ondary solvation spheres may reduce all equilibrium constants with the larger constants being affected more; one would expect an apparent decrease in the observed macrocyclic effect in this case when water is added to the methanol solvent. Although the change in solvents does not conclusively point to a specific microscopic cause, the changes in the observed macrocyclic effect are real and significant, and these experiments do show that the specific inner sphere solvation of the noncyclic polyether *is not* the dominant factor which causes the changes in the macrocyclic effect when water is added to the methanol solvent.

The small heats of dilution of the free ligands taken together with the decrease in the observed macrocyclic effect when water is added to methanol has led us to search for an explanation for the macrocyclic effect other than increased solvation of the noncyclic ligand. The macrocyclic effect for the systems we studied was caused by less favorable enthalpic factors for the noncyclic ligand. Changing from K^+ to Na^+ or changing from 100% MeOH to 90% MeOH both caused a decrease in the macrocyclic effect, and these *decreases were enthalpic* in origin. It seems to us that unfavorable conformational enthalpic factors associated with the coordination of the pentaglyme can explain most of the 4–6 kcal/mol in ΔH required to account for the macrocyclic effect in these polyether ligands.

In three systems reported by Margerum and co-workers, macrocyclic effects were measured to be about 10^4 (Cu^{2+}/tetramine in H_2O), 10^2 (Ni^{2+}/tetrathioether in CH_3NO_2), and 10^6 (Ni^{2+}/tetraamine in H_2O).[2,4,5] For the last system, the ΔH and ΔS contributions to ΔG were determined, and it was found that the enthalpy term was the one which contributed to the magnitude of the macrocyclic effect. As noted earlier, they rationalized that the conformational enthalpy associated with the noncyclic ligand was much too small to contribute to the 14 kcal/mol difference which they observed between the binding of the cyclic and noncyclic ligands to Ni^{2+}. Hence, they attributed most of this 14 kcal/mol difference to the additional solvation (two inner-sphere H_2O molecules) of the noncyclic tetraamine as compared to the cyclic tetraamine. However, we, like Paoletti and co-workers,[7,9] emphasize the importance of conformational enthalpies of the ligands. During the synthesis of cyclic ligands, a certain amount of conformational strain is built into the macrocycle. The positions of the ligating donor atoms in the macrocycle are such that these atoms find themselves in either *more or less* favorable orientations for binding to a particular metal ion. One does not know a priori if the cyclization process will increase or decrease the enthalpies of ligand–metal binding.

Conclusion. Our experimental results show that the macrocyclic effect is operative in five linear/cyclic polyether combinations when methanol is used as a solvent and that this effect is the result of more favorable *enthalpy* factors. We have also shown that the magnitude of this effect is dependent on the "reference" linear polyether used and on how well the cation size and ligand cavity size are matched. We know that changing the solvent from methanol to methanol/water (90/10) and changing from K^+ to Na^+ causes a decrease in the macrocyclic effect which in each case is enthalpic in origin. Like other workers,[2,4,5,8] our initial belief that the macrocyclic effect was caused, at least in part, by unfavorable conformational entropy changes in the linear ligand upon complexation must remain unsubstantiated in the case of polyethers in methanol. Our results do not conclusively point to any single microscopic source for the macrocyclic effect in polyethers, but they do indicate that unfavorable conformational enthalpy changes of the linear polyethers are important factors. Given the wide range of solvents, ligand sizes, numbers and types of donor atoms, metals, etc., which have been studied, we believe that a combination of factors at the molecular level is responsible for the presence *or absence* of the macrocyclic effect; in a specific case, one of these factors may predominate.

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Molybdenum(IV)–Oxo Complexes with Oxygen, Nitrogen, and Sulfur Ligands. Syntheses and Electrochemical Studies

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New Mo(IV)–oxo complexes with tri- and tetradentate oxygen, nitrogen, and sulfur ligands have been synthesized (MoOLL′, L = salicylaldehyde *o*-hydroxyanil, salicylaldehyde *o*-mercaptoanil, L′ = α,α-bipyridyl, *o*-phenanthroline, dmf; MoOL, L = *N*,*N*′-bis(2-mercapto-2-methylpropyl)ethylenediamine) by phosphine oxo abstraction from Mo(VI)–dioxo complexes, ligand displacement from known Mo(IV)–oxo complexes, and reaction with $MoCl_4$ in methanol. Electrochemical properties have been determined by cyclic voltammetry and controlled-potential coulometry, and electronic and IR spectra were obtained. The complexes are oxidized to Mo(V)–oxo complexes and undergo one-electron reductions at a platinum electrode in DMF. The limitations of the synthetic methods and the implications of the electrochemical results for molybdenum enzymes are discussed.

