

Electrochemical Studies of Oxo- and Sulfido-Bridged Binuclear Molybdenum(V) Complexes in Aprotic Media

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The electrochemistry of di- μ -oxo-bis(8-quinolinolatooxopyridinemolybdenum(V)) [$\text{Mo}^{\text{V}}_2\text{O}_4\text{Q}_2(\text{py})_2$] and μ -(2-mercaptoethanolato-*S:O*)- μ -oxo-bis(8-quinolinolatooxomolybdenum(V)) [$\text{Mo}^{\text{V}}_2\text{O}_3(\text{me})\text{Q}_2$] has been studied in dimethyl sulfoxide using cyclic voltammetry and controlled-potential coulometry at a platinum electrode. Redox mechanisms are proposed on the basis of the electrochemical data for the complexes and their electrolysis products. Both the reduction and oxidation of $\text{Mo}^{\text{V}}_2\text{O}_4\text{Q}_2(\text{py})_2$ are two-electron processes. The reduced and oxidized dimers immediately fragment into identical monomers. The reduction of $\text{Mo}^{\text{V}}_2\text{O}_3(\text{me})\text{Q}_2$ occurs in two one-electron steps to give a mixed oxidation state dimer with a transient lifetime. The monomeric Mo(IV) reduction products of both compounds reduce the solvent and water present in the solvent. Comparisons are made with the redox properties of other oxo- and sulfido-bridged binuclear molybdenum(V) complexes formed by chloride ion, 8-quinolinolate, *N,N*-diethyldithiocarbamate, riboflavin radical anion, and the dianion of 1,2-dimercaptoethane. Dioxo-bridged complexes in general are reduced by a two-electron process, while monooxo- and disulfido-bridged compounds and the triply bridged compound are reduced by successive one-electron processes. The results indicate the effects that stabilize mixed oxidation state dimers and may provide insight to the chemistry of biological molybdenum.

There has been much interest recently in the chemistry and structure of binuclear bridged molybdenum(V) complexes, particularly with respect to model compounds for molybdenum-containing enzymes. Molybdenum is known to occur in at least five enzymes: xanthine oxidase,¹ aldehyde oxidase,² nitrate reductase,³ sulfite oxidase,⁴ and nitrogenase.⁵ All of these enzymes catalyze redox type chemical reactions which involve the transfer of two or more electrons per substrate molecule. In each case the enzyme appears to contain two atoms of molybdenum and, in the cases of xanthine oxidase, aldehyde oxidase, and possibly nitrate reductase, two molecules of flavin as well.⁴

Although some molybdenum(V) has been detected by ESR in four of the enzymes in the presence of substrate,^{2,3,6-8} the oxidation state(s) of the molybdenum atoms in the native enzyme is not known. The chemistry of molybdenum(V) complexes is dominated by both terminal oxo and bridged oxo binuclear species in solution under conditions of biological acidity, but the degree of association of the two molybdenum atoms in the enzymes is not known. On the basis of the observed ESR signals in xanthine oxidase,⁴ the two molybdenum atoms are believed to be far apart because bridged binuclear molybdenum(V) complexes are diamagnetic. However, the presence of the molybdenum atoms in mixed oxidation state dimers (either V-IV or V-VI) would explain the ESR signals and still allow close association.

Because all of the molybdenum-containing enzymes catalyze oxidation-reduction reactions, electrochemistry is a particularly useful method for the study of the redox behavior of molybdenum model compounds. The possible importance of binuclear bridged molybdenum(V) species as model compounds for the active sites of these enzymes, along with the possible importance of direct molybdenum-flavin interactions⁹ has led to several studies of the molybdenum complexes formed with 8-quinolinol^{10,11} and with the riboflavin anion radical¹² in aprotic solvents. 8-Quinolinol has been chosen as a ligand because of its structural similarity to the flavins but without the drawback of having a rather complicated electrochemistry of its own. The results of these studies indicate that the inner coordination sphere about the molybdenum ion has a profound effect on the complexes' redox chemistry.

The presence of extensive amounts of inorganic sulfur in several of the molybdenum-containing enzymes has led us to consider sulfur ligands as an alternative to terminal and bridging oxygen ligands for biological molybdenum. Recent

electrochemical studies of molybdenum complexes that are formed with dithiocarbamate ligands and bridging oxygen and bridging sulfur groups also have confirmed the importance of the nature of the ligands on the redox chemistry of the complexes.¹³

In an effort to more fully understand the dependence of the redox chemistry on structure, we have undertaken a study of how the electrochemistry of bridged binuclear molybdenum(V) complexes is affected by systematic changes in the ligands occupying the inner coordination sphere. The concept of functional groups to describe the various types of molybdenum(V) dimeric linkages is useful at this point. A schematic representation of several such functional groups appears in Figure 1. The remaining molybdenum coordination sites that are not shown in the figure can be occupied by any other ligands, although our interest centers on complexes having bidentate "capping" ligands and other monodentate ligands as necessary (including solvent molecules) to fill the remaining coordination sites.

Molybdenum(V) dimers are known to exist with three different degrees of bridging, having either one, two, or three donor atoms shared equally by the two molybdenum atoms. The triply bridged species represented by functional group III is unique because the only well-characterized compound with this linkage is $\text{Mo}_2\text{O}_3(\text{me})\text{Q}_2$ (me is the dianion of 2-mercaptoethanol; Q is the anion of 8-quinolinol).¹⁴ The remainder of the functional groups are simply variations of types I and II where sulfur atoms have replaced either terminal oxygen atoms or bridging oxygen atoms or both. Compounds with functional groups I, II, V, and VI also have been reported. Although examples of functional groups IV, VII, VIII, and IX have not been reported, attempts to synthesize and characterize compounds with these linkages are in progress in this laboratory.

Ideally, a systematic study should involve a series of complexes with the same capping ligands and each type of functional group. Unfortunately, even for those functional groups which are known, an entire series with the same capping ligand has not been reported. The 8-quinolinolate complexes of functional groups I-III have been prepared, and the electrochemical behavior in DMSO at a platinum electrode of the monooxo-bridged compound, $\text{Mo}_2\text{O}_3\text{Q}_4$, has been discussed.¹⁰ The electrochemical behavior of the dioxo-bridged compound, $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$, and the triply bridged compound, $\text{Mo}_2\text{O}_3(\text{me})\text{Q}_2$, in DMSO solution at a platinum electrode is

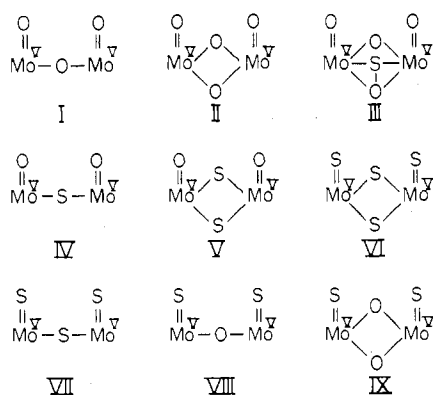


Figure 1. Bridged binuclear Mo(V) functional groups.

summarized in the present paper.

