Inorg. Chem. **1990**, *29*, 2261–2267

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Synthesis and Characterization of Mononuclear Oxomolybdenum(V) Complexes with Aliphatic Diolato, Dithiolato, or Alkoxo Ligands: Effect of Chelate Ring Size on the Properties of the Metal Center

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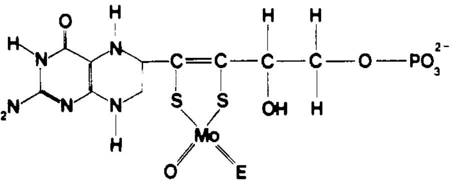
Received April 20, 1989

A series of mononuclear (diolato)- or (dithiolato)oxomolybdenum(V) complexes, LMoO[$E-(CH_2)_n-E$] (L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; E = O, S; $n = 2$–4), and bis(alkoxo) complexes, $LMoO(OR)_2$ (R = Me, Et, ^{n}Pr), have been synthesized and characterized by elemental analysis, mass spectrometry, electron paramagnetic resonance spectroscopy (EPR), cyclic voltammetry, and IR and electronic absorption spectroscopy. The lowest energy electronic absorption bands for the diolato complexes can be assigned as d → d transitions. However, the lowest energy electronic absorptions for the dithiolato complexes have substantial charge-transfer character. Hypsochromic and bathochromic effects are observed upon increasing the ring size for the dithiolato and diolato complexes, respectively. The value of $\langle g \rangle$ becomes smaller with increasing ring size in the diolato complexes, which correlates with the red-shift data obtained from the electronic spectra. All of these complexes exhibit quasi-reversible one-electron reduction waves. The diolato complexes with six- and seven-membered metallacycle rings and bis(alkoxo) complexes also show one-electron oxidation waves. The dithiolato complexes are more easily reduced than analogous diolato complexes. Both series of complexes show remarkable decreases in the Mo(V)/Mo(IV) reduction potential with increasing chelate ring size (0.12–0.22 V/additional CH_2 group).

Introduction

Molybdenum is a biologically important trace element that occurs in the redox-active sites of over a dozen molybdoenzymes that are involved in nitrogen, sulfur, or carbon metabolism.[2-10] The "oxo-type" molybdoenzymes catalyze biological two-electron redox reactions that involve a change in the number of oxygen atoms in the substrate.[11] These oxo-type molybdoenzymes possess a common molybdenum cofactor, Mo-co, which is proposed to coordinate to the molybdenum center through its dithiolene function, as represented in I.[12-15]



I

EXAFS (extended X-ray absorption fine structure) studies of the oxidized enzymes[16] show that the molybdenum atoms are also coordinated to terminal oxo and sulfido groups; E = O for sulfite oxidase (SO) and nitrate reductase (NR), and E = S for xanthine oxidase (XO), xanthine dehydrogenase (XDH), and aldehyde oxidase (AO). Additional ligands may be coordinated to the molybdenum, but their identity is still uncertain.

Previous studies of model complexes for Mo-co of oxo-type molybdoenzymes have been mainly directed toward duplicating the redox properties, the EPR spectra, the EXAFS spectra, and the chemical reactions of such molybdoenzymes.[17-23] To date, little attention has been given to the role that the ligand backbone and side chains of the metallacycle may play in determining the redox and spectroscopic properties of a molybdenum center. In this research,[24] we show that changes in the ligand backbone (Figure 1) can produce surprisingly large effects in the reduction potentials and spectroscopic properties of the metal center.

Experimental Section

Materials. Reactions were carried out under an atmosphere of dry argon; solvents were thoroughly degassed before use. Subsequent workup was carried out in air. Solvents were purified by distillation as follows: acetonitrile from calcium hydride; dichloromethane from calcium hydride; hexanes and pentanes from sodium hydride; tetrahydrofuran from potassium/benzophenone; triethylamine from potassium. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KL) and $LMoOCl_2$ were prepared according to literature methods.[25,26] Silica gel used in adsorption chromatography was obtained from Fluka and Sigma Chemical Co. and used as received. Molybdenum pentachloride was obtained from

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(1) (a) University of Arizona (b) University of Manchester.

(2) Rajagopalan, K. V.; Handler, P.; Palmer, G.; Beinert, H. *J. Biol. Chem.* **1968**, *243*, 3784–3796.

(3) Cohen, H. J.; Fridovich, I. *J. Biol. Chem.* **1971**, *246*, 367–373.

(4) Bray, R. C. In *The Enzymes*, 3rd ed.; Boyer, P. D., Ed.; Academic Press: New York, 1975; Vol. 12, Part B, pp 299–419.

(5) Eady, R. R.; Smith, B. E. In *A Treatise on Dinitrogen Fixation*; Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds.; John-Wiley: New York, 1979; Section II, Chapter 2, pp 399–490.

(6) Johnson, J. L. In *Molybdenum and Molybdenum Containing Enzymes*; Coughlan, M. P., Ed.; Pergamon Press: New York, 1980; pp 345–383.

(7) Takagi, M.; Tsuchiya, T.; Ishimoto, M. *J. Bacteriol.* **1981**, *148*, 762–768.

(8) Barber, M. J.; Coughlan, M. P.; Siegel, L. M. *Biochemistry* **1982**, *21*, 3561–3568.

(9) Tatsumi, K.; Kitamura, S.; Yamada, H. *Biochim. Biophys. Acta* **1983**, *747*, 86–92.

(10) Kröger, A.; Winkler, E.; Innerhoffer, A.; Hackenberg, H.; Schägger, H. *Eur. J. Biochem.* **1979**, *94*, 465–475.

(11) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943–953.

(12) Johnson, J. L.; Rajagopalan, K. V. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 6856–6860.

(13) Cramer, S. P.; Stiefel, E. I. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; John-Wiley: New York, 1985; Chapter 8, pp 411–441.

(14) Kramer, S. P.; Johnson, J. L.; Riberiro, A. A.; Millington, D. S.; Rajagopalan, K. V. *J. Biol. Chem.* **1987**, *262*, 16357–16363.

(15) Kramer, S. P. Ph.D. Dissertation, Duke University, 1987.

(16) (a) Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979**, *101*, 2772–2774. (b) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721–7727. (c) Tullius, T. D.; Kurtz, D. M., Jr.; Conradson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc.* **1979**, *101*, 2776–2779.

(17) Taylor, R. D.; Todd, P. G.; Chasteen, N. D.; Spence, J. T. *Inorg. Chem.* **1979**, *18*, 44–48.

(18) Garner, C. D.; Lambert, P.; Mabbs, F. E.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1191–1198.

(19) Farchione, F.; Hanson, G. R.; Rodrigues, C. G.; Bailey, T. D.; Bagchi, R. N.; Bond, A. M.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 831–832.

(20) Hanson, G. K.; Wilson, G. L.; Bailey, T. D.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 2609–2616.

(21) Cramer, S. P.; Gray, H. B.; Scott, N. S.; Barber, M.; Rajagopalan, K. V. In *Molybdenum Chemistry of Biological Significance*; Newton, W. E., Ed.; Plenum Press: New York, 1979; pp 157–168.