Introduction

The molybdenum center of the molybdenum oxidases and nitrate reductase appears to cycle between the 6+, 5+, and 4+ states during catalysis of electron transfer between substrates and electron donors or acceptors.[1,2] The most recent EXAFS data for reduced xanthine dehydrogenase and reduced sulfite oxidase indicates the presence of a single terminal oxo ligand, two to three thiolate ligands, and possibly a thioether, oxygen, or nitrogen ligand in the Mo(IV) coordination sphere.[3]

(1) R. C. Bray, *Enzymes*, **12**, 299 (1975).

(2) R. C. Bray in "Molybdenum Chemistry of Biological Significance", W. E. Newton and S. Otsuka, Eds., Plenum Press, New York, 1980, p 117.

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Table I. Properties of Complexes

complex	IR ν(Mo-O), cm^{-1}	electrochemistry E_{pa}[a]	n[b]	E_{pc}[c]	n[b]	electronic spectra λ,[d] nm
MoO(sip)(dmf)	950	−0.17	1.05	−1.17 (−0.86)	0.96	440 (10 000), 307 (20 000)
MoO(sip)(phen)	929	−0.13 (−1.15)	0.73	−1.29 (−1.19, −0.88)	1.07	712 (9200), 467 (10 400), 369 sh
MoO(sma)(phen)	923	+0.11 (−0.93)	0.79	−1.36 (−0.51)	*e*	667 (8100), 475 (5100), 412 (7100), 312 sh
MoO(sma)(bpy)	921	+0.06 (−0.97)	0.98	−1.32 (−0.48)	0.99	678 (5500), 604 (7300), 376 (6800), 293 (24 000)
MoO(sma)(dmf)	957	+0.11	0.81	−0.96 (−0.41)	0.97	465 (10 000), 320 sh
MoO(mpe)	950	−0.30 (−0.44)	0.71	−1.42 (−0.84)	*e*	367 (3300)

[a] Oxidation peak. Cyclic voltammogram: V vs. SCE; standard deviation ±0.015 V; 0.10 M $[Et_4N]Cl$ in DMF; scan rate 0.100 V/s. Values in parentheses are coupled reduction peaks observed with complete CVA cycle. [b] Electrons/molecule; average of two or more determinations. Standard deviation = ±0.05. [c] Reduction peak. Values in parentheses are coupled oxidation peaks observed with complete CVA cycle. [d] Extinction coefficients in M^{-1} cm^{-1} in parentheses. [e] Number of electrons/molecule could not be determined because of high background currents.

Data from well-characterized Mo(IV)–oxo complexes with oxygen, nitrogen, and sulfur ligands are therefore of considerable importance in efforts to model the Mo site of these enzymes.

The chemistry of biologically relevant Mo(IV)–oxo complexes has not been explored to the same extent as for Mo(VI)–dioxo and Mo(V)–oxo complexes.[4] This is owing, in part, to difficulties in synthesis and the great sensitivity of Mo(IV)–oxo species to H_2O and oxygen. We have sought general methods which might prove useful for the synthesis of Mo(IV)–oxo complexes with a variety of ligands. We report here the synthetic utility and limitations of several methods and the synthesis and electrochemical properties of six new Mo(IV)–oxo complexes with oxygen, nitrogen, and sulfur ligands. The Mo(VI)–dioxo and Mo(V)–oxo complexes with three of the ligands have been prepared previously. Thus, all three of the biologically relevant molybdenum oxidation states for oxo complexes with these ligands are known, allowing examination of electron transfer between them.

Results

Synthesis. Three synthetic methods have been explored for the preparation of Mo(VI)–oxo complexes reported here. In most cases, the complexes may be obtained by more than one of these methods. Attempts to prepare complexes with several other ligands of interest, however, were unsuccessful.

Oxo Abstraction with PPh_2Et. The use of a phosphine to abstract an oxygen from Mo(VI)–dioxo complexes to obtain Mo(IV)–oxo complexes with dithiocarbamate and dithiophosphinate ligands has been described by Chen, et al.[5] With a number of other ligands (8-hydroxyquinoline, e.g.), μ-oxo Mo(V) dimers were obtained. We have obtained the complexes MoO(sip)(phen), MoO(sip)(dmf), MoO(sma)(phen), Mo(sma)(bpy), MoO(sma)(dmf), and MoO(mpe) by this method:[6]

$$MoO_2(mpe) + PPh_2Et \rightarrow MoO(mpe) + OPPH_2Et \quad (1)$$

Prolonged reaction times (>4 h) with a moderate (>3×) excess of phosphine resulted in loss of both oxo groups, giving non oxo Mo(IV) complexes of unknown composition.

Ligand Displacement. Previously, we obtained limited success by ligand displacement with bidentate ligands using $MoOCl_2(PPh_2Me)_3$ as starting material;[7] this left one PPh_2Me ligand in the product, a somewhat undesirable result from the biomimetic viewpoint. In the case of tridentate ligands, however, all phosphine ligands are replaced:

$$MoOCl_2(PPh_2Me)_3 \xrightarrow[\text{sip}]{\text{DMF}} MoO(sip)(dmf) + 2HCl + 3PPh_2Me \quad (2)$$

Again, prolonged reaction times (>3 h) resulted in oxo abstraction by the displaced PPh_2Me giving non-oxo Mo(IV) products.