Important aspects of the electrochemical studies include the relative ease of oxidation and reduction of the compounds, the number of electrons transferred during oxidation and reduction, and the reversibility of the electron-transfer process. In addition there is the important question of the stability of mixed oxidation state dimers formed by the one-electron oxidation or reduction of each dimer. Finally, for those compounds which do not undergo reversible electrochemical reactions and thus undergo either gross structural changes or fragmentation reactions upon electron transfer, the nature of the rearrangements or postchemical reactions is of interest.

Experimental Section

Materials and Measurements. The cyclic voltammetric experiments were performed using a versatile instrument constructed from Philbrick operational amplifiers.¹⁵ A Wenking Model 61RH potentiostat was used for controlled-potential electrolysis studies. Coulometry was accomplished by integrating the current-time curve with a K&E Model 62005 compensating polar planimeter. A Beckman platinum-inlay electrode was used as the working electrode for cyclic voltammetry and a platinum gauze electrode was employed in the coulometric experiments. The reference electrode consisted of a Ag/AgCl electrode in aqueous tetramethylammonium chloride solution (0.000 V vs. SCE) placed in a glass tube which made contact through a cracked glass bead junction with bulk solution in a Luggin capillary. The platinum-flag auxiliary electrode was isolated from the bulk solution by a fine-porosity frit. For cyclic voltammetry experiments, the auxiliary compartment was filled with the bulk solution; for coulometric experiments, the auxiliary compartment was filled with solvent and supporting electrolyte only.

Dimethyl sulfoxide (DMSO) (J. T. Baker analyzed reagent grade) was obtained in pint bottles to minimize water contamination; the water content as specified by the source varied from 0.02 to 0.06%. DMSO was degassed with Ar in the electrochemical cell prior to the addition of the compound to be studied. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte in all of the electrochemical studies in a (50–100)-fold excess over the concentration of the electroactive species. TEAP was prepared according to the procedure of House et al.¹⁶

Ammonium paramolybdate(VI) was obtained from the Mallinckrodt Chemical Works. 2-Mercaptoethanol (H_2me) and 8-quinolinol were obtained from MC/B. Ammonium pentachloro-oxomolybdate(V) was prepared by the method of Saha and Banerjee.¹⁷ All solvents were reagent grade and used without further purification. Argon gas was dried by passing it through a tower of Aquasorb (Mallinckrodt).

Preparation of the Complexes. 1. Di- μ -oxo-bis(8-quinolinolato-oxopyridinemolybdenum(V)), $Mo_2O_4Q_2(py)_2$. The complex was prepared by a modification of the method of Dutta and Chatterjee.¹⁸ The ligand, 0.32 g of HQ (2.3 mmol), was dissolved in 15 ml of 70% ethanol in water. The metal salt, 0.65 g of $(NH_4)_2MoOCl_5$ (2.0 mmol), was dissolved in 25 ml of 70% ethanol in water and this solution was added immediately to the ligand solution. Next, 3 ml of pyridine (38 mmol) was added and the reaction mixture was refluxed with stirring for 20 min. During this time some orange-red solid precipitated

from the solution. The reaction mixture was cooled at $-28^\circ C$ for 24 h, the product filtered, and the solid washed with water and acetone and air-dried. The compound was purified by recrystallization from dichloromethane-acetone solution at $-28^\circ C$. For the synthetic conditions described in the original paper,¹⁸ only the monooxo-bridged compound $Mo_2O_3Q_4$ was isolated.

2. μ -(Mercaptoethanolato-S:O)- μ -oxo-bis(8-quinolinolato-oxomolybdenum(V)), $Mo_2O_3(me)Q_2$. The compound was prepared by the method of Gelder et al.,¹⁴ except the ethanol solvent was degassed with argon prior to the reaction and the reaction was carried out in a Schlenk tube under an atmosphere of dry argon.

Results

To understand the electrochemistry of the binuclear molybdenum(V) groups in DMSO solution the electrochemical behavior of the free ligands in this solvent must be known so that it can be distinguished from that of the complexes. The electrochemistry of 8-quinolinol (HQ) has been described previously.¹⁰ The neutral ligand is reduced by a one-electron process at -1.78 V vs. SCE to produce $0.5 H_2$ and Q^- ; Q^- is not reduced at potentials as negative as -2.0 V. The H_2 that is formed is oxidized at -0.59 V and Q^- is oxidized at $+0.06$ V by a one-electron process. The product of the oxidation is not electrochemically active and probably is Q_2 . HQ is not oxidized at potentials below $+1.25$ V.

The cyclic voltammogram of 2-mercaptoethanol (H_2me) exhibits an initial cathodic peak at -1.65 V followed by anodic peaks at -0.40 and $+0.70$ V. For an initial anodic scan there is a broad peak at $+0.73$ V followed by cathodic peaks at -0.57 , -1.65 , and -1.91 V. Because neither ethanol nor ethylene glycol is electrochemically active in the potential range of interest, attention can be focused on the mercapto end of the molecule. The initial reduction at -1.65 V corresponds to the reduction of protons bonded to the sulfur atom to form $R-S^-$ and $0.5 H_2$. The anion is a strong base and is partially hydrolyzed by the water present to form $R-SH$ and OH^- . The H_2 formed in this reduction is oxidized at -0.40 V to form H^+ . The absence of any H^+ reduction when the scan direction is switched from positive to negative at -0.12 V is due to the basic nature of the solution after the initial reduction at -1.65 V. All of the H^+ formed during the oxidation of the H_2 is immediately neutralized by OH^- and $R-S^-$. H_2me is oxidized at $+0.73$ V to form the disulfide, $(R-S)_2$, and two H^+ ions. The H^+ ions are reduced at -0.57 V and the disulfide is reduced at -1.91 V.

$Mo_2O_4Q_2(py)_2$. The cyclic voltammogram of 10^{-3} M $Mo_2O_4Q_2(py)_2$ in DMSO with 0.1 M TEAP as supporting electrolyte is shown in Figure 2. For an initial negative scan at a scan rate of 0.1 V/s, there is a large reduction peak at -1.47 V which has a small shoulder at -1.39 V; reversal of the scan gives anodic peaks at -0.26 and $+0.64$ V. The peak at $+0.64$ V also is present in an initial positive scan; reversal of the scan gives cathodic peaks at -0.57 , -0.97 , -1.39 , -1.47 , and -1.78 V; a second reversal yields anodic peaks at -0.59 and -0.26 V. The cathodic peak at -0.57 V, which results from the initial oxidation at $+0.64$ V, is greatly reduced in intensity for an initial negative scan to -2.0 V followed by a positive scan.

Both the cathodic wave at -1.47 V and the anodic wave at $+0.64$ V appear to involve the transfer of 2 mol of electrons/mol of molybdenum dimer, based on the large peak currents and steep initial slopes of the waves. The anodic peak at -0.26 V and the cathodic peaks at -0.57 and -0.97 V are only half as high and appear to involve the transfer of 1 mol of electrons/mol of dimer.