(22) Howie, J. K.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1892–1899.

(23) Topich, J.; Berger, N. *Inorg. Chim. Acta* **1982**, *65*, L131–134.

(24) Preliminary reports of portions of this work have been presented at the 196th National Meeting of the American Chemistry Society, Los Angles, CA, Sept 25–30, 1988; Abstract No. INOR 0235.

(25) Cleland, W. E.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017–1025.

(26) Trofimenko, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.

0020-1669/90/1329-2261$02.50/0

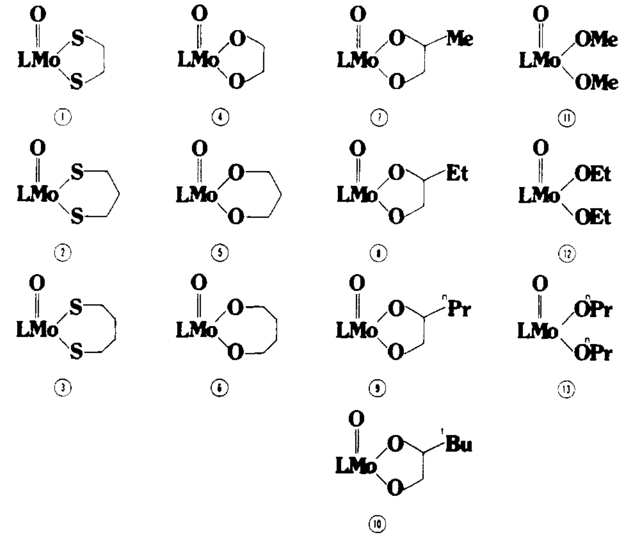

Figure 1. Model compounds **1**–**13**. L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate.

Aldrich Chemical Co. The dithiols and diols were purchased from Aldrich Chemical Co. Tetrabutylammonium tetrafluoroborate was recrystallized several times from aqueous ethanol and dried in vacuo for a few days before use. The purity of isolated compounds and the progress of the reactions were monitored by thin-layer chromatography. Elemental analyses were peformed by Atlantic Microlab Inc., Atlanta, GA.

Preparation of Compounds 1–13. To a $LMoOCl_2$ solution[25] (1 g in 200 mL of toluene) at 30 °C was slowly added either a mixture of 0.64 mL (4.6 mmol) of triethylamine and 2.3 mmol of appropriate diol (or 4.6 mmol of alcohol) or 2.3 mmol of potassium salt of dithiol in 10 mL of toluene, and the mixture was heated slowly to suitable reaction temperature. Reactions were monitored by TLC. Upon completion (2–5.5 h for **1**–**6** at 75–85 °C; 3.5–9 h for **7**–**10** at 65–75 °C; 2–7.5 h for **11**–**13** at 50–60 °C) the reaction mixture was cooled to room temperature, filtered, and evaporated to dryness in vacuo and then either chromatographed on silica gel or recrystallized as described below. Purified compounds were stored in an inert-atmosphere box.

$LMoO[S-(CH_2)_2-S]$ (1).[25] The crude product was dissolved in a minimum amount of toluene, and the mixture was chromatograhed on silica gel to give a dark green-brown product; yield 80%.

$LMoO[S-(CH_2)_3-S]$ (2). The crude product was dissolved in a minimum amount of toluene, and the mixture was chromatographed on silica gel with toluene. The compound eluted as a dark green-brown band, and the eluate was evaporated to dryness; yield 53%.

$LMoO[S-(CH_2)_4-S]$ (3). The crude product was dissolved in a minimum amount of toluene, and the mixture was chromatographed on silica gel with toluene. The desired compound eluted as a deep green band; yield 19%.

$LMoO[O-(CH_2)_2-O]$ (4).[25] The crude product was redissolved in a minimum amount of tetrahydrofuran, and the mixture was chromatographed on silica gel with tetrahydrofuran. The product eluted as a pale gray-blue band. Yields were 84–90%.

$LMoO[O-(CH_2)_3-O]$ (5). The reaction mixture was redissolved in a minimum amount of tetrahydrofuran, and the solution was chromatographed on silica gel with tetrahydrofuran. The desired compound eluted as a pale blue band. Yields were 55–60%.

$LMoO[O-(CH_2)_4-O]$ (6). The reaction mixture was redissolved in a minimum amount of tetrahydrofuran, and the solution was chromatographed on silica gel with tetrahydrofuran. The desired compound eluted as a blue band. Yields were 10–18%.

$LMo[O-(CH(CH_3)CH_2)-O]$ (7). The crude product was dissolved in a minimum amount of tetrahydrofuran, and the mixture was chromatographed on silica gel with tetrahydrofuran–toluene (1:9). The compound eluted as a pale gray-blue band, which was evaporated to dryness. The solid was redissolved in minimum amount of tetrahydrofuran, the solution was added to 100 times volume of stirring *n*-hexane, and the solid was then filtered out, washed several times with *n*-hexane, and dried in vacuo. The yield was 76%.

$LMoO[O-(CH(Et)CH_2)-O]$ (8). The purification method used for this compound was similar to that as described for **7**, except that the elution solvent used was 1:14 tetrahydrofuran–toluene. The yield was 74%.

$LMoO[O-(CH(^{n}Pr)CH_2)-O]$ (9). The purification procedure used was similar to that described for **7**, except that the elution solvent used in chromatography was 1:19 tetrahydrofuran–toluene. Yields were 65–78%.

$LMoO[O-(CH(^{t}Bu)CH_2)-O]$ (10). The purification procedure used was similar to that described for **9**. Yields were 63–70%.

$LMoO(OCH_3)_2$ (11).[25] The crude product was washed several times with a minimum amount of *n*-pentane to remove yellow-green byproducts until the filtrate from the final washing was colorless. The blue solid that remained was redissolved in dichloromethane, the solution was added to 100-fold volume excess of stirring *n*-pentane, and the solid was filtered out, washed several times with *n*-pentane, and dried in vacuo. The yield was 95%.

$LMoO(OEt)_2$ (12). This compound was purified by the method described above for **11**, and the final blue product was dried in vacuo. The yield was 83%.

$LMoO(O^{n}Pr)_2$ (13). The purification method used was the same as described for **11**, and the final desired blue compound was dried in vacuo. The yield was 62%.