In a similar manner, Cl^- and PPh_2Me in $MoOCl_2(bpy)(PPh_2Me)$ can be displaced by a tridentate ligand (eq 3). Both MoO(sma)(bpy) and MoO(sip)(dmf), the latter resulting from displacement of bpy by DMF solvent, were obtained in this way.

$$MoOCl_2(bpy)(PPh_2Me) + sip \rightarrow MoO(sip)(bpy) + PPhMe + 2HCl \quad (3)$$

$MoCl_4$ in MeOH. The use of $MoCl_4$ in MeOH has been described.[8] The nature of the reactive species formed when $MoCl_4$ reacts in MeOH is unknown, but an oxygen is presumably abstracted from the alcohol in an analogous fashion to the reaction of $MoCl_5$ in MeOH (eq 4).

$$MoCl_4(MeOH) + sip(dmf) \rightarrow MoO(sip)(dmf) \quad (4)$$

The mee ligand[6] is closely related to the mpe ligand, but all attempts to obtain MoO(mee) gave instead the μ-oxo Mo(V) dimer $Mo_2O_3(mee)_2$ or polymeric materials of unknown composition. This complex, however, has recently been obtained in small yield by reduction of $MoO_2(mee)$ with a large excess of thiophenol.[9]

Of particular interest is the series of complexes with the ligands mae, mab, and map[6] since the Mo(VI)–dioxo and Mo(V)–oxo complexes with these ligands have redox behavior similar to that of xanthine oxidase.[10] The Mo(V)–oxo complexes with these ligands ($[Et_4N][MoO(mae)]$, e.g.) have deprotonated amino groups, and since they are electrochemically reversibly reduced to Mo(IV) species,[10] an Mo(IV)–oxo complex with deprotonated amino groups, $[MoO(mae)]^{2-}$, might be expected. It has not been possible, however, to isolate an Mo(IV)–oxo complex with these ligands by any of the methods used. Initial reaction of PPh_2Et with the Mo(VI)–dioxo complex, e.g., gives a brown solution, identical in visible spectrum with that obtained by electrochemical reduction of the Mo(V)–oxo complex.[10] This is followed, however, by rapid formation of a black solid, which has no $Mo-O_t$ IR bands and appears to be polymeric. All attempts to isolate

(3) S. P. Cramer, R. Wahl and K. V. Rajagopalan, *J. Am. Chem. Soc.*, **103**, 7721 (1981).
(4) E. I. Stiefel, *Prog. Inorg. Chem.* **22**, 1 (1977).
(5) G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
(6) Abbreviations used for ligands: phen = *o*-phenanthroline, bpy = α,α'-bipyridyl, sip = salicylaldehyde *o*-hydroxyanil, sma = salicyladehyde *o*-mercaptoanil, mpe = *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenediamine, mee = *N,N'*-bis(2-mercaptoethyl)ethylenediamine, mae = *N,N'*-bis(2-mercaptophenyl)-1,2-diaminoethane, map = *N,N'*-bis(2-mercaptophenyl)-1,2-diaminopropane, mab = *N,N'*-bis(2-mercaptophenyl)-2,3-diaminobutane, and dmf = dimethylformamide.
(7) C. A. Rice and J. T. Spence, *Inorg. Chem.*, **19**, 2845 (1980).
(8) M. Novotny and S. J. Lippard, *Inorg. Chem.*, **13**, 828 (1974).
(9) C. Pickett, S. Kumar, P. Vella, and J. Zubieta, in press.
(10) J. T. Spence, M. Minelli, and P. Kroneck, *J. Am. Chem. Soc.*, **102**, 4538 (1980).

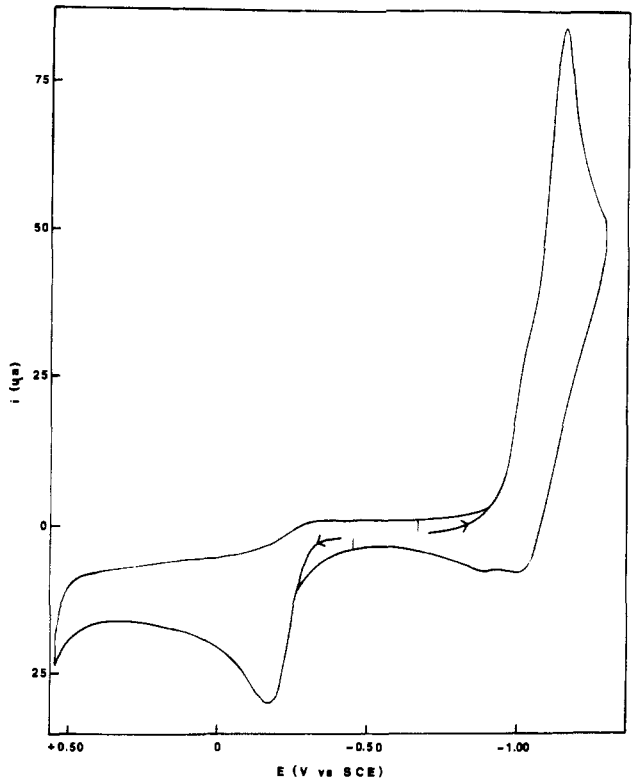


Figure 1. Cyclic voltammogram (5.00×10^{-4} M in DMF, 0.10 M $[Et_4N]Cl$) of MoO(sip)dmf. Scan rate = 0.100 V/s.

a product from the brown solution before formation of the black precipitate by rapid cooling or addition of large cation (Ph_4As^+) failed. Likewise, the other methods described produced only black nonoxo products.