Controlled-potential coulometry at -1.50 V indicates that n , the number of moles of electrons transferred per mole of dimer, is 2 for the initial reduction process. Cyclic voltammograms of the reduced solution have anodic peaks at -0.26 , -0.08 , and $+0.64$ V. Switching scan direction after either of

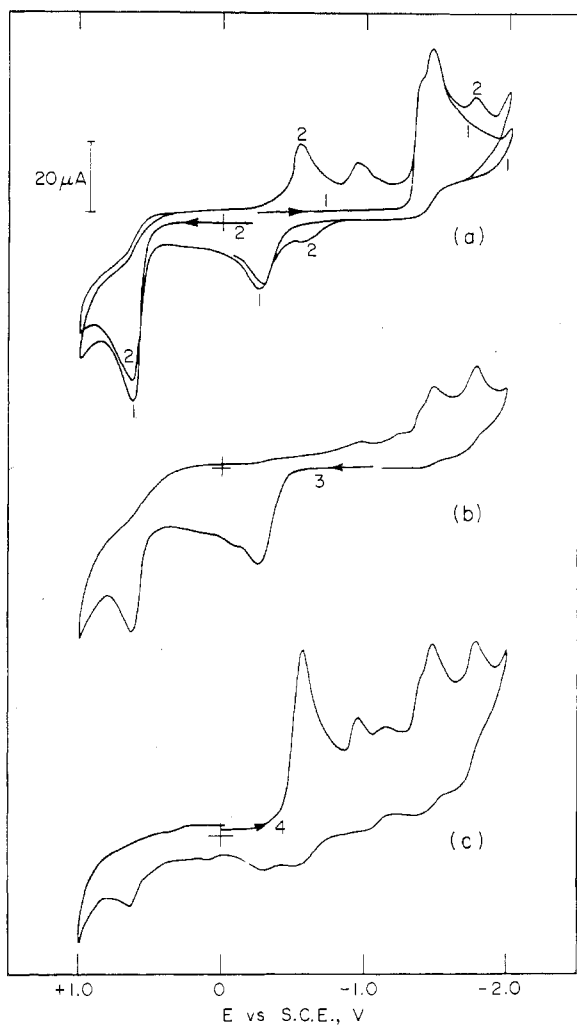


Figure 2. Cyclic voltammograms of 10^{-3} M $\text{MoV}_2\text{O}_4\text{Q}_2(\text{py})_2$ in 0.1 M TEAP in DMSO at a platinum electrode; scan rate 0.1 V/s: (a) before coulometric reduction or oxidation; (b) after coulometric reduction at -1.50 V; (c) after coulometric oxidation at $+0.64$ V; 1 and 4, initial cathodic scans; 2 and 3, initial anodic scans.

the first two anodic peaks gives cathodic peaks at -1.39 and -1.47 V, which correspond to the reduction of the starting material, plus a new cathodic peak at -1.78 V. Switching scan direction after the anodic peak at $+0.64$ V gives, in addition to the cathodic peaks just mentioned, reduction peaks at -0.97 and -1.17 V. Controlled-potential coulometry at -0.25 V after controlled-potential coulometry at -1.50 V indicates that n is 1 for this oxidation. However, if controlled-potential coulometry is then repeated at -1.50 V on the same solution, n is 1.6.

Controlled-potential coulometry at $+0.64$ V indicates that the value of n for the oxidation process is 1 on the coulometric scale instead of 2 (which it appears to be on the cyclic voltammetric time scale). Cyclic voltammograms of the oxidized solution have cathodic peaks at -0.57 , -0.97 , -1.15 , -1.49 , and -1.78 V; scan reversal gives anodic peaks at -0.97 , -0.55 , -0.26 , and $+0.64$ V. Switching scan direction after the cathodic peak at -0.57 V gives an anodic peak at -0.35 V. This couple is characteristic of the reduction of H^+ in DMSO and the reoxidation of the H_2 formed. Controlled-potential coulometry at -0.60 V after coulometry at $+0.64$ V indicates that n is 1 for this process as well.

The cathodic shoulder at -1.39 V increases in intensity when HClO_4 is added to the solution and decreases in intensity when tetraethylammonium hydroxide (TEAOH) is added. The

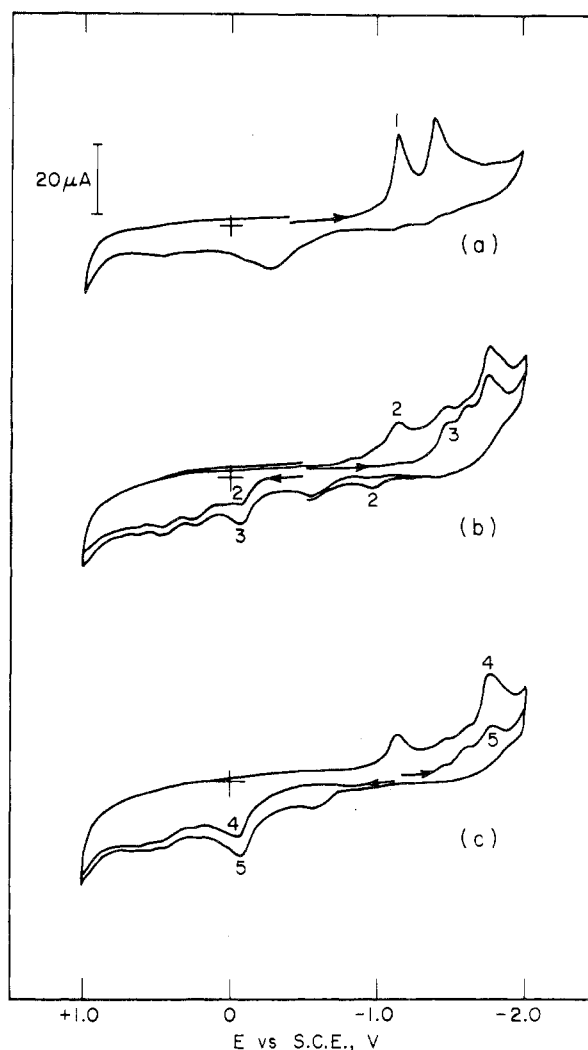


Figure 3. Cyclic voltammograms of 10^{-3} M $\text{MoV}_2\text{O}_3(\text{me})\text{Q}_2$ in 0.1 M TEAP in DMSO at a platinum electrode; scan rate 0.1 V/s: (a) before coulometric reduction; (b) after coulometric reduction at -1.16 V; (c) after coulometric reduction at -1.42 V; 1, 3, and 5 initial cathodic scans; 2 and 4, initial anodic scans.

cathodic peak at -0.57 V, which appeared after oxidation at $+0.64$ V, is eliminated by the addition of 1 equiv of base. There also is a new anodic peak at -0.08 V in the presence of base.

$\text{MoV}_2\text{O}_3(\text{me})\text{Q}_2$. Cyclic voltammograms of 10^{-3} M $\text{MoV}_2\text{O}_3(\text{me})\text{Q}_2$ in DMSO with 0.1 M TEAP as supporting electrolyte are shown in Figure 3. For an initial negative scan at a scan rate of 0.1 V/s cathodic peaks occur at -1.16 and -1.42 V; reversal of the scan gives peaks at -1.31 , -1.08 , -0.51 (all small), -0.27 , -0.08 V and very small peaks at $+0.28$ and $+0.45$ V. At a scan rate of 1.0 V/s the same initial cathodic peaks at -1.16 and -1.42 V are present, but there is only one anodic peak at -0.20 V. Whether the cathodic peaks at -1.16 and -1.42 V are quasi-reversible is questionable because the return anodic peaks are extremely flat. Because there is a small anodic peak at -0.08 V at fast scan rates, the first reduction process probably is transiently reversible. However, the anodic wave is so poorly defined that it is not possible to determine kinetic parameters for the species formed by reduction at -1.16 V.