Physical Measurements. Infrared spectra of the powdered samples (KBr pellets) were recorded on a Perkin-Elmer PE 983 spectrometer. Electronic absorption spectral information was obtained on a IBM 9420 spectrophotometer, with the near-infrared region (900–2000 nm) being scanned on a Cary 14 spectrophotometer. Mass spectra were obtained with a Finnigan 3300 quadrupole gas chromatographic/mass spectrometer (GC/MS) with an INCOS data system. Electron paramagnetic resonance (EPR) spectra of the fluid solutions (at room temperature) or frozen glasses in toluene (at liquid-nitrogen temperature) were obtained at X-band frequencies with a Varian E-3 spectrometer or at Q-band frequencies with a Varian E112 spectrometer. All of the EPR spectra were calibrated with DPPH standard. Cyclic voltammetric measurements were performed in acetonitrile solutions (ca. 1–2 mM) over the potential window of +2.0 to −2.0 V with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte. The electrochemical cell used employed a platinum-disk electrode as the working electode, a platinum-wire counter electrode, and a Hg/Hg_2Cl_2 reference electrode (SCE). Scans were taken on an IBM EC 225 voltammetric analyzer equipped with an IBM 742 MT X-Y-T recorder. Potentials were calibrated[27] by addition of ferrocene as an internal standard after each experiment. Potentials are reported with respect to the SCE. The peak-to-peak separation (ΔE_p) between the cathodic and anodic peaks and the ratio of the cathodic and anodic currents (i_{pc}/i_{pa}) were used as criteria for the reversibility of the redox processes. Controlled-potential coulometry of compounds in dichloromethane solution was performed in a three-compartment cell with a graphite working electrode, a platinum-flag auxiliary electrode, and a $Ag/AgNO_3/CH_3CN$ reference electrode.

Results and Discussions

Characterization. The characterization data with elemental analyses and mass spectrometry are set out in Tables S1 and S2, respectively (see supplementary material). The mass spectral data support the mononuclear formulation for complexes **1**–**13**. Each compound shows a multiplet around the parent ion peak (P), and the mass number in Table S2 refers to the peak of maximum intensity within this multiplet. The multiplets mainly result from the natural abundance distribution of isotopes of molybdenum and boron in the [LMoO] moiety. Every compound shows a strong peak due to the cation of [LMoO] at $m/z = 411$, corresponding to the loss of dithiolato (compounds **1**–**3**), diolato (compounds **4**–**6**), monosubstituted ethanediolato (compounds **7**–**10**), or two alkoxo ligands (compounds **11**–**13**). In addition, all of these compounds exhibit features that can be assigned to loss of one pyrazole ring.

Infrared Spectra. The infrared spectra of the complexes in KBr disks are summarized in Table S3 (in supplementary material). All of the compounds exhibit the characteristic bands for the hydrotris(3,5-dimethyl-1-pyrazolyl)borate group, metal–ligand vibrations, and a strong Mo=O stretching peak at lower frequency than that of starting material, $LMoOCl_2$, which has $\bar{\nu}_{Mo=O} = 961$ cm^{-1}. This result implies that bonding between the terminal oxo group and the molybdenum atom is slightly weakened in compounds **1**–**13** compared to that of $LMoOCl_2$.

Electronic Absorption Spectra. Table I gives the peak maxima and molar extinction coefficients for the lowest energy electronic absorption band of each of the compounds. The variation of the energy of the first electronic transition with increasing ring size

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(27) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

Table I. Electronic Absorption Data for the Lowest Energy Absorption Band for Model Compounds **1–13**[a]

compd	$\tilde{\nu}$, 10^3 cm^{-1}	λ, nm	ε, L·mol^{-1}·cm^{-1}
1	12.05	830	264
2	13.72	729	957
3	15.95	627	1426
4	15.63	640	25
5	15.04	665	24
6	13.53	739	33
7	15.50	645	23
8	15.48	646	20
9	15.36	651	25
10	15.43	648	22
11	13.89	720	34
12	13.50	741	32
13	13.46	743	30

[a] CH_3CN solution.

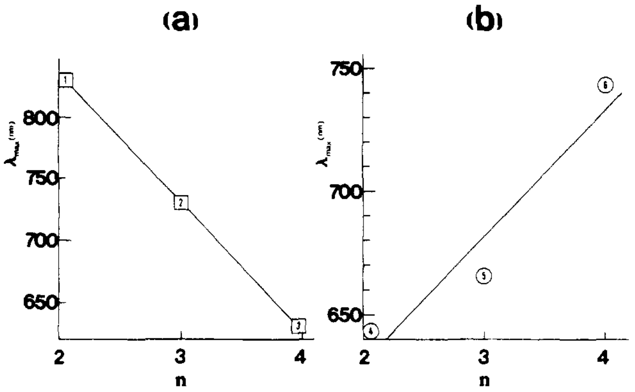


Figure 2. Correlation of λ_{max} vs *n*, where *n* is the number of methylene groups that are involved in the metallacycle ring: (a) for compounds **1–3**; (b) for compounds **4–6**.

is shown in Figure 2. For the dithiolato complex series (**1–3**), a hypsochromic shift is observed with increasing ring size (Figure 2a); furthermore, a substantial increase in the molar extinction coefficient (ε) of this lowest energy band also occurs. The values of ε (≈200–1400 L·mol^{-1}·cm^{-1}) suggest that the first electronic transition in compounds (**1–3**) has substantial charge-transfer character. Near-infrared spectroscopy (900–2000 nm) shows only weak overtone peaks of C–H vibrations, and there is no evidence for ligand field bands in this region for dithiolato complexes. The presence of sulfur donor atoms and a high value of ε for the lowest energy absorption is quite similar to the situation in $[NEt_4][MoO(SAr)_4]$, where the first band is at 598 nm (ε = 660, Ar = phenyl) and 610 nm (ε = 710, Ar = *p*-tolyl).[28] Similar results were also found for $LMoO(SEt)_2$ (λ_{max} = 718 nm, ε = 360) and $LMoO(SPh)_2$ (λ_{max} = 735 nm, ε = 1650).[25] In xanthine oxidase, an absorption maximum at 580 nm has been tentatively assigned to a molybdenum chromophore.[29]

For compounds **4–6**, the diolato series, a bathochromic shift is observed with increasing metallacycle ring size (Figure 2b). The small value of ε (<40) suggests that for these compounds the lowest energy electronic transition is primarily d → d in character. A similar band with ε = 14–25 occurs in the range 625–850 nm in systems such as $[Mo(OR)Cl_5]^-$, $[Mo(OR)_2Cl_4]^-$ (R = CH_3, C_2H_5, C_3H_7),[30] and $MoOCl_3Z_2$ (Z = triphenylphosphine oxide, tris(dimethylamino)phosphine oxide)[18] and has been assigned to a d → d transition.

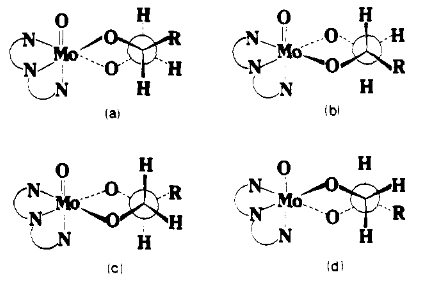
The absorption spectra of compounds **7–10** are similar to one another and show a slight bathochromic shift relative to **4**, which has no alkyl substituents on the chelate ring. Similar results are observed for the bis(alkoxo) complexes, $LMoO(OR)_2$ (compounds **11–13**), where the absorption spectra for R = Et and R = ^{n}Pr are similar in both energy and intensity, but the spectrum for R = Me has slightly higher absorption energy for the first electronic transition.