Electrochemistry. Cyclic voltammograms for all the complexes have both an oxidation and a reduction peak. Controlled-potential coulometry and analysis of the cyclic voltammograms indicate these are one-electron processes. In all cases but one (MoO(mpe)), the redox processes are highly irreversible, as determined by ΔE for coupled oxidation–reduction peaks and the shape of the cyclic voltammograms. Controlled-potential coulometric oxidation, as determined by the cyclic voltammograms and electronic spectra of the oxidized products, gives the known Mo(V)–oxo complexes. The electrochemical behavior of the complexes is discussed below. Electrochemical data are summarized in Table I.

MoO(sip)(dmf) and MoO(sma)(dmf). The cyclic voltammograms for these complexes in 0.10 M $[Et_4N]Cl$ (Figure 1) have oxidation and reduction peaks at essentially the same potentials as for the known Mo(V)–oxo complexes $[Et_4N][MoOCl_2(sip)]$[11] and $[Et_4N][MoOCl_2(sma)]$,[12a] respectively. One-electron coulometric oxidation at a potential slightly more positive than the oxidation peak near 0.00 V produces these Mo(V)–oxo complexes, as determined by the cyclic voltammograms and electronic spectra of the oxidized solutions. This oxidation peak is, therefore, assigned to process 5. The reduction peak near −1.00 V represents a one-electron process, while the reduction peak near the same potential for the Mo(V)-oxo complexes corresponds to a two-electron process,[11,12a] both determined by coulometry. Further, the reduced products for both Mo(IV)–oxo and Mo(V)–oxo complexes have identical electronic spectra. Thus, the reductions for both oxidation states occur at or near the same potential and give the same product. Consequently, the Mo(V)–oxo complexes cannot be reduced to the corresponding Mo(IV)–oxo complexes under these conditions.[12b,c] Since the same oxidation peak near 0.00 V is present in both the anodic and cathodic scans (Figure 1), it appears the broad oxidation peak near −1.00 V, coupled to the one-electron reduction, represents the reoxidation of the one-electron-reduced species[12c] to the initial Mo(IV)–oxo complex.

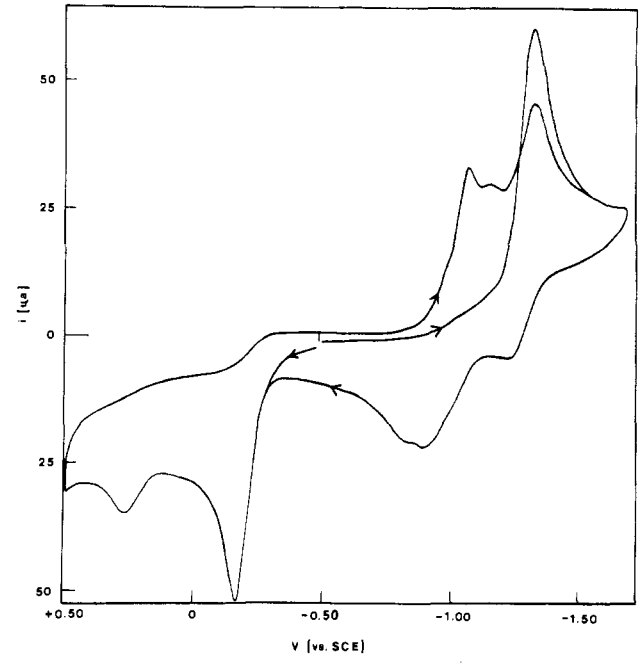


Figure 2. Cyclic voltammogram (5.00×10^{-4} M in DMF, 0.10 M $[Et_4N]Cl$) of MoO(sip)(phen). Scan rate = 0.100 V/s.

$$MoO(L)(dmf) + 2Cl^- \rightarrow MooCl_2(L)^- + dmf + e^- \quad L = sip, sma \qquad (5)$$