Controlled-potential coulometry at -1.16 V indicates that n is 1 for the initial reduction process, but the cyclic voltammograms of the reduced solution indicate a complicated set of products. For an initial negative scan, the cathodic peak previously at -1.42 V is replaced by a smaller peak at -1.49

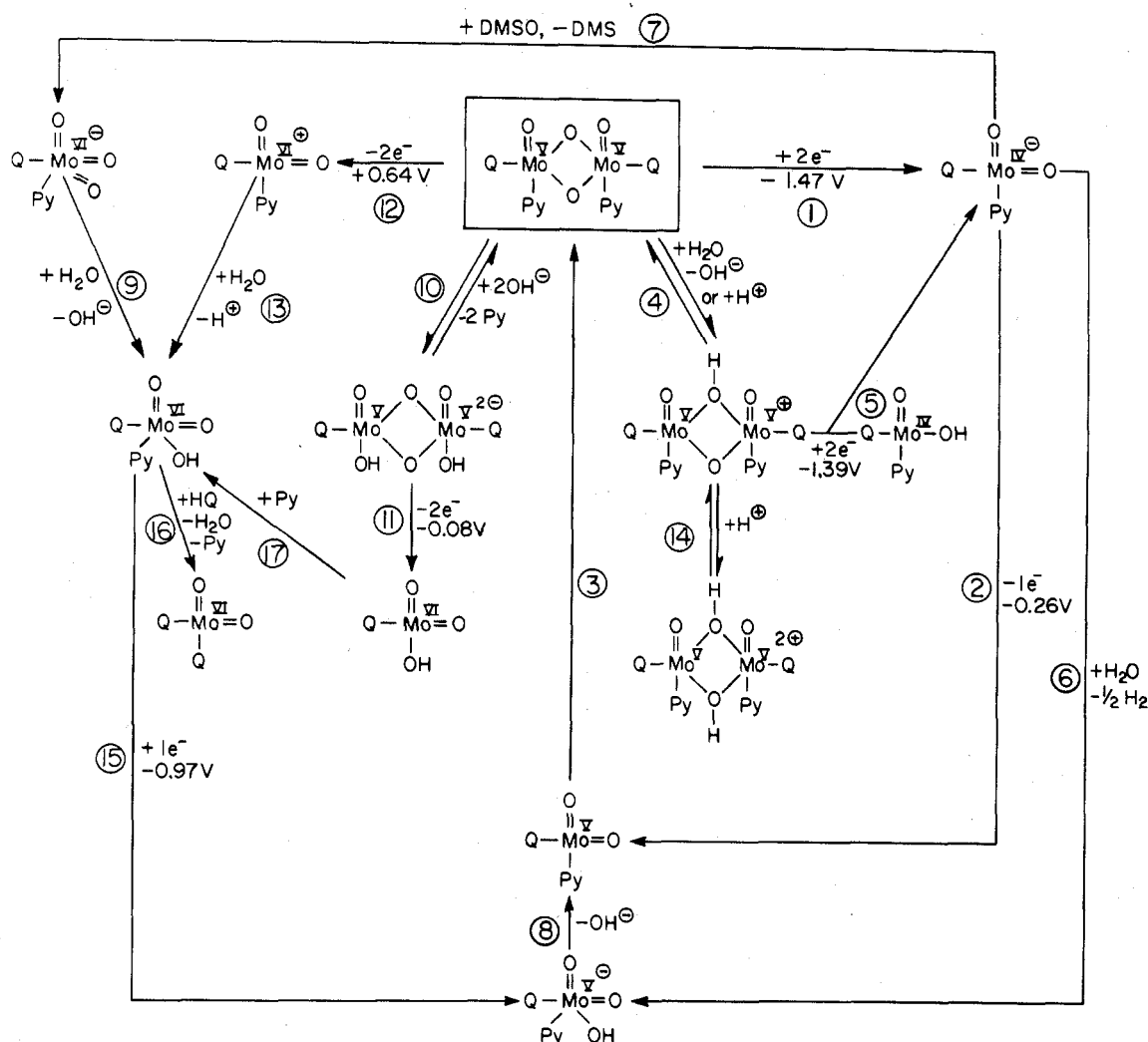


Figure 4. Redox mechanism for $\text{Mo}^{\text{V}}_2\text{O}_4\text{Q}_2(\text{py})_2$ in DMSO solution.

V. Additional cathodic peaks are observed at -1.62 and -1.77 V; scan reversal yields anodic peaks at -0.55 , -0.08 , $+0.22$, and $+0.46$ V. For an initial positive scan, anodic peaks occur at -0.08 , $+0.22$, and $+0.46$ V; scan reversal gives a cathodic peak at -1.15 V along with all of the other initial cathodic peaks. The cathodic peak at -1.15 V is coupled to an anodic peak at -0.97 V.

Controlled-potential coulometry at -1.42 V of a fresh solution of the dimeric complex indicates that n is 2 for this process. Because n is 1 for the reduction at -1.16 V and the number of moles of electrons transferred at -1.42 V will be the sum of the number transferred at -1.16 and -1.42 V, n actually is 1 for the second reduction process (reduction of product from -1.16 -V electrolysis). Cyclic voltammograms obtained after electrolysis at -1.42 V are similar to those obtained after electrolysis at -1.16 V, although all of the peaks are broader and thus less well defined.

Discussion and Conclusions

$\text{Mo}^{\text{V}}_2\text{O}_4\text{Q}_2(\text{py})_2$. A self-consistent mechanism for the oxidation and reduction of this compound appears in Figure 4. The dioxo-bridged dimer is irreversibly reduced at -1.47 V by a two-electron process to give two Mo(IV) monomer anions (reaction 1). Even at scan rates of 1.0 V/s, there is no indication of a coupled oxidation peak until the anodic wave at -0.26 V. The product of the reduction, $[\text{Mo}^{\text{IV}}\text{O}_2\text{Qpy}]^-$, is oxidized to $\text{Mo}^{\text{V}}\text{O}_2\text{Qpy}$ at -0.26 V (reaction 2). The Mo(V) monomers then recombine to form the dimeric starting compound (reaction 3).

The cathodic shoulder at -1.39 V corresponds to the reduction of the hydrolytically produced species $[\text{Mo}_2\text{O}_3(\text{OH})\text{Q}_2(\text{py})_2]^+$, which is formed by reaction of the parent compound with water (reaction 4). The concentration of water in Baker reagent grade DMSO is approximately 30 mM, about 30 times the concentration of the complex. The reduction of the protonated dimer probably is a two-electron process to give $[\text{Mo}^{\text{IV}}\text{O}_2\text{Qpy}]^-$ and $\text{Mo}^{\text{IV}}\text{O}(\text{OH})\text{Qpy}$ (reaction 5). The positively charged protonated species would be easier to reduce than the neutral species.

On the basis of coulometry, the two-electron reduction at -1.50 V followed by the one-electron oxidation at -0.25 V should give back only half as much starting material as was originally present. However, controlled-potential coulometry at -1.50 V after coulometry first at -1.50 V and then at -0.25 V indicates that n is 1.6 instead of the expected value of 1 . Therefore, some of the electrochemically produced Mo(IV) species is being chemically oxidized to Mo(V) or Mo(VI) and subsequently converted to $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$.

