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Synthesis and Characterization of *cis*-Dioxomolybdenum(VI) Complexes with Sterically Bulky Tripodal Tetradentate Ligands

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Abstract

A new series of sterically bulky tripodal tetradentate ligands have been synthesized. The ligands were found to react readily with $MoO_2(acac)_2$ in absolute methanol to yield the corresponding *cis*-dioxoMo(VI) complexes. These complexes were characterized by IR, ^1H and ^{13}C NMR, UV–Vis spectroscopy, elemental analysis and cyclic voltammetry (CV). Cyclic voltammetry was performed in DMF and CH_2Cl_2. In CH_2Cl_2 the ease of reduction was found to decrease in the order $MoO_2[L{-}NO_2{-}(SCH_3)] > MoO_2[L{-}NO_2{-}(OCH_3)] > MoO_2[L{-}NO_2{-}(N(CH_3)_2)]$. The CV results are consistent with that expected for a S,O,N substitution pattern.

Introduction

Molybdenum is an important element both from a chemical [1] and biological [2, 3] viewpoint. Biologically, molybdenum has been incorporated into a number of enzymes known as the molybdoenzymes [4]. One class of these enzymes, the oxo-transferases, has been studied using Electron Paramagnetic Resonance (EPR) [5] and Extended X-ray Absorption Fine Structure (EXAFS) [6–9] spectroscopy. The results of such investigations on the oxidized forms of sulfite oxidase and nitrate reductase indicate that the *cis*-MoO_2^{2+} unit is coordinated by at least two thiolate sulfur ligands. The presence of other ligands such as nitrogen, oxygen or thioether can not be ruled out.

A number of dioxoMo(VI) complexes [4] have been prepared and studied as possible bioinorganic models for the molybdenum-cofactor (Mo-co). One of the most successful models to date is the [2,6-bis(2,2-diphenyl-2-thioethyl)pyridinato]dioxoMo(VI) complex synthesized by Berg and Holm [10]. This complex exhibits both structural and reaction chemistry that very closely models that of the oxo-transferases [11]. The *cis*-dioxoMo core is complexed with a tridentate ligand. This resulted in the Mo complex having an available coordination site to which a solvent molecule is bound.

Tripodal tetradentate ligands can be used which enable one to carry out a detailed systematic study of the effects on chemical properties of different ligand donor atoms. In addition, the lability of ligand donor groups *trans* to an oxo oxygen may allow competitive solvent or substrate binding. Previous studies using tripodal tetradentate ligands [12] have been unsuccessful as Mo-co models due to the formation of biologically irrelevant μ-oxoMo(V) dimers. This formation of μ-oxoMo(V) dimers may be prevented by incorporation of sterically bulky groups into the ligand framework. Such ligands when coordinated to molybdenum may prove to be excellent candidates as bioinorganic models for the Mo-co.

In this report we describe the synthesis, characterization and electrochemistry of *cis*-dioxoMo(VI) complexes coordinated by sterically bulky tripodal tetradentate ligands possessing different ligand donor atom sets.

Experimental

Materials

All ligand precursors (methylbromoacetate, 2-methoxyethylamine, 2-dimethylaminoethylchloride hydrochloride, iminodiacetic acid, *p*-toluenesulfonic acid, 2-chloroethylmethylsulfide, phenylmagnesium chloride and phenyllithium) were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was of HPLC grade and dried over lithium aluminum hydride. Dichloromethane and hexanes used for recrystallization were of reagent grade. Dichloromethane used for cyclic voltammetry was of puriss.p.a. grade (Fluka). *N,N*-Dimethylformamide (DMF), obtained from Burdick and Jackson, was stored over type 3 Å molecular sieves and deaerated with N_2 prior to use. $MoO_2(acac)_2$ was prepared according to a literature procedure [13] and characterized by its IR spectrum.