Table II. Electron Paramagnetic Resonance Data[a]

compd	g_1	g_2	g_3	$\langle g \rangle$	$\langle A \rangle^b$
1	2.018	1.971	1.939	1.976	36.9
2	2.017	1.951	1.926	1.967	37.7
3	2.017	1.954	1.927	1.970	37.3
4	1.975	1.964	1.910	1.950	38.5
5	1.965	1.955	1.902	1.940	46.8
6	1.970	1.939	1.882	1.928	48.7
7	1.973	1.961	1.906	1.948	40.5
8	1.974	1.963	1.907	1.949	41.3
9	1.974	1.963	1.907	1.949	40.6
10	1.973	1.961	1.906	1.948	40.4
11	1.967	1.939	1.900	1.936	47.0
12	1.966	1.942	1.897	1.934	47.2
13	1.967	1.941	1.897	1.935	47.2
c	2.006	1.949	1.940	1.965	37.8
d	1.955	1.947	1.926	1.940	44.1
e	2.012	1.997	1.975	1.999	30.3
f	2.0037	1.9720	1.9658	1.9800	
g	1.9872	1.9641	1.9531	1.9700	

[a] Data for compounds **1–13** use the mean of measurements at X- and Q-band frequencies: the mean values fall in the range *g* ± 0.002 and *A* ± 1.0 × 10^{-4} cm^{-1}. [b] ^{95,97}Mo, ×10^{-4} cm^{-1}. [c] Data for MoCl(SNNS) from ref 32. [d] Data for *trans*-MoCl{(sal)$_2$phen} from ref 34a. [e] Frozen-solution X-band data for $[MoO(SCH_2CH_2S)_2]^-$ from ref 34b. [f] Data for sulfite oxidase at low pH from ref 35. [g] Data for sulfite oxidase at high pH from ref 35.

Chart I



EPR Spectra. The isotropic and anisotropic *g* values and isotropic ^{95,97}Mo hyperfine parameter, $\langle A \rangle$, for each complex appear in Table II. The EPR spectra for the complexes in fluid and frozen toluene solutions indicate that for each compound only one EPR-active molybdenum species is present. Both the poor ligating ability of the solvent (toluene) and the intrinsic kinetic inertness of these complexes ensure that the values of Table II are the molecular parameters of the listed compounds. Chart I shows that compounds **7–10** have two chiral centers, the molybdenum atom and one of the carbon atoms in the backbone of the diolato chelate ligand, and that four stereoisomers are in principle possible depending upon the relative configuration of the R group and the $[LMo^VO]^{2+}$ fragment. In Chart I, where $N\frown N\frown N$ represents the tridentate ligand L, the species a/c and b/d are enantiomers and a/b and c/d are diastereomers. There is no evidence for diastereomers in the EPR spectra of **7–10**; however, such splitting would likely be too small to be detected by EPR spectroscopy.[31]

Figure 3 shows the typical inverse correlation between isotropic spin-Hamiltonian parameters $\langle g \rangle$ and $\langle A \rangle$.[32a] Compounds containing ligands with sulfur donor atoms show large isotropic *g* parameters and small isotropic hyperfine values; whereas,

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(28) Boyd, I. W.; Dance, I. G.; Murry, K. S.; Wedd, A. G. *Aust. J. Chem.* **1978**, *31*, 279–284.

(29) Garbett, K.; Gillard, R. D.; Knowles, P. F.; Stangroom, J. E. *Nature* **1967**, *215*, 824–828.

(30) Rillema, D. P.; Brubaker, C. H., Jr. *Inorg. Chem.* **1969**, *8*, 1645–1649.

(31) At Q-band frequencies, a small splitting of the g_2 component was observed for compounds **10**, **12**, and **13** but not for others. The detailed reasons for this are still not clear.

(32) (a) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–362. (b) Spence, J. T.; Minelli, M.; Kroneck, P.; Scullane, M. I.; Chasteen, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 8002–8004.

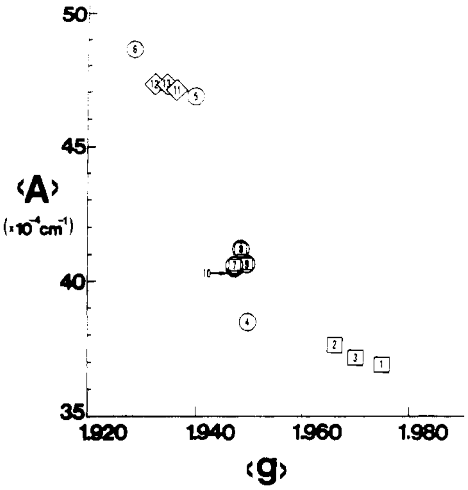

Figure 3. Correlation of $\langle g \rangle$ and $\langle A \rangle$ (^{95,97}Mo) for model compounds **1**–**13**. See Table II for the identities of individual compounds.

compounds coordinated by oxygen donor ligands give rise to smaller values of $\langle g \rangle$ associated with larger $\langle A \rangle$ parameters. However, the diolato complexes (**4** and **7**–**10**) with a five-membered metallacycle ring have larger values of $\langle g \rangle$ and smaller values of $\langle A \rangle$ than those of the other diolato compounds (**5** and **6**) and bis(alkoxo) compounds (**11**–**13**).

The point group symmetry of a transition-metal complex determines the allowed intermixing of the metal d orbitals. Such intermixings of d orbitals can result in significant noncoincidence of the principal axes of the **g** and metal atom **A** tensor.[33] Complexes with no symmetry elements (C_1) are not required to have any of their **g**- or **A**-tensor axes coincident. Furthermore, the compounds studied here possess a strong trigonal field from L, and the usual assumption that the oxo ligand dominates the electronic structure of $[\mathrm{Mo^VO}]^{3+}$ centers may no longer be valid.[25] In this paper, only the isotropic molybdenum hyperfine splitting constants are discussed because of the possible complicated angular relationship between the **g** and **A** tensors.

Among all of these model compounds **1**–**13**, the point symmetry at the molybdenum atom can be no higher than C_s; therefore, complete anisotropy in the principal components of the **g** tensors is possible.[25] In most cases, the isotropic g values, $\langle g \rangle$, obtained directly from fluid solution measurements at room temperature are in good agreement with $\sum g_i/3$ obtained by direct measurement from the frozen-solution EPR spectra. Compounds **1**–**3** containing two sulfur donor atoms possess one g_i component greater than 2.010. In contrast, compounds **4**–**13**, which contain two ligand oxygen atoms, all exhibit one component of g_i that is smaller than 1.915.