The Mo(IV) anion apparently is a good reducing agent and reduces both water (reaction 6) and DMSO (reaction 7). When water is reduced, the product $[\text{Mo}^{\text{IV}}\text{O}_2(\text{OH})\text{Qpy}]^-$ can lose a hydroxyl group (reaction 8) and then dimerize back to the parent compound (reaction 3). When DMSO is reduced, the product ($[\text{Mo}^{\text{VI}}\text{O}_3\text{Qpy}]^-$) can undergo a hydrolytic step (reaction 9) to form $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Qpy}$, which can then react with Mo(IV) monomers (not yet chemically oxidized) to form the parent compound. The reaction with DMSO is indicated at least to some extent because the solution smells of dimethyl

sulfide (DMS) during electrolysis at -1.50 V. The overall reaction then is



This can either be viewed as a two-electron reduction or as an oxygen atom transfer reaction. This may be of biological significance because the redox reactions catalyzed by xanthine oxidase, sulfite oxidase, and nitrate reductase also can be viewed as oxygen atom transfers.¹⁹

That a postchemical oxidation of the product from the electrochemical reduction at -1.47 V is competing with the electrochemical oxidation at -0.26 V becomes evident when the ratio of the peak currents of the cathodic and anodic processes is examined as a function of scan rate. Hence, as the scan rates are increased, the ratio of cathodic to anodic peak currents is decreased.

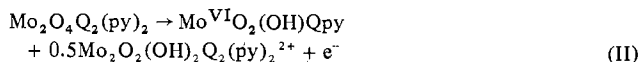
After controlled-potential coulometry at -1.50 V, there is, in addition to the anodic peak at -0.26 V, a smaller anodic peak at -0.08 V which is not present in the cyclic voltammograms of the parent compound. This same anodic peak at -0.08 V is observed in initial anodic cyclic scans of solutions of $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ to which additional OH^- ion has been added. The new species, $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$, is formed by the nucleophilic displacement of the pyridine ligands by OH^- ions (reaction 10). The anodic peak at -0.08 V corresponds to the two-electron oxidation of the dianion to $\text{Mo}^{\text{VI}}\text{O}_2\text{Q}(\text{OH})$ (reaction 11). The dianion, because of its double negative charge, is not reduced at potentials less negative than -2.0 V. The formation of $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ accounts for the 80% recovery of the original compound after the sequence of electrolyses at -1.50 , -0.25 , and -1.50 V. Some 20% of the starting material is converted to the dianion during the initial electrolysis at -1.50 V. The OH^- ions necessary for this reaction are supplied as products of the chemical reactions of $[\text{Mo}^{\text{IV}}\text{O}_2\text{Qpy}]^-$ with water and DMSO.

The initial anodic process at $+0.64$ V is totally irreversible and appears to involve the transfer of 2 mol of electrons/mol of starting material on the cyclic voltammogram time scale. However, controlled-potential coulometry at $+0.64$ V indicates that n is 1 for this process. Interrupted coulometry, where the electrolysis is periodically stopped and the concentration of unoxidized $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ is determined from peak currents of cyclic voltammograms, also yields consistent values of n equal to 1, even after only 10% of the original dimer has been oxidized.

An analysis of the products formed during the oxidation and subsequent hydrolytic reactions can account for the coulometric results. $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ is oxidized by a two-electron process at $+0.64$ V to form two $[\text{Mo}^{\text{VI}}\text{O}_2\text{Qpy}]^+$ monomers (reaction 12). The monomers undergo a hydrolytic reaction to form $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Qpy}$ and H^+ (reaction 13); the H^+ ions formed in this reaction are reduced at -0.60 V. Controlled-potential coulometry at -0.60 V after coulometry at $+0.64$ V indicates that one H^+ ion is formed for every electron transferred in the initial oxidation. Because the parent compound has a strong affinity for protons (it will abstract them from water), the protons formed in the hydrolytic reaction protonate unoxidized $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ to form $[\text{Mo}_2\text{O}_3(\text{OH})\text{Q}_2(\text{py})_2]^+$ (reaction 4) initially and then $[\text{Mo}_2\text{O}_2(\text{OH})_2\text{Q}_2(\text{py})_2]^{2+}$ (reaction 14). The latter, because of its double positive charge, is more difficult to oxidize than the neutral species and is not oxidized at potentials below $+1.0$ V. The effect of protonation of the parent compound on the oxidation potential has been confirmed by experiments in which H^+ ion is added to a solution of $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$; the anodic peak current at $+0.64$ V decreases in intensity.

Thus, the oxidation at $+0.64$ V actually is a two electron/mol of dimer process, but only half of the original dimer is oxidized because each electron transferred generates an H^+

ion which protonates the remaining starting material. Because of the diprotonated dimer is not oxidized at this potential, the overall process amounts to the transfer of 1 mol of electrons/mol of dimer



The $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Qpy}$ formed from oxidation at $+0.64$ V is reduced at -0.97 V to $\text{Mo}^{\text{V}}\text{O}_2(\text{OH})\text{Qpy}$ (reaction 15). The latter compound can then lose an OH^- group and dimerize to form the starting material again (reactions 8 and 3). The base released in the dimerization reaction neutralizes the unoxidized diprotonated dimer with the net result that most of the starting material is again available for reduction at -1.39 and -1.47 V. Some decomposition accompanies either the initial oxidation at $+0.64$ V or the reduction of the oxidation product at -0.97 V, and Q^- is released to the solution. The Q^- anion is a strong base and is hydrolyzed to form HQ and OH^- ion. The HQ formed is reduced at -1.77 V. On the longer coulometric time scale, some of the HQ that is formed attacks $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Qpy}$ to give $\text{Mo}^{\text{VI}}\text{O}_2\text{Q}_2$ (reaction 16); the electrochemical behavior of the latter species has been discussed in a previous paper.¹⁰ After controlled-potential coulometry at $+0.64$ V, both a cathodic peak at -1.15 V and a coupled anodic peak at -0.97 V are observed. These correspond to the quasi-reversible reduction of $\text{Mo}^{\text{VI}}\text{O}_2\text{Q}_2$ to $[\text{Mo}^{\text{V}}\text{O}_2\text{Q}_2]^-$.

The H^+ reduction peak at -0.60 V is greatly reduced in intensity when the oxidation at $+0.64$ V is preceded by an initial negative scan to -2.0 V. This occurs because the postchemical reactions that follow the reduction of the parent compound produce OH^- ions which subsequently neutralize the H^+ ions that are formed during the oxidation at $+0.64$ V.