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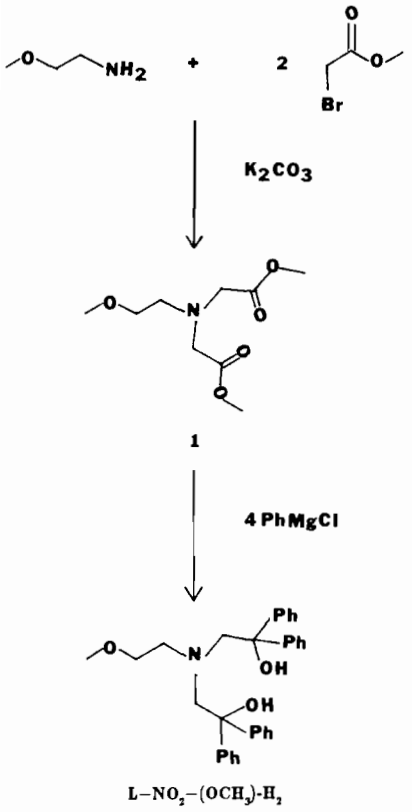
Synthesis

I. Ligands

A. N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-methoxyethane (L–NO_2–(OCH_3)–H_2, Scheme 1)

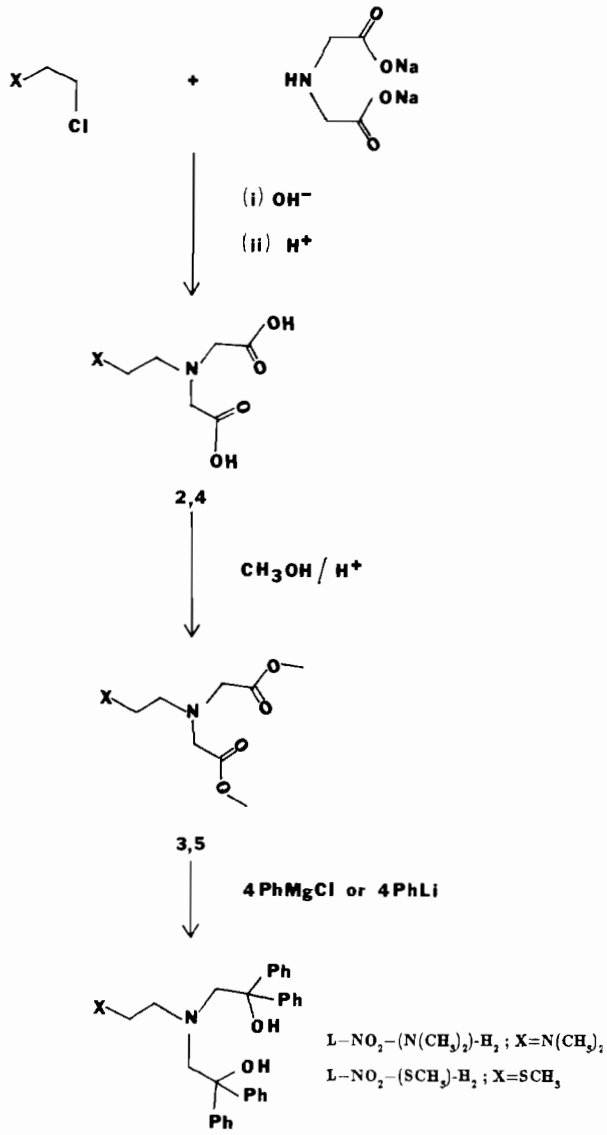
(i) N,N-Bis(methylethanoate)-1-amino-2-methoxyethane (1). **1** was synthesized from 2-methoxyethylamine and methylbromoacetate in the presence of potassium carbonate according to the method of Schwarzenbach *et al.* [14].



Scheme 1.

(ii) N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-methoxyethane. 12.0 g (55 mmol) of **1** was dissolved in 20 ml THF and then added in a slow dropwise manner to 110 ml of an ice cooled 2 M solution of phenylmagnesium chloride in THF. After refluxing for 1 h the reaction was cooled to 0–4 °C and hydrolyzed with 220 ml saturated ammonium chloride solution. The organic layer was removed, dried with anhydrous magnesium sulfate and filtered. Removal of the THF *in vacuo* yielded a viscous oil. 6.0 g of the ligand was isolated by dissolving the oil in methanol and allowing the solution to stand overnight at room temperature. The ligand was recrystallized for chemical characterization from hot methanol to yield pure white crystals, melting point (m.p.) = 145.0–146.2 °C dec. *Anal.* Calc. for $C_{31}H_{33}NO_3$: C, 79.63; H, 7.11; N, 3.00. Found: C, 79.70; H, 7.13; N, 2.96%. ^{1}H NMR in $CDCl_3$: δ 2.567 (t, 5.16 Hz, 2H, $-CH_2N$), 3.157 (t, 5.16 Hz, 2H, OCH_2), 3.268 (s, 3H, CH_3O), 3.561 (s, 4H, $N(CH_2-)_2$, 4.805 (s br, 2H, –OH), and 7.184–7.468 (m, 20H, C_6H_5) ppm; ^{13}C NMR in $CDCl_3$: δ 55.85 ($-CH_2N$), 58.71 (CH_3O), 67.28 ($N(CH_2-)_2$), 70–73 (OCH_2), 76.60 (C–OH), 146.52 (PhC_2), 126.74 (PhC_4), 128.13 (PhC_3), 126.14 (PhC_4) ppm.