MoO(sip)(phen), MoO(sma)(phen), MoO(sma)(bpy). Anodic scans of these complexes exhibit well-defined oxidation peaks near 0.00 V (Figure 2, Table I). A complete cycle shows two major reduction peaks, of approximately equal height, the first coupled to the oxidation peak near 0.00 V. An initial cathodic scan, however, shows only one reduction peak, corresponding in potential to the more negative peak. Upon a second cathodic cycle, both reduction peaks are again observed. Controlled-potential coulometry indicates the more negative peak is a one-electron process. A broad oxidation peak, coupled to this reduction is observed near −0.90 V. Again, since the same oxidation peak near 0.00 V is observed for both anodic and cathodic scans, it appears the broad oxidation peak near −0.90 V is for the reoxidation of the one-electron-reduced species to the initial Mo(IV)–oxo complex. Controlled-potential oxidation at potentials slightly more positive than the oxidation peak near 0.0 V gives solutions with cyclic voltammograms and electronic spectra identical with those of $[Et_4N][MoOCl_2(sip)]$ and $[Et_4N][MoOCl_2(sma)]$. Clearly, on the coulometric time scale, the initial one-electron oxidation product, which is responsible for the more positive of the two reduction peaks seen in the complete cyclic voltammograms,

(11) (a) R. D. Taylor, J. P. Street, M. Minelli, and J. T. Spence, *Inorg. Chem.*, **17**, 3207 (1978) (the correct value of λ_{max} for MoO(mpe) is 367 nm); (b) D. T. Sayer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley, New York, 1974, p 340.

(12) (a) M. Minelli, Dr.rer.nat. Dissertation, Universität Konstanz, Konstanz, Germany, 1980; (b) The cyclic voltammogram for $[Et_4N][MoOCl_2(sma)]$ in DMF with $[n\text{-}Bu_4N][BF_4]$ as electrolyte shows two one-electron reduction peaks of approximately equal height, the first ~0.40 V more positive than the second. It appears in the absence of excess $[Et_4N]Cl$, a Cl^- dissociates from $MoOCL_2(sma)^-$ resulting in the shift of the Mo(V/IV) peak to more positive values: J. T. Spence, unpublished results. (c) The one-electron-reduced products of the Mo(IV)–oxo complexes and the two-electron-reduced products of the Mo(V)–oxo complexes are most likely Mo(III) species since the ligands are not reduced at these potentials and disproportionation reactions to produce lower oxidation states of Mo (Mo(II), e.g.) are unlikely.[4]

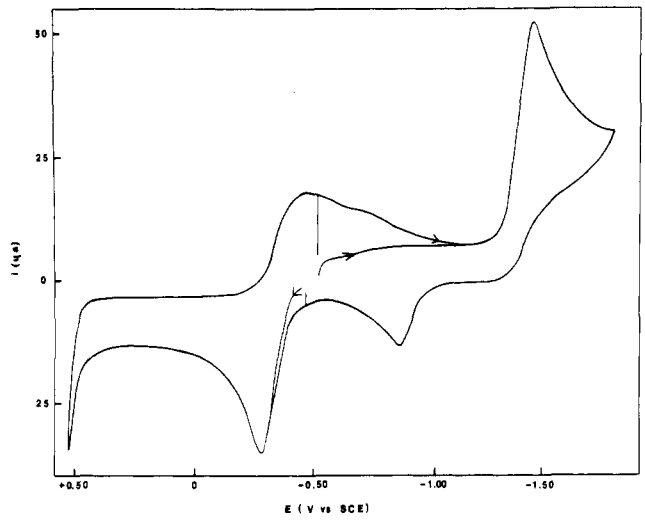
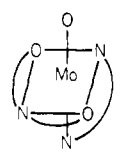


Figure 3. Cyclic voltammogram (5.00×10^{-4} M in DMF, 0.10 M $[Et_4N]Cl$) of MoO(mpe). Scan rate = 0.100 V/s.

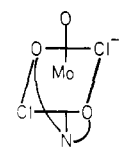
is converted to these Mo(V)–oxo complexes by Cl^- displacement of the phen and bpy ligands.

MoO(mpe). This complex has an initial cathodic peak at −1.37 V coupled to an oxidation peak at −0.85 V. Both complete anodic and cathodic scans show an oxidation peak at −0.30 V with a coupled reduction peak at −0.44 V (Figure 3). Upon controlled-potential coulometric oxidation at −0.25 V, a process which yields one electron, the yellow color of the Mo(IV) complex changes to the violet of the previously reported Mo(V)–oxo complex MoOCl(mpe),[11a,13] and the cyclic voltammogram is essentially identical with that of this Mo(V)–oxo complex. The oxidation peak at −0.85 V, coupled to the initial one-electron reduction peak at −1.37 V, most likely represents the reoxidation of the one-electron-reduced species to the original Mo(IV) complex since both anodic and cathodic scans show the same oxidation peak near −0.30 V. As demonstrated by coulometry, the quasi-reversible couple at $E_{1/2}$ −0.37 V, is for the Mo^V/Mo^{IV} couple.