The EPR parameters are influenced not only by the nature and geometry of the ligands but also by the charge distribution and electron delocalization. The compounds in Table II can be classified into four groups: (1) dithiolato complexes **1**–**3**, (2) diolato complexes (**4**–**6**), (3) five-membered ring-substituted diolato complexes (**7**–**10**), and (4) bis(alkoxo) complexes (**11**–**13**). EPR parameters of several other mononuclear oxomolybdenum(V) complexes are also included in Table II. The average parameters for MoOCl(SNNS)[32b] are most similar to those for LMoO[S–(CH$_2$)$_3$–S], while the average parameters for *trans*-MoCl{(sal)$_2$phen}[34a] (probable N_2O_2 equatorial ligands) are similar to those for LMoO(OMe)$_2$. The similarity between the EPR parameters of these latter pairs of compounds indicates that the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand does not produce any grossly unusual effects in the magnitudes of these parameters.

Table III. Electrochemical Data[a,b]

	Mo(V) ⇌ Mo(VI) + e⁻			Mo(V) + e⁻ ⇌ Mo(IV)		
compd	$E_{1/2}$, V	ΔE_p, mV	i_{pc}/i_{pa}	$E_{1/2}$, V	ΔE_p, mV	i_{pc}/i_{pa}
1				−0.367	75	0.93
2				−0.503	61	1.00
3				−0.621	111	1.02
4				−1.160	120	1.02
5	0.865	99	0.95	−1.328	165	1.04
6	0.648	86	0.93	−1.546	210	1.03
7				−1.175	99	1.02
8				−1.064	80	1.00
9				−0.954	80	0.99
10				−1.180	114	1.00
11	0.550	74	0.96	−1.275	96	1.05
12	0.520	76	0.95	−1.341	104	1.02
13	0.501	57	1.01	−1.383	75	1.02

[a] Conditions: cyclic voltammetry, Pt electrode, 1–2 mM solutions in CH$_3$CN, 0.1 M Bu$_4$NBF$_4$ supporting electrolyte. [b] Potentials vs Hg/Hg$_2$Cl$_2$, 25 °C.

A comparison of the EPR spectra of the dithiolato complexes (**1**–**3**) and square-pyramidal {MoO[S–(CH$_2$)$_2$–S]$_2$}$^-$ [34b] shows that all have similar g_1 values but that {MoO[S–(CH$_2$)$_2$–S]$_2$}$^-$ has larger values for g_2 and g_3 and hence for $\langle g \rangle$. The EPR data for {MoO[S–(CH$_2$)$_2$–S]$_2$}$^-$ follow the general rule that increasing the number of thiolato-type sulfur atoms in a complex appears to increase $\langle g \rangle$ and decrease $\langle A \rangle$.[32]

A comparison of the g parameters for the model compounds with those of sulfite oxidase[35] reveals that none of the model compound parameters exactly match all the anisotropic g_i values of enzyme, but five-membered metallacycle dithiolato (compound **1**) and diolato (compounds **4** and **7**–**10**) complexes have values similar to those of sulfite oxidase in low- and high-pH conditions, respectively. However, the g_3 components for these model compounds (**1**, **4**, and **7**–**10**) are smaller than that of sulfite oxidase.

Table II shows that there is a decrease of ≈0.010 in the value of the isotropic g parameter with an increase of one methylene unit in the diolato complexes (**4**–**6**). It should be possible to correlate the principal g_i values with changes in the electronic absorption spectra by using eq 1,[36–38] where each summation is

$$g_i = 2.0023 - \sum\left(\frac{\xi_{\mathrm{Mo}}F}{\Delta E^*}\right) + \sum\left(\frac{\xi_{\mathrm{Mo}}G}{\Delta E}\right) \tag{1}$$

over all appropriate excited states, ξ_{Mo} is the single-electron spin–orbit coupling constant for an electron in a metal d orbital, F and G are terms that depend on the composition of the molecular orbitals in the ground and excited states and ligand spin–orbit coupling contributions, ΔE^* is the d → d transition energy, and ΔE is the energy associated with a single-electron excitation from a filled molecular orbital of mainly ligand character to the half-filled metal d orbital of the ground state. For diolato complexes (**4**–**6**), the dominant contributing term for the anisotropic g_i values is expected to be the d → d transition energy (ΔE^*); therefore, at least one of the g_i values should decrease with increasing ring size due to the bathochromic shift in the first electronic band. However, if the charge-transfer energy term (ΔE) contribution to a particular g component is comparable to the contribution from the d → d term (ΔE^*), as probably occurs in the dithiolato complexes (**1**–**3**), then the g value might not show any regular trend.

Electrochemistry. Cyclic voltammetry and controlled-potential coulometry were used to examine the electrochemical behavior of the model complexes, and the data are summarized in Table III. All complexes exhibit quasi-reversible one-electron reduction waves as demonstrated by $\Delta E_p > 59$ mV, by i_{pc}/i_{pa} close to 1.0,

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(33) Collison, D.; Mabbs, F. E.; Enemark, J. H.; Cleland, W. E., Jr. *Polyhedron* **1986**, *5*, 423–425.

(34) (a) Scullane, M. I.; Taylor, R. D.; Minelli, M.; Spence, J. T.; Yamanouchi, K.; Enemark, J. H.; Chasteen, N. D. *Inorg. Chem.* **1979**, *18*, 3213–3219. (b) Ellis, S. R.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1483–1485.

(35) Lamy, M. T.; Gutteridge, S.; Bray, R. C. *Biochem. J.* **1980**, *185*, 397–403.

(36) Glarum, S. H. *J. Chem. Phys.* **1963**, *39*, 3141–3144.

(37) Garner, C. D.; Hiller, I. H.; Mabbs, F. E.; Taylor, C.; Guest, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2258–2261.

(38) Garner, C. D.; Mabbs, F. E. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1125–1127.

and by plots of the peak current vs square-root of the sweep rate (not shown here), which give straight lines passing through the origin. The peak separation values (ΔE_p) range from 61 to 210 mV at a scan rate of 100 mV/s; all approach the theoretical value (59 mV) at slower scan rates.[39] Similar results have been observed for various other $[\mathrm{Mo^VO}]^{3+}$ complexes.[25] Controlled-potential coulometry for these model complexes shows 1.00 ± 0.07 e/Mo atom,[40] verifying the one-electron nature of the reduction waves and further confirming the formation of the analogous Mo(IV) monoanion. The wide range of the reduction potentials of these complexes (ca. 1.2 V) indicates the sensitivity of the reduction potential of the $[\mathrm{LMo^{(V)}O}]^{2+}$ core to the nature of the remaining two ligands.

The series **1**–**3** and **4**–**6** show surprisingly large *decreases* in the potential of the Mo(V)/Mo(IV) couple as the size of the chelate ring *increases*. For the dithiolato complexes (**1**–**3**), the reduction potential decreases by 0.118 and 0.136 V as the number of CH_2 groups in the chelate ring increases from 2 to 3 and from 3 to 4, respectively. For the diolato complexes (**4**–**6**), even larger decreases in the reduction potential (0.168 and 0.218 V; see Table III) accompany the increases in chelate ring size. The results for these two series of complexes clearly show that the Mo(V) reduction potential is sensitive to the ligand backbone and demonstrate the possibility of "fine tuning" the potential for a fixed set of donor atoms by perturbation of the ligand backbone.