B. N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-(N',N'-dimethylamino)ethane (L–NO_2–($N(CH_3)_2$)–H_2, Scheme 2)



Scheme 2.

(i) N,N-Bis(ethanoic acid)-1-amino-2-(N',N'-dimethylamino)ethane (2). This synthesis was adapted from the method of Morris *et al.* [15]. 28.8 g (0.20 mol) 2-dimethylaminoethyl chloride hydrochloride in 100 ml 50% aqueous methanol was added slowly to a solution containing 26.6 g (0.20 mol) iminodiacetic acid and 21.2 g (0.53 mol) sodium hydroxide in 300 ml 50% aqueous methanol maintained at 60 °C. When half of the above addition had taken place an additional 13.2 g (0.33 mol) sodium hydroxide was added to the mixture. After stirring overnight the methanol was removed *in vacuo* and the remaining aqueous phase acidified to pH 2.5 with concentrated HCl. Removal of the water yielded a white solid (NaCl) and a viscous residue. The NaCl was removed by the addition of methanol followed by filtration. Removal of methanol from the filtrate yielded the organic acid as a viscous oil.

(ii) N,N-Bis(methylethanoate)-1-amino-2-(N',N'-dimethylamino)ethane (3). 10 g of **2** was added to 300 ml of benzene. To this solution were added 50 ml of methanol and sufficient *p*-toluenesulfonic acid to adjust the pH to 1–2. The resultant solution was refluxed for 3 days using a Dean-Stark trap [16, 17]. On cooling, the reaction mixture was adjusted to pH 10 with an aqueous 10% Na_2CO_3 solution. The benzene layer was separated, dried with anhydrous $MgSO_4$ and filtered. Removal of the benzene *in vacuo* yielded the desired ester (2.5 g). ^{1}H NMR in $CDCl_3$: δ 2.20 (s, 6H, $(CH_3)_2N$), 2.84/2.40 (m, 4H, NCH_2-CH_2N), 3.57 (s, 4H, CH_2CO), 3.67 (s, 6H, OCH_3) ppm. IR ($CHCl_3$, sealed cell) ν(C=O stretch) 1775 cm^{-1}.

(iii) N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-(N',N'-dimethylamino)ethane. 4.6 g (20 mmol) of **3** was suspended in 20 ml of anhydrous diethyl ether and added in a slow dropwise manner to 40 ml of an ice cooled 2 M solution of phenyllithium in cyclohexane/diethyl ether (70/30). After refluxing for 3 h the reaction was cooled to 4 °C and hydrolyzed with 120 ml saturated aqueous ammonium chloride solution. An additional 60 ml of diethyl ether was added to the reaction mixture before the organic layer was removed. The aqueous layer was extracted with 3 X 50 ml of diethyl ether. The combined organic layers were dried with anhydrous $MgSO_4$ and filtered. Removal of the solvent *in vacuo* yielded a viscous oil. 1.1 g of the ligand was isolated by dissolving the oil in 95% ethanol and allowing it to stand overnight at room temperature. The ligand was recrystallized for chemical characterization from hot 95% ethanol to yield pure white crystals, m.p. = 162.5–164.0 °C dec. *Anal.* Calc. for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.38. Found: C, 80.10; H, 7.56; N, 5.79%. ^{1}H NMR in $CDCl_3$: δ 2.108 (s, 6H, $(CH_3)_2N$–), 2.093 (t, 2H, CH_2N), 2.426 (t, 2H, CH_2N) 3.414 (s, 4H, $N(CH_2-)_2$), ~5.5 (s vbr, 2H, –OH), and 7.164–7.392 (m, 20H, C_6H_5) ppm; ^{13}C NMR in $CDCl_3$: δ 44.95 ($(CH_3)_2N$), 53.45/57.45 (NCH_2CH_2N), 67.43 ($N(CH_2-)_2$), 75.73 (C–OH), 126.17 ($PhC_{2,6}$), 126.50 (PhC_4), 127.98 ($PhC_{3,5}$), 146.95 (PhC_1) ppm.