The number of electrons that are transferred during the oxidation at $+0.64$ V probably could be increased by adding OH^- ions prior to the electrolysis. This would neutralize the H^+ ions as they are formed and prevent protonation of the parent compound. However, the nucleophilic substitution reaction (reaction 10) is rapid and any OH^- added to the solution prior to electrolysis will react with the starting material to form $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$. Controlled-potential coulometry at $+0.64$ V of a solution of $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ that contains 1 equiv of OH^- is the same as oxidizing 0.5 equiv of $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ at -0.08 V and 0.5 equiv of $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ at $+0.64$ V. Both oxidations ultimately yield the same product, $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Qpy}$, because the $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Q}$ that is formed in reaction 11 will add a pyridine molecule (reaction 17). However, the $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ species is oxidized without the release of any protons. Thus, during controlled-potential coulometry at $+0.64$ V all of the $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ is oxidized (0.5 mol of compound \times 2 electrons/mol = 1 mol of electrons), and half of the remaining $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ is oxidized (0.25 mol of compound \times 2 electrons/mole = 0.5 mol of electrons) before 0.5 mol of protons is released to protonate the other 0.25 mol of $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$. In the presence of 1 mol of OH^- ions and 1 mole of parent compound, 1.5 mol of electrons should be transferred. This has been confirmed by experiment. In addition, only half as much H^+ is generated during the electrolysis as in the absence of base.

$\text{Mo}^{\text{V}}\text{O}_3(\text{me})\text{Q}_2$. A self-consistent mechanism for the oxidation and reduction of this compound appears in Figure 5. Its electrochemical behavior can be divided into two categories: those reactions which occur on the cyclic voltammogram time scale and those which occur on the coulometric time scale. For the short time scale the complex is reduced at -1.16 V by a one electron/mol of dimer process (reaction

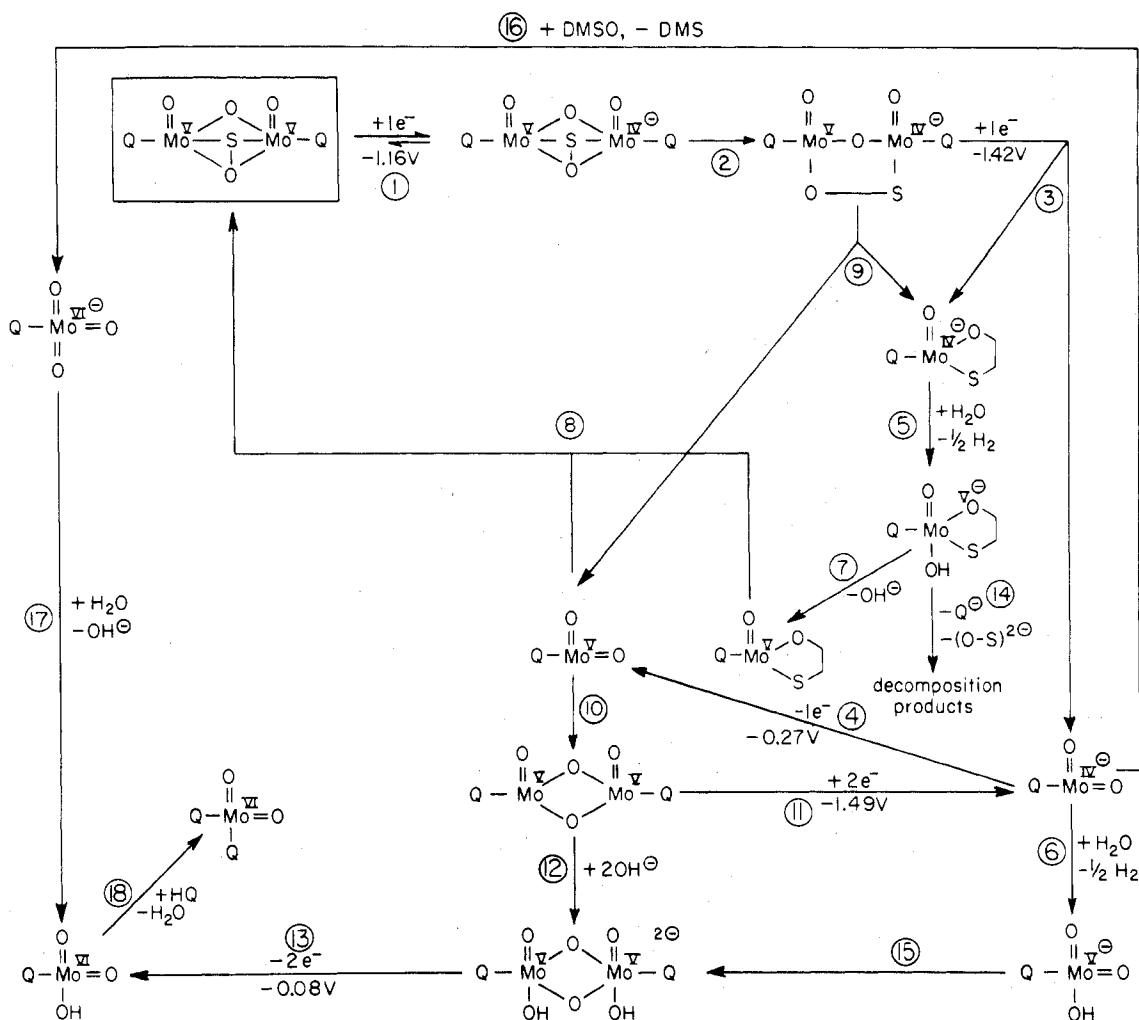


Figure 5. Redox mechanism for $\text{Mo}^{\text{V}}_2\text{O}_3(\text{me})\text{Q}_2$ in DMSO solution.

1); the number of electrons transferred is confirmed by coulometry. The product of the reduction is not oxidized at potentials as positive as +1.0 V. (There is a small anodic peak at -0.27 V which is the product of the second reduction at -1.42 V; some of the second reduction inevitably occurs because of the proximity of the two cathodic peaks.) The electron-transfer process is transiently reversible because there is a small coupled anodic peak at -1.08 V, but the one-electron reduced dimer apparently undergoes a gross structural change before being reduced further at -1.42 V. The symmetrically disposed bridging 2-mercaptoethanol dianion, upon reduction, probably rotates 90° so that the oxygen end of the ligand is coordinated exclusively to one molybdenum atom and the sulfur end to the other (reaction 2). Because the Mo(IV) oxidation state exhibits a preference for sulfur over oxygen, the structure in Figure 5 is believed to be reasonable. The asymmetric mixed oxidation state dimer anion is further reduced by a one-electron process at -1.42 V (reaction 3). The irreversibility of this electron-transfer process indicates that the dimer dissociates into two Mo(IV) anions after the second reduction. The products of the reduction are $[\text{Mo}^{\text{IV}}\text{O}(\text{me})\text{Q}]^-$ and $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$; the remainder of the inner coordination spheres probably are filled with either water or DMSO ligands.

The anodic peak at -0.27 V corresponds to the oxidation of $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$ to $\text{Mo}^{\text{V}}\text{O}_2\text{Q}$ (reaction 4). The potential is almost the same as for the oxidation of $[\text{Mo}^{\text{IV}}\text{O}_2\text{Ppy}]^-$ to $\text{Mo}^{\text{V}}\text{O}_2\text{Ppy}$ (discussed earlier, -0.26 V). Because reversal of scan direction after the oxidation peak indicates that most of the starting material has been regenerated, this again is a case

where Mo(IV) anions appear to reduce either the solvent or water (reaction 5). For example, $[\text{Mo}^{\text{IV}}\text{O}(\text{me})\text{Q}]^-$ may reduce water to form $[\text{Mo}^{\text{V}}\text{O}(\text{OH})(\text{me})\text{Q}]^-$, which in turn would release OH^- ion (reaction 7) to form $\text{Mo}^{\text{V}}\text{O}(\text{me})\text{Q}$. The latter then reacts with the $\text{Mo}^{\text{V}}\text{O}_2\text{Q}$ that is produced electrochemically in reaction 4 to form the parent compound (reaction 8). This hypothesis might be checked by performing successive coulometry at -1.42, -0.27, and then again at -1.42 V to confirm that more parent compound is regenerated than can be accounted for by the electrochemistry. However, other reactions which are slow on the cyclic voltammetric time scale but significant on the coulometric time scale completely eliminate all of the $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$ that is formed by the reduction at -1.42 V.