For the complexes containing dithiolato or diolato ligands, the reduction potential of the Mo(V)/Mo(IV) couple increases in the order: butanediolato (**6**) < propanediolato (**5**) < ethanediolato (**4**) < butanedithiolato (**3**) < propanedithiolato (**2**) < ethanedithiolato (**1**). This trend may reflect the relative abilities of these ligands to stabilize the complexes in the Mo(IV) oxidation state. For corresponding pairs of the dithiolato and diolato compounds, the half-wave reduction potential of the dithiolato complex is ca. 800–930 mV more positive. Similar behavior is found for the reduction potentials of other oxomolybdenum complexes upon substitution of O for S in complexes with otherwise identical ligands.[25,41,42]

Compounds **7**–**10** show the effect of attaching an alkyl group (R) to one of the carbon atoms of the ethanediolato ligand of **4**. For the electron-releasing substituent series of R = Me (**7**), Et (**8**), and ^{n}Pr (**9**), each succeeding complex becomes increasingly easy to reduce as the size of R increases. However, substitution of a ^{t}Bu group (**10**) reverses the trend and gives a Mo(V)/Mo(IV) potential which is not significantly different from that for **7**. Nonetheless, the observed potentials for this series (Table III) clearly show that changing a single CH_2 group in a side chain of a chelate ring can also result in changes of the Mo(V)/Mo(IV) potential of 0.1 V or more.

The Mo(V)/Mo(IV) reduction potentials of complexes with simple monodentate alkoxide ligand sets (**11**–**13**) show relatively small variations with chain length compared to the effects observed for complexes of chelating ligand discussed above.

Changes in the chelate ring size and in the nature of the groups attached to the chelate ring skeleton can alter the interaction of the donor atoms of the chelating ligand with the Mo atom by (1) changing the bite angle of chelate ring and (2) changing the conformation of the chelate ring and hence the torsional angles at the heteroatom coordinated to the Mo atom. Both of these factors will change the interaction between the half-filled ground-state d-orbital combination of the molybdenum atom and the filled ligand π-type group orbitals of the dithiolato, diolato, or alkoxo ligand, assuming that a constant half-filled orbital is defined by the $[\mathrm{LMoO}]^{2+}$ moiety. This repulsive interaction determines the final energy of the HOMO for the complexes as depicted in Scheme I, where a ground state of $(4d_{xy})^1$ is *assumed*.

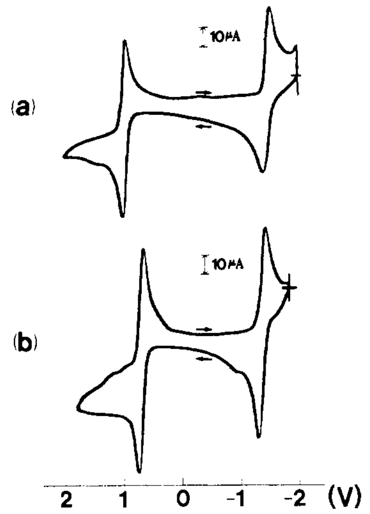
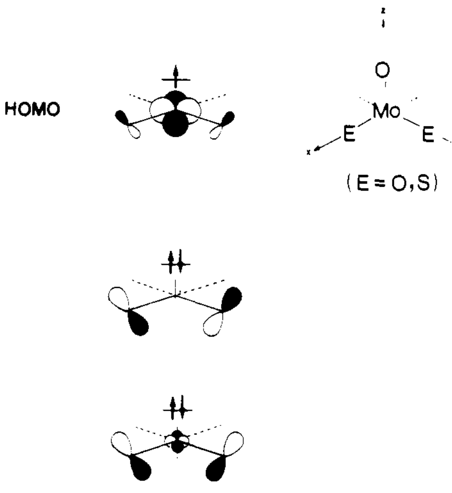


Figure 4. Cyclic voltammograms of model compounds of (a) LMoO-[O–$(CH_2)_4$–O] (compound **6**) and (b) $\mathrm{LMoO(OEt)_2}$ (compound **12**) in CH_3CN at 25 °C (scan rate 100 mV/s). The wave at lower potential is the Mo(V)/Mo(IV) couple; the wave at higher potential is the Mo(V)/Mo(VI) couple. Compounds **5**, **11**, and **13** (not shown here) exhibit similar behavior.

Scheme I



For all of the complexes (**1**–**13**), the pyrazolylborate ligand and the terminal oxo ligand may be assumed to make a fixed contribution to the overall ligand field. Consequently, only the contribution from the group orbitals of the donor atoms from the variable ligands have been considered in Scheme I, which illustrates the d_π–p_π interaction between the singly occupied $4d_{xy}$ orbital of the Mo atom and the filled π orbitals of the ligand that lie in the xy plane. The larger the d_π–p_π interaction, the more the HOMO will be destabilized and the more difficult it becomes to reduce the complexes.[43] This scheme will be necessarily modified if (i) $[\mathrm{LMo^VO}]^{2+}$ does not contribute a fixed electronic arrangement to the overall complex and/or (ii) the description of the half-filled (ground-state) orbital, which is strictly a symmetry-determined linear combination of the metal 4d orbitals, varies between complexes in this molecular series.

Compounds **5**, **6**, and **11**–**13** also exhibit quasi-reversible one-electron oxidation waves from Mo(V) to Mo(VI) (cyclic voltammograms for compounds **6** and **12** are shown in Figure 4). Controlled-potential coulometry of these compounds at a potential ≈200 mV beyond the anodic peak potential of the appropriate

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(39) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

(40) After coulometric reduction, the cyclic voltammograms for these compounds are similar to those of their Mo(V) complexes.

(41) Taylor, R. D.; Street, J. P.; Minelli, M.; Spence, J. T. *Inorg. Chem.* **1978**, *17*, 3207–3211.

(42) (a) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917–925. (b) Boyd, I. W.; Spence, J. T. *Inorg. Chem.* **1982**, *21*, 1602–1606.

(43) Chang, C. S. J.; Rai-Chaudhuri, A.; Lichtenberger, D. L.; Enemark, J. H. *Polyhedron*, in press. The ionization potentials of the valence orbitals of compounds **4**–**6** and **11**–**13** were measured by the gas-phase He I photoelectron spectroscopy method. The results obtained support the suggestions discussed here.