C. N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-methylthioethane (L–NO_2–(SCH_3)–H_2, Scheme 2)

(i) N,N-Bis(ethanoic acid)-1-amino-2-methylthioethane (4). **4** was synthesized from 2-chloroethylmethylsulfide and iminodiacetic acid in a manner analogous to that used for **2**. Acidification of the aqueous phase to pH 2.5 yielded the acid as a white solid. The acid was filtered, washed successively with water, methanol, and ether and then allowed to air dry (41% yield), m.p. = 194–196 °C dec. ^{1}H NMR in D_2O: δ 2.18 (s, 3H, CH_3S–), 2.92/3.58 (2 X t, 4H, SCH_2CH_2N), 4.20 (s, 4H, CH_2CO) ppm, IR (KBr disk) ν(C=O stretch) 1695 cm^{-1}.

(ii) N,N-Bis(methylethanoate)-1-amino-2-methylthioethane (5). **5** was synthesized in an analogous manner to that used for **3** except that 8 g of **4** was used to yield 5.5 g of product. ^{1}H NMR in $CDCl_3$: δ 2.12 (s, 3H, CH_3S), 2.80 (m, 4H, SCH_2CH_2N), 3.58 (s, 4H, CH_2CO), 3.70 (s, 6H, OCH_3) ppm. IR ($CHCl_3$, sealed cell) ν(C=O stretch) 1755 cm^{-1}.

(iii) N,N-Bis(2-hydroxy-2,2-diphenylethyl)-1-amino-2-methylthioethane. This was synthesized in an analogous manner to that used for L–NO_2-(OCH_3)–H_2. However, 95% ethanol was used to obtain the ligand from the oil (26% yield). The ligand was recrystallized for chemical characterization from hot 95% ethanol to yield pure white crystals, m.p. = 128.5–134.5 °C dec. *Anal.* Calc. for $C_{31}H_{33}NO_2S$: C, 76.98; H, 6.88; N, 2.90. Found: C, 77.08; H, 6.89; N, 2.89%. ^{1}H NMR in $CDCl_3$: δ 1.682 (s, 3H, CH_3S), 2.177–2.415 (m, 4H, SCH_2CH_2N), 3.536 (s, 4H, $N(CH_2-)_2$), 4.386 (s, 2H, –OH), 7.167–7.518 (m, 20H, C_6H_5) ppm; ^{13}C NMR in $CDCl_3$: δ 15.20 (CH_3S), 30.50 (SCH_2), 55.72 (CH_2N), 66.32 ($N(CH_2-)_2$), 76.39 (C–OH), 126.03 ($PhC_{2,6}$), 126.94 (PhC_4), 128.24 ($PhC_{3,5}$), 146.02 (PhC_1) ppm.

II. Molybdenum(VI) complexes

All of the *cis*-dioxoMo(VI) complexes were prepared in a similar manner from $MoO_2(acac)_2$ and the ligand in anhydrous methanol. A typical preparation follows:

[N,N-Bis(2-oxy-2,2-diphenylethyl)-1-amino-2-methoxyethane]dioxoMo(VI) (Mo(VI)O_2-[L–NO_2–(OCH_3)]). 2.00 g L–NO_2–(OCH_3)–H_2 was dissolved in 80 ml refluxing anhydrous methanol.

TABLE I. Cyclic Voltammetry, Spectroscopic, and Elemental Analysis Data for *cis*-Dioxomolybdenum(VI) Complexes

Mo(VI) complex	E_{pc} (V)[a]		ν(Mo=O) (cm^{-1})	Analysis: found (calc.) (%)		
	DMF	CH_2Cl_2[b]		C	H	N
$Mo(VI)O_2[L-NO_2-(SCH_3)]$	−1.70	−1.61	910	60.96 (61.08)	5.15 (5.13)	2.28 (2.30)
$Mo(VI)O_2[L-NO_2-(OCH_3)]$	−1.70	−1.82	895	62.64 (62.72)	5.31 (5.27)	2.36 (2.36)
$Mo(VI)O_2[L-NO_2-(N(CH_3)_2)]$	−2.00	<−2.08	895	63.55 (63.36)	5.70 (5.65)	4.67 (4.62)

[a]Volts *vs.* NHE with reference to the Fc^+/Fc redox couple (scan rate = 100 mV/s). [b]Small oxidation peak observed at −0.15 V for $Mo(VI)O_2[L-NO_2-(OCH_3)]$ and −0.12 V for $Mo(VI)O_2[L-NO_2-(SCH_3)]$.