IR Spectra. The infrared absorption frequencies for the Mo–O_t bands are found in Table I. They occur in the 920–960-cm^{-1} region. The coordination of the neutral bidentate nitrogen donor ligands (bpy, phen) has the effect of lowering the Mo–O_t stretch from the value observed in the corresponding six-coordinate Mo(V) complexes $[Et_4N][MoOCl_2(sip)]$ and $[Et_4N][MoOCl_2(sma)]$.[12a] This anomalous result[4] may be due to a difference in structure. The six-coordinate complexes most likely have octahedral geometry, and, since both ligands are planar, a nitrogen of the bidentate ligand is in the trans position to the oxo ligand. $[Et_4N][MoOCl_2(sip)]$, on the other hand, has the sip ligand nitrogen trans to oxo, with the chlorides in cis positions.[14,15] This difference in structure may explain the anomalous Mo–O_t frequencies.



MoO(sip)(phen)
[ν(Mo-O_t) 929 cm^{-1}]



$MoOCl_2(sip)^-$
[ν(Mo-O_t) 940 cm^{-1}]

As expected, the five-coordinate Mo(IV) complexes have higher ν(Mo–O_t) for MoO(sip)(dmf) and MoO(sap)(sma) than the corresponding six-coordinate Mo(V) complexes;[12a] the ν(Mo–O_t) observed for MoO(mpe), which is lower than ν(Mo–O_t) for MoOCl(mpe),[10,12a] is also anomalous.[4]

Discussion

The complexes prepared in this study can be synthesized by a number of methods, as described above. The most useful method is oxo abstraction from the appropriate Mo(VI)–dioxo complex by PPh_2Et. As discussed by Chen et al.,[5] its success depends on reaction 7 being an equilibrium, rather than going

$$MoO_2(mpe) + PPh_2Et \rightarrow MoO(mpe) + OPPhEt \quad (6)$$

$$MoO_2(mpe) + MoO(mpe) \rightleftarrows Mo_2O_3(mpe)_2 \quad (7)$$

to completion. In this context, it is of some interest to compare the use of this method for the synthesis of the two closely related complexes MoO(mpe) and MoO(mee). While the method proved satisfactory for MoO(mpe), only the μ-oxo Mo(V) dimer was obtained from $MoO_2(mee)$. The difference may be a result of the steric effect of the methyl groups on the carbon atoms adjacent to sulfur in mpe. Molecular models indicate these methyl groups interact sterically in the μ-oxo-bridged dimer $Mo_2O_3(mpe)_2$, thus destabilizing it to some degree and thereby possibly shifting equilibrium 7 to the left. If so, rather small differences in ligand structure may determine the outcome of a synthesis by this method. This suggests the synthesis of Mo(IV)–oxo complexes by oxo abstraction by phosphine from Mo(VI)–dioxo complexes may be more successful if the ligands have bulky groups adjacent to the coordination sites.

The electrochemical and spectral results with MoO(sip)(dmf), MoO(sma)(dmf), and MoO(mpe) clearly indicate these complexes are electrochemically oxidized to $[Et_4N][MoOCl_2(sip)]$,[11a] $[Et_4N][MoOCl_2(sma)]$,[12a] and MoOCl(mpe),[11a,13] respectively, under the conditions used. Thus, for these complexes, all members of the series (Mo(VI), -(V), -(IV)) have been obtained and their electrochemical properties determined under identical conditions.[16] It is evident they do not form simple electron-transfer series. The Mo(V)–oxo complexes are not obtainable electrochemically from the Mo(VI)–dioxo complexes nor are the Mo(IV)–oxo complexes obtainable by one-electron reduction of the Mo(V)–oxo complexes, while both the Mo(V)–oxo and Mo(IV)–oxo complexes give the same product upon reduction.[12c]

The results with the mixed-ligand complexes MoO(sip)(phen), MoO(sma)(phen), and MoO(sma)(bpy) indicate they lose their bidentate ligands upon electrochemical oxidation in the presence of Cl^- on the coulometric time scale, giving the known $MoOCl_2(sip)^-$[11a] and $MoOCl_2(sma)^-$[12a] complexes (eq 8). This may be a result of unfavorable charge since positively

$$MoO(sip)(phen) + 2Cl^- \rightarrow MoOCl_2(sip)^- + phen + e^- \quad (8)$$

charged species $(MoO(sma)(bpy)^+$, e.g., which may be the initial product of one-electron oxidation) might be expected to be less stable than anionic species for complexes of molybdenum in high oxidation states.