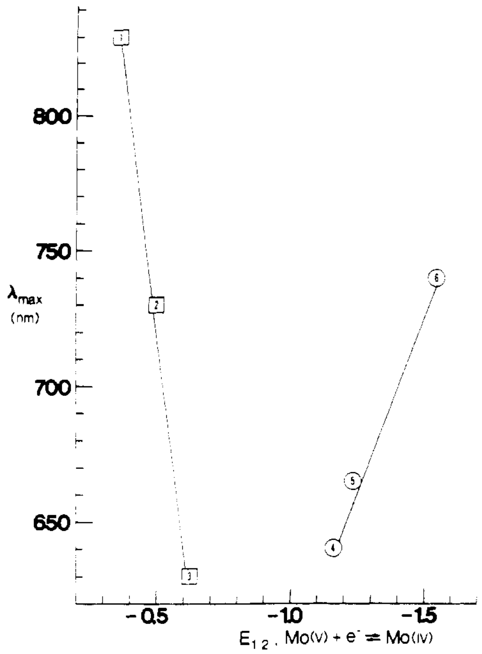

Figure 5. Correlation of λ_{max} with the reduction half-wave potential between Mo(V) and Mo(IV) states for compounds **1**–**6**.

cyclic voltammogram indicated 1.04 ± 0.12 e/Mo atom.[44] This electrochemical behavior is unusual for monooxomolybdenum(V) complexes and demonstrates the accessibility of several complexes containing the $[LMo^{VI}O]^{3+}$ core that may be isolable through stabilization by appropriate ligands with hard-base donor atoms and small inherent strain, such as compounds **5**, **6**, and **11**–**13**. Our present results for monooxomolybdenum complexes contrast with previous electrochemical studies of *cis*-dioxomolybdenum(VI) complexes,[45-49] which have generally shown irreversible or quasi-reversible behavior. Spence[41] has pointed out that monomeric oxomolybdenum(V) complexes cannot be obtained by electrochemical reduction of the corresponding dioxomolybdenum(VI) complexes in nonaqueous solvents. Likewise, monomeric oxomolybdenum(V) complexes cannot be electrochemically oxidized to analogous dioxomolybdenum(VI) complexes. The reason for the failure of such redox processes is probably due to the difficulty in adding (or removing) an oxygen atom from an oxomolybdenum core during the oxidation (or reduction) in nonaqueous solvents.

Figure 5 plots the lowest energy absorption band versus the Mo(V)/Mo(IV) reduction potential for the dithiolato and diolato complex series. The two series show opposite slopes. This behavior contrasts with the variation of reduction potential, which becomes more negative with increasing ring size for both series. The energy of the first electronic transition for the dithiolato complexes increases with ring size whereas for the diolato complexes the reverse occurs. A consistent rationalization for all these observations can be developed from consideration of Scheme I. The half-occupied HOMO is the orbital most likely to accept an electron in electrochemical reduction. Increasing the chelate ring size will allow torsional angles at the ligand heteroatoms (O or S) that are more favorable for the d_π–p_π interactions shown in Scheme I. Stronger d_π–p_π interactions will raise the energy of the HOMO, which is d_π–p_π antibonding, and make the complexes more difficult to reduce. Destabilization of the HOMO by enhanced d_π–p_π interactions should decrease the separation between the HOMO, which is mainly $4d_{xy}$ in character, and the other unoccupied metal 4d orbitals, thereby decreasing the energy of the first observed ligand field band with increasing ring size, as observed in the diolato complexes. On the other hand, an increased d_π–p_π interaction should increase the separation between filled ligand orbitals and the HOMO. An increase in energy of the first electronic transition with increasing ring size for the dithiolato complexes is consistent with the first band being largely charge transfer in character (vide supra).

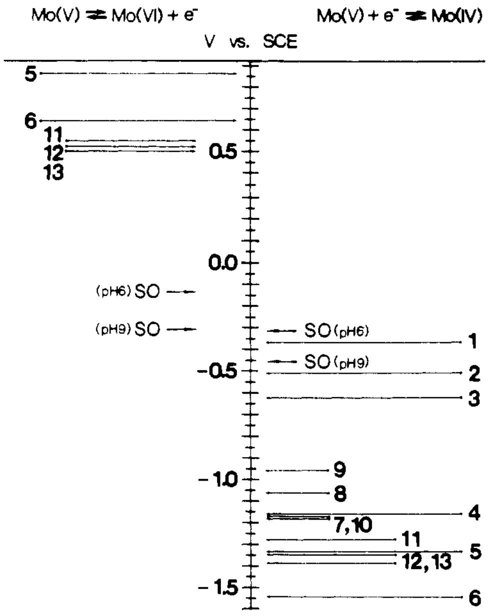

Figure 6. Relationship for Mo(V)/Mo(VI) and Mo(V)/Mo(IV) couples among model compounds **1**–**13** in CH_3CN. The corresponding potentials for sulfite oxidase in aqueous buffer are also shown.

The relationships among the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) reduction potentials for the model complexes as well as for sulfite oxidase[50] at pH = 6 and 9 are shown in Figure 6. Several complexes with diolato and alkoxo ligands (**5**, **6**, **11**–**13**) show two one-electron processes separated by about 2.0 V. Although the potentials for the compounds and for sulfite oxidase cannot be directly compared due to medium effects arising from differing solvent systems, this potential range is much too large to be a viable pathway for two-electron changes in biological systems. For example, the potential range for sulfite oxidase is less than 0.3 V.[50] The importance of the ligand type in Mo(IV)/Mo(V)/Mo(VI) oxidation–reduction reactions is further illustrated by the incompatibility of the ArS⁻ ligand with two-electron changes in the redox-related series $[MoO(SAr)_4]^{n-}$, where n = 0–2.[51]

Summary and Conclusions

Only a limited number of mononuclear dithiolato or diolato oxometal complexes have been previously reported,[52] especially

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(44) For compounds **5** and **6**, the cyclic voltammograms recorded after coulometric electrolysis are the same as those observed before electrolysis. Attempts to isolate the oxidized monocations of compounds **5** and **6** are in progress. The cyclic voltammograms of the oxidized Mo(VI) complexes of analogous compounds **11**–**13** are often different from the voltammograms of the parent complexes, indicating that compounds **11**–**13** may only be stable on the cyclic voltammetry time scale.

(45) (a) Topich, J.; Lyon, J. T., III. *Polyhedron* **1984**, *3*, 55–60. (b) Topich, J.; Lyon, J. T., III. *Inorg. Chem.* **1984**, *23*, 3202–3206.

(46) (a) Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 660–664. (b) Rajan, O. A.; Chakravorty, A. *Inorg. Chim. Acta* **1979**, *37*, L503–L504.

(47) Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Inorg. Chem.* **1980**, *19*, 773–775.

(48) Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1983**, *22*, 1322–1327.

(49) Roberts, S. A.; Young, C. G.; Kipke, C. A.; Cleland, W. E., Jr.; Yamanouchi, K.; Enemark, J. H. Manuscript submitted to *Inorg. Chem.*

(50) Spence, J. T.; Kipke, C. A.; Enemark, J. H.; Sunde, R. A. Manuscript submitted to *Biochemistry.*

(51) Collison, D.; Ellis, S. R.; Garner, C. D. *J. Chem. Soc., Dalton Trans.*, in press.

(52) (a) Wiggins, R. W.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1313–1315. (b) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297–3302. (c) Davison, A.; DePamphilis, B. V.; Faggiani, R.; Jones, A. G.; Lock, C. J. L.; Orvig, C. *Can. J. Chem.* **1985**, *63*, 319–323. (d) Smith, J. E.; Byrne, E. F.; Cotton, F. A.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 5571–5572. (e) Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1052–1053. (f) Phillips, F. L.; Skapski, A. C. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1814–1818.

for chelating butanedithiolato or butanediolato ligands. We have synthesized a series of oxomolybdenum(V) complexes with similar chemical environments but varying chelate ligand backbones. This series has provided an opportunity to investigate the effect of systematic ligand variations on the spectroscopic properties and reduction potentials of mononuclear oxomolybdenum(V) centers.