1.40 g $MoO_2(acac)_2$ was added as the solid and the solution was refluxed for 30 mins. After cooling to room temperature the white solid was filtered, washed with absolute methanol and allowed to air dry, yield 2.40 g. Pure $Mo(VI)O_2[L-NO_2-(OCH_3)]$ was obtained by recrystallization from dichloromethane/hexanes, followed by vacuum drying at 111 °C.

Elemental analyses were performed by Atlantic Microlab, Atlanta, Ga.

Physical Measurements

Cyclic voltammetry measurements were made with a Bioanalytical Systems CV-1B potentiostat. The working electrode was a Bioanalytical Systems glassy carbon electrode and the auxiliary electrode was a Pt wire. An Ag wire was used as a pseudo reference electrode. All potentials were referenced to the ferrocenium/ferrocene couple (0.400 V *versus* NHE) [18]. The ferrocene concentration was $\sim 3 \times 10^{-4}$ M. All cyclic voltammetry measurements were done in dry and deaerated DMF or CH_2Cl_2 with tetrabutylammonium perchlorate (TBAP, $\sim 5 \times 10^{-2}$ M) as the supporting electrolyte and with a molybdenum complex concentration $\sim 10^{-3}$ M. IR spectra were obtained using a Perkin-Elmer Model 283 spectrophotometer. A Beckman Acta M VII spectrophotometer was used to obtain UV–Vis data. ^{1}H NMR data were obtained using a Varian EM360A, Jeol FX-90Q or Bruker IBM 270 MHz spectrometer. ^{13}C NMR data were obtained solely on the Bruker IBM 270 MHz spectrometer. Tables I and II contain electrochemical, spectroscopic, and elemental analysis data for the Mo complexes.

Results and Discussion

Sterically bulky tripodal tetradentate ligands containing O, N and/or S donor atoms and two potential ionizable hydrogens have been synthesized. The ligands underwent a rapid exchange reaction with the acetylacetonate monoanion ligands of $MoO_2(acac)_2$ to form the corresponding *cis*-dioxoMo(VI) complexes. All three Mo complexes displayed typical IR active terminal oxo stretches for the *cis*-dioxo MoO_2^{2+} cation. There was no evidence of oligomers in the solid state due to Mo=O····Mo bridging [19].

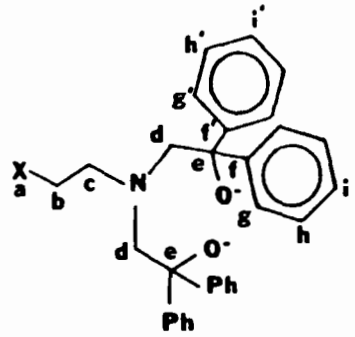
^{1}H NMR spectroscopy revealed the presence of an AB quartet for all of the Mo complexes. This is thought to arise from the geminal coupling of the methylene protons adjacent to the alkoxide donor groups. This means that the methylene protons are diastereotopic. For this to be the case, the two alkoxide donor groups must be situated *trans* to one another and *cis* to the oxo oxygens. This configuration places the alkoxide ligand donor groups *cis* to oxo atoms where they can more effectively compete for available empty d orbitals [10]. This would place the methoxy, methythio or dimethylamino ligand substituents *trans* to an oxo atom. This position has been shown to be very labile [20].

^{13}C NMR spectroscopy for the three Mo complexes reflected the steric constraints imposed upon them. Non-equivalence of the bulky phenyl groups was observed especially at $PhC_{f,f'}$ and $PhC_{g,g'}$ (Table II). This implies that free rotation of the phenyl groups is hindered thus making the ligands excellent candidates for the formation of mononuclear Mo complexes (especially Mo(V) complexes). Such species may be relevant to the EPR-active sites of Mo oxo-transfer enzymes [5].