The results demonstrate Mo(IV)–oxo complexes are obtainable, by synthesis from Mo(VI)–dioxo complexes and from Mo(IV) starting materials. The results also indicate, as with other ligands,[10,11,12a,16] Mo(VI)–dioxo complexes are generally reducible to Mo(IV)–oxo complexes (although subsequent reaction of the Mo(IV) complex with the Mo(VI) complex in most cases produces μ-oxo Mo(V) dimers), with the loss

(13) J. T. Spence, M. Minelli, P. Kroneck, M. I. Scullane, and N. D. Chasteen, *J. Am. Chem. Soc.*, **100**, 8002 (1978).
(14) M. I. Scullane, R. D. Taylor, M. Minelli, J. T. Spence, K. Yamanouchi, J. H. Enemark, and N. D. Chasteen, *Inorg. Chem.*, **18**, 3213 (1979).
(15) K. Yamanouchi and J. H. Enemark, unpublished results.
(16) In addition to the complexes reported here, all three members of the series (Mo(VI), -(V), -(IV)) are known with the ligands 8-hydroxyquinoline, 8-mercaptoquinoline, and *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine.

of one oxo group. Mo(V)–oxo complexes, on the other hand, are obtained by one-electron oxidation of Mo(IV)–oxo complexes but cannot be obtained by reduction of Mo(VI)–dioxo complexes.[11a] These results are in general agreement with current hypotheses concerning electron-transfer mechanisms of molybdenum enzymes.[17] They differ, however, with recent suggestions based on EXAFS data concerning the structure of the molybdenum center in the reduced (Mo(IV), Mo(V)) states for sulfite oxidase, in which an oxo group is converted to a ligated hydroxyl group upon reduction.[3] Work is in progress to obtain complexes which may better model the reduced enzymatic molybdenum environment.

Experimental Section

Materials. Methanol was purified and dried by refuxing over Mg turnings and freshly distilled before use. DMF and MeCN were purified as described previously.[11a,b] PPh_2Me and PPh_2Et were purchased from Strem Chemicals, α,α'-bypiridyl and *o*-phenanthroline from Aldrich, $Na_2MoO_4 \cdot 2H_2O$ from J. T. Baker, and salicylidene-*o*-phenol from Pfaltz and Bauer. $MoCl_4$ was obtained from Alfa.

Syntheses. Ligands. *N,N'*-Dimethyl-*N,N'*-bis(2-mercaptoethyl)-ethylenediamine (mee) was synthesized by the procedure of Karlin and Lippard.[18] Salicylaldehyde 2-mercaptoanil (sma) was prepared by the method of Muto.[19] *N,N'*-Bis(2-mercapto-2-methylpropyl)-ethylenediamine (mpe) and the ligands *N,N'*-bis(2-mercaptophenyl)-1,2-diaminoethane (mae), *N,N'*-bis(2-mercaptophenyl)-1,2-diaminopropane (map), and *N,N'*-bis(2-mercaptophenyl)2,3-diaminobutane (mab) were kindly supplied by Dr. Peter Kroneck, Fakultät für Biologie, Universität Konstanz, and were synthesized according to the procedures of Corbin and Work.[20,21]

Starting Materials. $MoOCl_2(PMePh_2)_3$ was synthesized according to the method of Butcher and Chatt[22] and $MoOCl_2(bpy)(PPh_2Me)$ according to the method of Rice and Spence.[7] $MoO_2(sma)$,[12] $MoO_2(sip)$,[11] $MoO_2(mee)$,[11] $MoO_2(mpe)$,[11] $MoO_2(mae)$,[23] $MoO_2(mab)$,[23] and $MoO_2(map)$[23] were synthesized by methods previously described.

Mo(IV) Complexes. All manipulations were performed under an atmosphere of prepurified dinitrogen (99.997%) with standard Schlenk techniques.

MoO(sip)(dmf). 1. To a solution of PPh_2Et (0.5 cm^3, ~2.3 mmol) in MeCN (30 cm^3) was added a solution of $MoO_2(sip)$ (0.40 g, 1.18 mmol) in DMF (10 cm^3). The resultant yellow-brown solution was refluxed for 0.5 h to produce a deep reddish brown solution containing a crystalline solid. After the solution was cooled to −20 °C, the brown crystals were filtered off, washed with MeCN, and dried in vacuo; yield 0.30 g (70%). Anal. Calcd for $MoC_{16}H_{16}N_2O_4$: C, 48.50; H, 4.07; N, 7.07. Found: C 48.31; H, 4.07; N, 7.16.

2. To a slurry of $MoCl_4$ (0.5 g, 2.10 mmol) in MeOH (40 cm^3) was added a solution of salicylidene *o*-aminophenol (0.45 g, 2–10 mmol) in DMF (40 cm^3). The mixture was stirred for a few hours and then cooled to −20 °C. The solid was filtered off, washed with MeOH, and dried in vacuo; yield 0.40 g (48%).

3. To a slurry of $MoOCl_2(bpy)(PPh_2Me)$ (0.44 g, 1.07 mmol) in MeCN (20 cm^3) was added a solution of salicylidene *o*-aminophenol (0.23 g, 1.07 mmol) and triethylamine (0.30 cm^3, 2.14 mmol) in DMF (5 cm^3). The solution was stirred for a couple of hours during which time the violet mixture became brown. After the solution was cooled to −20 °C, the brown microcrystalline solid was filtered off, washed with MeCN, and dried in vacuo; yield 0.30 g (71%).

4. $MoOCl_2(PPh_2Me)_3$ can be used instead of $MoOCl_2(bpy)(PPh_2Me)$ by using a method identical with the one above.

