesting structural subtleties should be noted at this point. First, in previous work it has been shown[8,11–13] that the S_2C_2 fragment of a dithiolate ligand often does not lie in the MS_2 chelate plane of the trigonal prism but can be at a small angle to it. This seems to be a common observation in dithiolene chemistry wherein the symmetry is reduced to C_{3h} in the tris systems. In a cis *o*-aminobenzenethiolate complex of type B the symmetry would be further reduced to C_3.

Second, the proton of the coordinated amino groups has been assumed to lie in the ligand plane as it presumably does in the $Ni(abt)_2$ complex. However, this need not be the case and the proton could well lie outside of the ligand plane. In fact, location of the amino proton could introduce considerable insight into the bonding of these complexes. Location in the plane of the ligand would indicate the importance of the extended π system of the ligand (the vertical system, π_v) in stabilizing the complex, whereas location of the proton out of the plane places the lone pair of the nitrogen out of position to participate in the ligand π_v system and implies that in-plane π bonding between metal and ligand (π_h bonding) is important. Coupled with the ability of the dithiolene ligands to bend about the S–S (or S–N) axes, this can lead to lowering of the symmetry of the complexes and may explain the complexity of the IR spectra.[36]

Despite the overall similarity, the electronic spectra of the rhenium and molybdenum amidothiolate complexes show some differences when compared to the spectra of the corresponding tris(dithiolene) complexes. These differences in energy of excitation and in extinction coefficients are probably reflections of the lower symmetry of the abt complexes and the differing donor ability of the RNH^- moiety as compared to the RS^- moiety. Changes in the coordination geometry are also possible due to the smaller bite of the *o*-aminobenzenethiolate ligand.[10] In light of this, only preliminary analysis of the electronic spectra has been attempted.[36] This has involved appropriate modification of the molecular-orbital scheme previously presented,[28] but in view of the structural uncertainties the detailed assignments are clearly speculative.[36]

Electrochemistry. The electrochemical characteristics of the neutral complexes were studied by means of dc polarography and cyclic voltammetry. Table IV gives the $E_{1/2}$ ($E_{1/2}$ here is defined as $(E_{pc} + E_{pa})/2$) values vs. a saturated calomel electrode and the peak-to-peak separation of the cyclic voltammetric reduction and oxidation waves.

The tris complexes show the reversible stepwise one-electron redox properties which are characteristic of the dithiolene complexes. The amidothiolate complexes are more difficult to reduce than the corresponding dithiolene systems in keeping with the results found in the bis systems.[14–18] The 4-chloro-2-amino thiolate complexes are easier to reduce than the corresponding unsubstituted system, consistent with the electron-withdrawing power of the chloro substituent, which should stabilize the reduced states. The electrochemical observations are consistent with an orbitally nondegenerate ground state for the neutral Re complexes based on arguments analogous to those presented for the corresponding dithiolene systems.[28]

Table IV. Polarography of ML_3 Complexes[a]

Complex	$1+ \rightarrow 0$	$0 \rightarrow 1-$	$1- \rightarrow 2-$
$Mo(abt)_3$		−0.190 (0.075)	−1.025 (0.080)
$Mo(abtCl)_3$[b]		−0.005 (0.10)	−0.935 (0.11)
$Re(abt)_3$	+0.395 (0.08)	−0.120 (0.08)	−1.825 (0.18)
$Re(abtCl)_3$	+0.530 (0.16)	+0.095 (0.12)	−1.608 (0.15)
$Ni(abt)_2$		−0.226 (0.08)	−1.073 (0.13)
$Mo(tdt)_3$		+0.277 (0.08)	−0.408 (0.10)

[a] 10^{-3} M in complex and 10^{-1} M tetraethylammonium perchlorate as supporting electrolyte in DMF. Voltages ($E_{1/2}$ values) measured vs. a saturated calomel electrode with dropping Hg working electrode. [b] In acetonitrile with a Pt electrode.