Cyclic voltammetry (CV) was used to obtain cathodic reduction potentials (E_{pc}). All three Mo complexes exhibited irreversible redox behavior. This is evidenced by no observable oxidation wave upon the reverse anodic CV scan. Electrochemical studies on other *cis*-dioxoMo(VI) complexes [19, 21–24] have generally shown irreversible or quasireversible behavior. The $MoO_2(LNS_2)$ complex of Berg and Holm [10] was found to approach chemical reversibility at −23 °C, however, their results indicated

TABLE II. ^{1}H and ^{13}C NMR Chemical Shift Data[a] for $MoO_2[L-NO_2-(X)]$

L–NO_2–$(X)^{2-}$ =



X = OCH_3, $N(CH_3)_2$, SCH_3

	$MoO_2[L-NO_2-(OCH_3)]$			$MoO_2[L-NO_2-(N(CH_3)_2)]$			$MoO_2[L-NO_2-(SCH_3)]$		
	^{1}H	J (Hz)	^{13}C	^{1}H	J (Hz)	^{13}C	^{1}H	J (Hz)	^{13}C
a	3.788		61.39	2.553		48.42	1.451		15.05
	2.969			2.679			2.250		
b	2.997	5.56	68.67	2.709	5.63	56.39	2.287	7.77	25.57
	3.025			2.735			2.328		
				b, c		b, c			
	2.678			2.020			2.844		
c	2.705	5.56	56.53	2.047	5.59	56.19	2.888	7.74	54.55
	2.733			2.076			2.922		
	4.268			4.312			3.695		
d	4.331	12.58	73.84	4.376	12.76	72.35	3.758	12.63	68.65
	4.350	(J_{AB})		4.442	(J_{AB})		4.330	(J_{AB})	
	4.412			4.506			4.393		
phenyl	7.089–7.606			7.003–7.630			7.124–7.552		
e			90.30			90.11			93.72
f, f'			146.63			146.66			144.65
			147.55			148.37			146.95
g, g'			124.36			124.02			124.89
			124.04			125.00			125.45
h, h'			128.50			128.49			128.22
									128.75
i, i'			126.88			126.47			127.14
						126.85			127.24

[a] ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker IBM 270 MHz spectrometer. All chemical shifts are in ppm and are referenced to TMS.

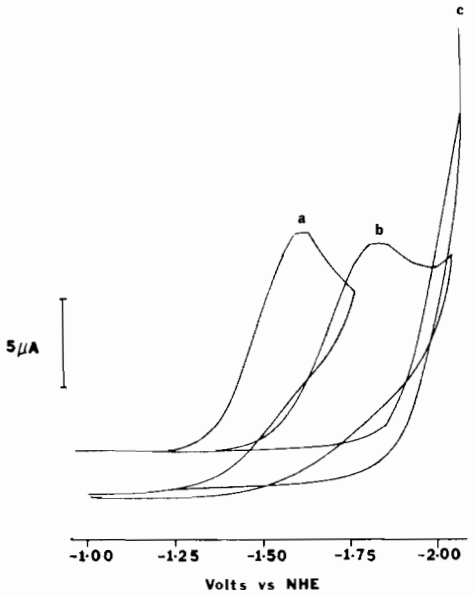


Fig. 1. Cyclic voltammograms for the Mo complexes in CH_2Cl_2. [Mo complex] $\simeq 1 \times 10^{-3}$ M; [TBAP] $\simeq 5 \times 10^{-2}$ M; scan rate = 100 mV/s. a = $MoO_2[L-NO_2-(SCH_3)]$; b = $MoO_2[L-NO_2-(OCH_3)]$; c = $MoO_2[L-NO_2-(N(CH_3)_2)]$.

that the initial reduction product reacted with the starting complex to yield an unidentified product lacking Mo–thiolate ligation. Other workers [25, 26] have observed Mo(IV) as an electrochemical product. Recently, reversible one-electron reductions have been observed for some Mo(VI) complexes [27, 28].

In DMF the cathodic reduction potentials for $MoO_2[L-NO_2-(OCH_3)]$ and $MoO_2[L-NO_2-(SCH_3)]$ were found to be identical to each other but more anodic than the corresponding $MoO_2[L-NO_2-(N(CH_3)_2)]$ complex. In CH_2Cl_2, however, all three complexes were found to exhibit distinct cathodic reduction potentials with the ease of reduction decreasing in the order $MoO_2[L-NO_2-(SCH_3)] > MoO_2[L-NO_2-(OCH_3)] > MoO_2[L-NO_2-(N-(CH_3)_2)]$ (Fig. 1).