MoO(sip)(phen). To a solution of *o*-phenanthroline (1.33 g, 7.38 mmol) and PPh_2Et (0.40 cm^3, ~1.85 mmol) in MeCN (25 cm^3) was added a solution of $MoO_2(sip)$ (0.25 g, 0.74 mmol) in DMF (5 cm^3). The yellow-brown solution was refluxed for 1.5 h by which time it had become green, with a precipitate present. After the solution was cooled to −20 °C, the green crystalline solid was filtered off, washed with MeCN, and dried in vacuo; yield 0.15 g (40%). Anal. Calcd for $MoC_{25}H_{17}N_3O_3$: C, 59.65; H, 3.40; N, 8.35. Found: C, 60.23; H, 3.26; N, 8.70.

MoO(sma)(phen). To a solution of *o*-phenanthroline (0.84 g, 4.66 mmol) and PPh_2Et (0.20 cm^3, ~0.93 mmol) and MeCN (25 cm^3) was added a solution of $MoO_2(sma)$ (0.165 g, 0.46 mmol) in DMF (5 cm^3). The resultant brown, then green solution was stirred for 30 min, by which time a precipitate was present. After the solution was cooled to −20 °C, the gray-green microcrystals were isolated, washed with MeCN, and dried in vacuo; yield 0.21 g (88%). Anal. Calcd for $MoC_{25}H_{17}N_3O_2S$: C, 57.81; H, 3.30; N, 8.09; S, 6.17. Found: C, 57.30; H, 3.37; N, 8.15; S, 5.10.

MoO(sma)(bpy). 1. To a solution of α,α'-bipyridyl (0.53 g, 6.8 mmol) and PPh_2Et (0.30 cm^3, ~1.5 mmol) in MeCN (25 cm^3) was added a solution of $MoO_2(sma)$ (0.24 g, 0.68 mmol) in DMF (5 cm^3). The orange-brown solution was refluxed for 1 h to produce dark green crystals, which after cooling to −20 °C, were isolated, washed with MeCN, and dried in vacuo; yield 0.24 g (70%). Anal. Calcd for $MoC_{23}H_{17}N_3O_2S$: C, 55.76; H, 3.46; N, 8.48; S, 6.47. Found: C, 55.50; H, 3.50; N, 8.67; S, 6.30.

2. To a slurry of $MoOCl_2(bpy)(PPh_2Me)$ (0.54 g, 1.00 mmol) in MeCN (30 cm^3) was added a solution of salicylaldehyde 2-mercaptoanil (0.23 g, 1.00 mmol) and triethylamine (0.28 cm^3, 2.00 mmol) in DMF (6 cm^3). The mixture was stirred, and after 5 min a green solution was present. The solution was stirred for a couple of hours and then cooled to −20 °C. The green solid was filtered off, washed with MeCN, and dried in vacuo; yield 0.30 g (60%).

MoO(sma)(dmf). To a solution of PPh_2Et (0.5 cm^3, 2.3 mol) in MeCN (25 cm^3) was added a solution of $MoO_2(sma)$ (0.36 g, 1.01 mmol) in DMF (5 cm^3). The orange-brown solution was stirred for a few hours, after which time the solution had become dark brown with the precipitation of a brown solid. After the solution was cooled to −20 °C, the brown microcrystals were filtered off, washed with MeCN, and dried in vacuo; yield 0.27 g (70%). Anal. Calcd for $MoC_{16}H_{16}N_2O_3S$: C, 46.61; H, 3.91; N, 6.79; S, 7.78. Found: C, 46.38; H, 4.07; N, 7.00; S, 7.52.

MoO(mpe). To a slurry of $MoO_2(mpe)$ (0.25 g, 0.69 mmol) in DMF (5 cm^3) was added a solution of PPh_2Et (0.90 cm^3, 4.2 mmol) in MeCN (25 cm^3). The resultant yellow slurry was refluxed for 3–4 h, giving orange crystals in a brown solution. After the solution was cooled to −20 °C, the orange crystals were filtered off, washed with MeCN, and dried in vacuo; yield 0.17 g (71%). Anal. Calcd for $MoC_{10}H_{22}ON_2S_2$: C, 34.68; H, 6.40; N, 8.09; S, 18.5. Found: C, 33.00; H, 6.03; N, 7.90; S, 17.6.

Electrochemistry. Electrochemistry measurements were made with a three-electrode system at a platinum electrode as described previously.[11a]

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Registry No. MoO(sip)(dmf), 80630-33-7; MoO(sip)(phen), 80630-32-6; MoO(sma)(phen), 80630-34-8; MoO(sma)(bpy), 80630-35-9; MoO(sma)(dmf), 80658-36-2; MoO(mpe), 80630-36-0; $MoO_2(sip)$, 67598-36-1; $MoO_2(sma)$, 75780-89-1; $MoO_2(mpe)$, 67598-35-0; $MoOCl_2(bpy)(PPh_2Me)$, 73953-23-8; $MoCl_4$, 13320-71-3.

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