For the longer coulometric time scale, several different processes occur. After controlled-potential coulometry at -1.16 V, the rearranged mixed oxidation state dimer completely dissociates into $\text{Mo}^{\text{V}}\text{O}_2\text{Q}$ and $[\text{Mo}^{\text{IV}}\text{O}(\text{me})\text{Q}]^-$ (reaction 9). The $\text{Mo}^{\text{V}}\text{O}_2\text{Q}$ dimerizes to form $\text{Mo}_2\text{O}_4\text{Q}_2$ (reaction 10), which is reduced by a two-electron process at -1.49 V to form $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$. This is similar to the potential at which $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$ is reduced (-1.47 V).

Reduction of water by $[\text{Mo}^{\text{IV}}\text{O}(\text{me})\text{Q}]^-$ produces OH^- ions (reactions 5 and 7), which attack some of the $\text{Mo}_2\text{O}_4\text{Q}_2$ to displace either water or DMSO ligands in the sixth coordination site to form $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ (reaction 12). The latter compound, which also is formed in the redox scheme for $\text{Mo}_2\text{O}_4\text{Q}_2(\text{py})_2$, is oxidized by a two-electron process at -0.08 V (reaction 13) to form $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Q}$. On the longer

coulometric time scale some of the $[\text{Mo}^{\text{V}}\text{O}(\text{me})\text{Q}]^-$ (formed as a result of the reduction of water) decomposes to give both Q^- and me^{2-} ligands (reaction 14). The ligand anions hydrolyze to form HQ and H_2me and more hydroxide ions. The cathodic peaks at -1.62 and -1.77 V, after controlled-potential electrolysis at -1.16 V, correspond to the reduction of H_2me and HQ, respectively. The small anodic peaks at $+0.22$ and $+0.46$ V can be attributed to the oxidation of the decomposed Mo(V)-containing species.

During controlled-potential coulometry at -1.42 V, reactions 1–3 occur rapidly. The $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$ that is formed reduces both water and DMSO. The reaction with water produces $[\text{Mo}^{\text{V}}\text{O}_2(\text{OH})\text{Q}]^-$ (reaction 6), which then dimerizes to form $[\text{Mo}_2\text{O}_4\text{Q}_2(\text{OH})_2]^{2-}$ (reaction 15). The production of this species accounts for the anodic peak at -0.08 V (reaction 13). The anion $[\text{Mo}^{\text{IV}}\text{O}_2\text{Q}]^-$ also reacts with DMSO to produce $[\text{Mo}^{\text{VI}}\text{O}_3\text{Q}]^-$ (reaction 16), which can undergo a hydrolytic step to produce $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Q}$ (reaction 17). The solution smells of DMS after controlled-potential electrolysis at -1.42 V.

Finally, during both of the controlled-potential coulometry experiments at -1.16 and at -1.42 V, Q^- is released and HQ formed by hydrolysis. After positive scans have oxidized all of the Mo(V)-containing species to $\text{Mo}^{\text{VI}}\text{O}_2(\text{OH})\text{Q}$, the latter is attacked by HQ to form $\text{Mo}^{\text{VI}}\text{O}_2\text{Q}_2$ (reaction 18). This accounts for the subsequent cathodic peak at -1.15 V that is coupled to the small anodic peak at -0.97 V.¹⁰

From the preceding discussion and from the previously published redox mechanism for $\text{Mo}_2\text{O}_3\text{Q}_4$,¹⁰ conclusions can be made about how the degree of bridging affects the redox behavior of binuclear bridged Mo(V) compounds with the same capping ligands. Table I summarizes the redox potentials for these compounds and other relevant Mo(V) compounds. The triply bridged compound and the monooxo-bridged compound are reduced at similar potentials, while the dioxo-bridged compound is reduced at a more negative potential.

The molecular orbitals in these compounds to which electrons are either added or removed are nonbonding and of essentially pure metal d character (in the absence of any metal–ligand π bonding). The energy difference of the highest filled MO and of the lowest unfilled MO and thus the redox potential (which, other things being equal, is proportional to this energy) will be strongly influenced by the extent and type of π bonding in the complex and its redox products. Metal d to ligand π^* electron transfer is expected to make the complex more easily reduced and more difficult to oxidize, whereas ligand π or π^* to metal d transfer will have the opposite effect.²⁰

Disulfido-bridged dithiocarbamate complexes are known to be easier to reduce than their dioxo-bridged analogues.¹³ The relative ease of reduction of sulfido-bridged complexes is perhaps surprising because sulfur, with its vacant low-energy d orbitals, might be expected to participate in metal-to-ligand π bonding. The ease of reduction of disulfido-bridged Mo(V) compounds probably is due to the strong affinity of Mo(IV) for sulfur, as in the highly unreactive MoS_2 compound. The ease of reduction of the monooxo compound may not be directly due to the bridge structure but rather to the presence of an additional 8-quinolinolate ligand on each molybdenum atom.

The monooxo and triply bridged species are each initially reduced by a one electron/mol of dimer process, while the dioxo compound is reduced by a two-electron process. Dioxo-bridged compounds in general are reduced by a two-electron process while monooxo-bridged compounds are reduced by a one-electron process. This phenomenon also is observed in the chloride,²¹ riboflavin radical anion,¹² and dithiocarbamate complexes.¹³

Table I. Voltammetric Peak Potentials of Bridged Binuclear Molybdenum(V) Complexes in DMSO (0.1 M TEAP) at a Platinum Electrode (Scan Rate 0.1 V/s)