A possible explanation for the lack of electrochemical discrimination observed in DMF is related to the lability of the ligand donor group *trans* to the terminal oxo oxygen. In the case of $MoO_2[L-NO_2-(N(CH_3)_2]$, the more basic dimethylamino ligand donor group is not readily displaced by the electrochemical solvent DMF. However, this may not be the situation with regards to the methylthio and methoxy ligand donor groups. In these two complexes the Mo may only experience tridentate chelation by the ligand with the remaining position *trans* to the terminal oxo group being occupied by a molecule of DMF. In this sence the cathodic reduction potential is very close to a similar complex synthesized by Berg and Holm [10], [2,6-bis(2,2-diphenyl-2-oxyethyl)-pyridinato] dioxoMo(VI), in which they observed irreversible behavior with an E_{pc} of −1.58 V *versus* NHE.

In CH_2Cl_2 it was demonstrated that variation of the ligand donor group *trans* to an oxo oxygen had a significant effect upon the cathodic reduction potential. The CV results are consistent with that expected for a S, O, N substitution pattern. The 0.21 V E_{pc} difference between $MoO_2[L-NO_2-(SCH_3)]$ and $MoO_2[L-NO_2-(OCH_3)]$ can be explained in terms of the availability of 3d orbitals which are much more accessible for S than O. In the presence of S, due to S 3d–Mo 4d interactions, there is a shift of electron density away from the Mo core thus making it more susceptible to reduction. The >0.26 V E_{pc} difference between the $MoO_2[L-NO_2-(OCH_3)]$ and $MoO_2(L-NO_2-(N(CH_3)_2)]$, however, can be explained on the basis of increased basicity of the N in the dimethylamino group. This increased basicity results in a shift of electron density onto the Mo core thus decreasing its susceptibility to reduction.

The trend in cathodic reduction potentials is also paralleled by the ^1H NMR data (Table III). These data show that an upfield shift of the protons present in the CH_3S ligand donor group occurs upon complexation of this group to the *cis*-dioxoMo(VI) core. This suggests that there is a shift of electron density away from the Mo core. In the case of CH_3O and $(CH_3)_2N$ ligand donor groups, a downfield shift is observed indicating a shift of electron density onto the Mo core.

The extremely cathodic potentials for these complexes can be explained in terms of (i) the lack of ligand delocalization and (ii) the presence of alkoxide donor groups. The former is corroborated by the

TABLE III. Comparison of ^1H NMR Chemical Shifts for Free and Complexed Ligands

Ligand donor group	^1H NMR chemical shifts (ppm *vs.* TMS)		
	Free ligand (L)	Mo(VI) complex (C)	Difference[a] (L–C)
CH_3S-	1.682	1.451	+0.231
CH_3O-	3.268	3.788	−0.520
$(CH_3)_2N-$	2.108	2.553	−0.445

[a]+ = upfield shift; − = downfield shift.

absence of any UV–Vis absorption bands above 260 nm which implies a lack of LMCT. Topich and Lyon [29] showed that ligand delocalization was one of several factors responsible for controlling the redox behavior of a series of tridentate Schiff base Mo(VI) complexes. The substitution of thiolate ligands with alkoxide ligands was shown by Berg and Holm [10] to cause a dramatic cathodic shift of 0.94 V for the reduction potential. Other workers [21, 29] have also observed similar effects, although not of the same magnitude, in which O-ligated Mo complexes are poorer oxidants than their S-ligated analogues.

Conclusions

Sterically bulky tripodal tetradentate ligands and their corresponding Mo(VI) complexes of the type discussed in this paper have potential as synthetic analogues of the Mo-co. The demonstrated lability of ligand donor groups *trans* to an oxo oxygen may allow competitive solvent or substrate binding. In addition, systematic variation of these ligand donor groups showed that the anodic shift of the cathodic reduction potential is dependent on sulfur. This is significant in view of the EXAFS evidence indicating that the *cis*-MoO_2^{2+} unit contained within the Mo-co is coordinated by at least 2 thiolate sulfur ligands. Incorporation of additional sulfur donor atoms into these tetradentate ligands is desirable and synthetic efforts toward this end are currently in progress. Finally, the presence of bulky phenyl groups impose steric constraints upon the Mo(VI) complexes and therefore may prevent upon reduction the formation of biologically irrelevant μ-oxo-Mo(V) dimers.

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