The effects of the chelate ring size and flexibility on the stability of metal complexes are well-known.[53] In this research, we have observed that the size of the chelate ring and of the alkyl substituents on the chelate ring backbone have substantial effects on the spectroscopic properties of $LMoO[S{-}(CH_2)_n{-}S]$ and $LMoO[O{-}(CH_2)_n{-}O]$ complexes and can lead to changes in the reduction potential of up to 0.2 V/CH_2 unit. In the absence of crystal structures for these complexes the geometrical effects from the changes in the ligand skeleton are unknown. However, the changes in the torsional angles of the donor heteroatom that result from changes in chelate ring size and ring substituents provide a promising mechanism for transmitting seemingly remote ligand effects to the properties of the metal center. This rationale has been used previously to account for the unusually low reactivity of $CpMo(NO)(SPh)_2$ and related compounds.[54]

Finally, it has not escaped our attention that the significant changes in metal properties which we have observed with changes in the ligand skeleton may be important for understanding the properties of the molybdenum cofactor (I), which is thought to possess a five-membered chelate ring with two side chains.

Acknowledgment. We thank Drs. S. A. Roberts and J. M. Mayer for helpful discussions and suggestions. Support of this research by the National Institutes of Health, Grant GM37773, is gratefully acknowledged. D.C. wishes to thank the Royal Society for financial support.

Supplementary Material Available: Listings of elemental analyses, mass spectral data, and infrared absorption data for compounds **1–13** (Tables S1–S3, respectively) (3 pages). Ordering information is given on any current masthead page.

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(53) (a) Romeo, R.; Minniti, D.; Lanza, S.; Tobe, M. L. *Inorg. Chim. Acta* **1977**, *22*, 87–91. (b) Pahor, N. B.; Calligaris, M.; Randaccio, L.; Romeo, R. *Inorg. Chim. Acta* **1978**, *26*, L13–L14.

(54) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730–733.

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Interactions of Vanadate with Mono- and Dicarboxylic Acids

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Received September 25, 1989

The condensation reactions between vanadate and a variety of mono- and dicarboxylic acids in aqueous solution have been investigated by ^{51}V NMR spectroscopy. Equilibration with acetate occurred rapidly, about 10^4 s^{-1}, to form predominantly a bis(acetato)vanadate (−541 ppm) although formation of a mono derivative could be detected. With pentanoic acid and the dicarboxylic acids, a product (−536 ppm) in slow equilibration with vanadate was formed. This product occurred in addition to a rapidly exchanging product and contained only one ligand (except possibly for the pentanoic acid derivative, which was not well characterized). In addition to the above products, succinic acid gave a product with a ^{51}V chemical shift at −548 ppm. This derivative also contained one ligand. Variation of the pH showed that product formation occurred from the acid form of the ligands and that no protons were required for generation of any of the products.

Introduction

Over the past few years the aqueous chemistry of vanadium(IV) and vanadium(V) oxoanions has been receiving increasing attention because of the relevance of these materials to the investigation of various biochemical processes. It may be that some of the function of vanadium derives from its role as a phosphate analogue. In addition to this, vanadium occurs at the active site of some seaweed bromoperoxidases[1] and is found in a secondary enzymic system for nitrogen fixation in some nitrogen fixing bacteria.[2,3]

In aqueous solution the vanadium(V) anion, vanadate, rapidly and spontaneously condenses with alcohols and phenols to form vanadate esters.[4,5] Beyond this it is well-known that vanadate undergoes self-condensation to form divanadate and other oligomers[6] and that it also condenses with other weak acids such as phosphate and arsenate.[7,8] Despite this evidence that aqueous vanadate readily forms products with a wide variety of hydroxyl-bearing ligands, it has often been stated or implied that it does not react with acetic acid (frequently used as a buffer) and, by extension, other monofunctional carboxylic acids. Of course, it is well-known that vanadium(V) in aqueous solution readily forms cyclic derivatives with a variety of multifunctional carboxylate-containing ligands such as the α-hydroxy carboxylates, the pyridine-2-carboxylates, and others.[9-16] The aspect of vanadate chemistry of primary interest here is the interaction of the vanadate ion, $VO_4H_2^-$, with carboxylate functionalities and is not concerned with peroxo and other derivatives of this anion. In a non-aqueous medium $VOCl_3$ reacts with alkane- and arenecarboxylic acids to form tris(carboxylato) derivatives.[17,18] Crystal structure analysis has shown that there is a bidentate coordination for each car-

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(1) de Boer, E.; van Kooyk, Y.; Tromp, M. G. M.; Wever, R. *Biochim. Biophys. Acta* **1986**, *869*, 48–53.

(2) Robson, L. R.; Eady, R. R.; Richardson, T. H.; Hawkins, M.; Postgate, J. R. *Nature* **1986**, *322*, 388–390.

(3) Hales, B. J.; Case, E. E.; Morningstar, J. E.; Dzeda, M. F.; Mauterer, L. A. *Biochemistry* **1986**, *25*, 7251–7255.

(4) Tracey, A. S.; Galeffi, B.; Mahjour, S. *Can. J. Chem.* **1988**, *66*, 2294–2298.

(5) Galeffi, B.; Tracey, A. S. *Can. J. Chem.* **1988**, *66*, 2565–2569.

(6) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.

(7) Gresser, M. J.; Tracey, A. S.; Parkinson, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 6229–6234.

(8) Tracey, A. S.; Gresser, M. J.; Liu, S. *J. Am. Chem. Soc.* **1988**, *110*, 5869–5874.

(9) Ehde, P. M.; Anderson, I.; Pettersson, L. *Acta Chem. Scand.* **1989**, *43*, 136–143.

(10) Caldeira, M. M.; Ramos, M. L.; Oliveiro, N. C.; Gil, V. M. S. *Can. J. Chem.* **1986**, *65*, 2434–2440.

(11) Djordjevic, C.; Lee, M.; Sinn, E. *Inorg. Chem.* **1989**, *28*, 719–723.

(12) Tracey, A. S.; Gresser, M. J.; Parkinson, K. M. *Inorg. Chem.* **1987**, *26*, 629–638.

(13) Galeffi, B.; Tracey, A. S. *Inorg. Chem.* **1989**, *28*, 1726–1734.

(14) Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand.* **1983**, *A37*, 709–714.

(15) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101–3110.

(16) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1973**, *12*, 829–831.

(17) Preuss, F.; Towae, W.; Woitschach, J. *Z. Naturforsch* **1980**, *35b*, 817–823.

(18) Rehder, D.; Preibsch, W.; von Oeynhausen, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1221–1222.

(19) Kustin, K.; Liu, S. -T. *J. Am. Chem. Soc.* **1973**, *95*, 2487–2491.

0020-1669/90/1329-2267$02.50/0