Conclusions and Biochemical Implications

The evidence presented above strongly indicates that the products of the reaction of molybdate and perrhenate with the amine thiol ligands are tris complexes in which the amine ligand is in various states of deprotonation. The isolation of these complexes with highly deprotonated amine ligands from *acid* solutions may at first seem unusual but is in line with general trends in Mo and Re coordination chemistry. For example, in the formal +6 oxidation state in acid solution Mo is usually present in the highly deprotonated state as the MoO_2^{2+} group (containing two doubly deprotonated aquo ligands) or in basic solution as MoO_4^{2-} (containing four doubly deprotonated aquo ligands). When the oxo groups are not present, the coordinated amines feel the full positive charge of the metal center and themselves become highly acidic. In the Re(VII) complex this effect seems sufficient to doubly deprotonate one amino group in the complex and to require acid solution to isolate the singly deprotonated species (see Scheme I). Viewed in a somewhat different way, deprotonated ligands stabilize higher oxidation states by virtue of their ability to act as π- as well as σ-donor ligands. In these complexes of Mo and Re the state of protonation is dependent on the state of oxidation. For other metals, examples of relatively deprotonated ligands associated with higher oxidation states have appeared in the recent literature.[37–39]

Several factors may contribute to the isolation of the amine deprotonated tris complexes in the present case. First, the high formal oxidation state of the metal *in the absence of coordinated oxo* will greatly decrease the pK_a of coordinated amine ligand. Second, the deprotonation allows the resultant $C_6H_4SNH^{2-}$ ligand to become similar to the analogous dithiolate donor, $C_6H_4S_2^{2-}$, and this allows the metal–ligand interaction to more closely resemble that of the dithiolene complex system. Clearly, oxo removal, amine deprotonation, and formation of the tris complex may all be involved in driving the observed reactions to completion. (Precipitation of the tris complexes formed does not appear to be a driving force insofar as in the preparation from $MoO_2(acac)_2$ in CH_3OH the green complex appears to be formed in homogeneous solution prior to crystallizing.)

The tris nonoxo complexes stand in sharp contrast to the MoO_2^{2+} species which contain N-substituted *o*-aminobenzenethiolate groups incorporated into a tetradentate ligand. Here, the amine serves as a neutral ligand, and it is clear that the acidity enhancing ability of the Mo(VI) oxidation state is expended on the aquo ligands which are in their doubly deprotonated oxo form. The strongly σ- and π-bonded O^{2-} ligands neutralize much of the formal positive charge on the Mo(VI) center.

The ability of Mo complexes to engage in proton- and electron-transfer processes may be viewed in light of the known behavior of molybdenum enzymes. There is now strong evidence that in some of the Mo oxidases, proton transfer from substrate to enzyme accompanies electron transfer in the same direction.[40,41] The results in this paper illustrate that it is natural for a transition-metal center to increase the protonation state of its coordinated ligands as the oxidation state of the metal decreases. This dependence of pK_a on oxidation state led us to propose a coupled electron–proton transfer as a general mechanism by which molybdo enzymes interact with substrates.[25,42] In support of this concept is the observation in four Mo enzymes of superhyperfine interaction from a single exchangeable proton.[40,43] In one case, that of xanthine oxidase, deuteration studies reveal the hydrogen atom in question to originate in the substrate xanthine. The observed superhyperfine splittings are large (9–14 G), and some felt it necessary to attribute this to the formation of a molybdenum hydride.[46] However, the observation of relatively large proton superhyperfine splitting in the ion $Mo(NHSC_6H_4)_3^-$ and in related complexes[44,45] reveals that protons on coordinated ligands can display relatively large isotropic superhyperfine coupling in Mo(V) EPR spectra. While these compounds *are not models* for Mo enzymes, they nonetheless demonstrate that protons on coordinated ligands can be both acidic and exchangeable and can show relatively large EPR superhyperfine splittings. These same features have each been established as key aspects of the action of Mo-containing enzymes.

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Registry No. $Mo(abt)_3$, 52820-25-4; $Mo(abtCl)_3$, 65354-51-0; $Re(C_6H_4NS)(C_6H_4NHS)_2$, 65354-50-9; $Re(abt)_3$, 65293-30-3; $[(C_6H_5)_4As^+][Re(abt)_3^-]$, 65293-54-1; $[Re(abt)_3^+][C_7H_7SO_3^-]$, 65293-52-9; $Re(C_6H_3ClNS)(C_6H_3ClNHS)_2$, 65354-52-1; $Re(abtCl)_3$, 65293-29-0; $[(C_6H_5)_4As^+][Re(abtCl)_3^-]$, 65293-38-1; $[Re(abtCl)_3^+][C_7H_7SO_3^-]$, 65293-36-9; $MoO_2(C_6H_4SNHCH_2CH_2NHSC_6H_4)$, 65293-34-7; $Mo_2(C_6H_4SNCH_2CH_2NSC_6H_4)_3$, 65378-49-6; $MoO_2(C_6H_4SNHCHCH_3CHCH_3NHSC_6H_4)$, 65293-33-6.

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