	E_{pc}, V vs. SCE	E_{pa}, V vs. SCE	$e/$ Mo_2
I. Mo–Q Complexes ^a			
$\text{Mo}_2\text{V}_2\text{O}_3(\text{me})\text{Q}_2 + e^- \rightarrow$	-1.16		1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3(\text{me})\text{Q}_2^-$			
$\text{Mo}_2\text{V}_2\text{Mo}^{\text{IV}}\text{O}_3(\text{me})\text{Q}_2^- + e^- \rightarrow$	-1.42		1
2Mo^{IV}			
$\text{Mo}_2\text{V}_2\text{O}_3\text{Q}_4 + e^- \rightarrow$	-1.21	-1.15	1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Q}_4^-$			
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3\text{Q}_4^- + e^- \rightarrow$	-1.54		1
$\text{Mo}^{\text{IV}}\text{V}_2\text{O}_3\text{Q}_4^{2-}$			
$\text{Mo}_2\text{V}_2\text{O}_3\text{Q}_4 \rightarrow$		+0.60	1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}\text{O}_3\text{Q}_4^+ + e^-$			
$\text{Mo}_2\text{V}_2\text{O}_3\text{Q}_2(\text{py})_2 + 2e^- \rightarrow$	-1.47		2
$2\text{Mo}^{\text{IV}}\text{O}_2\text{Qpy}^-$			
$\text{Mo}_2\text{V}_2\text{O}_3\text{Q}_2(\text{py})_2 \rightarrow$		+0.64	2
$2\text{Mo}^{\text{VI}}\text{O}_2\text{Qpy}^+ + 2e^-$			
II. Mo–Cl Complexes ^b			
$\text{Mo}_2\text{V}_2\text{O}_3(\text{OH})_2\text{Cl}_4^{2-} + e^- \rightarrow$	-1.00		1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_3(\text{OH})_2\text{Cl}_4^{3-}$			
$\text{Mo}_2\text{V}_2\text{O}_3\text{Cl}_4^{2-} + 2e^- \rightarrow$	-1.20		2
2Mo^{IV}			
$\text{Mo}_2\text{V}_2\text{O}_3(\text{OH})_2\text{Cl}_4^{4-} + 2e^- \rightarrow$	-1.80		2
2Mo^{IV}			
III. Mo–Rib Complexes ^c			
$\text{Mo}_2\text{V}_2\text{O}_4(\text{OH})_2\text{Rib}_2^{2-} + 2e^- \rightarrow$	-0.94	-0.67	2
$\text{Mo}^{\text{IV}}\text{V}_2\text{O}_4(\text{OH})_2\text{Rib}_2^{4-}$			
$\text{Mo}^{\text{IV}}\text{V}_2\text{O}_4(\text{OH})_2\text{Rib}_2^{4-} + 2e^- \rightarrow$	-1.45		2
$2\text{Mo}^{\text{IV}} + \text{Rib}^{2-}$			
IV. Mo–dtc Complexes ^d			
$2\text{Mo}_2\text{V}_2\text{O}_3\text{S}_2(\text{dtc})_2 + e^- \rightarrow$	-1.05 ^e	-0.95	1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_4\text{S}_4(\text{dtc})_4^-$			
$\text{Mo}_2\text{V}_2\text{O}_4(\text{dtc})_2 + 2e^- \rightarrow$	-1.23		2
$2\text{Mo}^{\text{IV}}\text{O}_2(\text{dtc})^-$	-1.49 ^e		
V. Mo–dme Complexes ^f			
$\text{Mo}_2\text{V}_2\text{O}_2\text{S}_2(\text{dme})_2^{2-} + e^- \rightarrow$	-1.85		1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_2\text{S}_2(\text{dme})_2^{3-}$			
VI. Mo–mnt Complexes ^g			
$\text{Mo}_2\text{V}_2\text{O}_2\text{S}_2(\text{mnt})_2^{2-} + e^- \rightarrow$	-1.46		1
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_2\text{S}_2(\text{mnt})_2^{3-}$	-1.56 ^e		
$\text{Mo}^{\text{V}}\text{Mo}^{\text{IV}}\text{O}_2\text{S}_2(\text{mnt})_2^{3-} + e^- \rightarrow$	-1.78		1
2Mo^{IV}	-1.71 ^e		

^a Q = 8-quinolinolate anion; me = 2-mercaptoethanol dianion; py = pyridine. ^b Reference 21. ^c Reference 12; Rib = riboflavin anion radical. ^d Reference 13; dtc = *N,N*-diethyldithiocarbamate. ^e DMF solution. ^f Reference 22; dme = 1,2-dimercaptoethane dianion. ^g Reference 23; mnt = 2,2-dicyanoethylene-1,1-dithiolate anion.

Oxo-bridged dimers which can fragment symmetrically into two identical monomers upon a two-electron reduction appear to be reduced by a two-electron process, while oxo-bridged compounds which cannot fragment symmetrically upon reduction are reduced initially by a one-electron process. The disulfido-bridged compounds formed with dithiocarbamate,¹³ 1,2-dimercaptoethanate,²² and 2,2-dicyanoethylene-1,1-dithiolate,²³ however, are reduced by a one-electron process. The ability of the disulfido-bridged compounds to undergo initial one-electron reductions instead of two-electron reductions is perhaps related to the ability of the bridging sulfur atoms to help delocalize the negative charge to the other Mo atom and its associated ligands.

The monooxo and triply bridged 8-quinolinolate complexes also form more stable reduced dimers than does the dioxo complex, which falls apart immediately upon reduction. The tendency of reduced dioxo-bridged compounds to fragment at once also is observed for the chloride²¹ and dithiocarbamate¹² complexes. The riboflavin radical anion complex

is an exception;¹² it forms a stable doubly reduced dimer.

A similar process may occur for oxidations of these complexes as well, although the number of compounds which can be oxidized within the potential window of DMSO is smaller. Of the three 8-quinolinolate capped compounds, the mono-oxo-bridged species is slightly more easily oxidized than is the dioxo-bridged species. The triply bridged compound is not oxidized at these potentials. The presence of sulfur in the bridging linkage or the presence of the additional bridging group makes the compound more difficult to oxidize as well as easier to reduce. Again, the mono-oxo-bridged complex (which cannot fragment symmetrically) undergoes a one-electron oxidation, and the resulting mixed oxidation state dimer has a transient lifetime. The dioxo-bridged species is oxidized by a two-electron process and immediately falls apart.

The Mo(IV) monomer anions that are formed after fragmentation of the reduced Mo(V) dimers in all three of the 8-quinolinolate complexes are potent reducing agents and are capable of reducing H₂O to H₂ and OH⁻. This is interesting because the nitrogenase enzyme generates H₂ in the absence of reducible substrate. Such behavior has also been observed recently in what is believed to be a monomeric molybdenum(IV)-cysteine complex.²⁴

The nature of the capping ligands also affects the redox potentials and the stability of oxidized and reduced species. A comparison of the changes in redox behavior as a function of capping ligand is best made on the dioxo-bridged compounds for which there are data on compounds with four different caps: chloride,²¹ 8-quinolinolate, dithiocarbamate,¹³ and riboflavin radical anion.¹² As the reduction potentials are strongly dependent on the charge of the molecule and as three of these molecules are negatively charged, the reduction potentials must be corrected for charge differences. An empirical rule of thumb is that for each increase of one negative charge, the reduction potential is shifted negatively by 0.3–0.4 V. Thus a compound like Mo₂O₄(OH)₂(Rib)₂²⁻ which is reduced at -0.94 V would be reduced at approximately -0.25 V if it were not for its double negative charge. Referring again to Table I, the riboflavin radical anion (Rib) complex is the most easily reduced, followed by the chloride complex, the dithiocarbamate complex, and the 8-quinolinolate complex. The relative ease with which the riboflavin radical anion compound is reduced can be attributed to the ligand's ability to participate in ligand π* to metal d π bonding. This is in sharp contrast to the 8-quinolinolate complex where the ligand has vacant π* orbitals and cannot participate in this type of π bonding. Comparison of the reduction potentials for the neutral quinolinolate and dithiocarbamate complexes indicates that sulfur-containing capping ligands make the compounds easier to reduce and more difficult to oxidize.

The riboflavin radical anion also produces the most stable reduced dimer of the dioxo-bridged compounds.¹² This probably is due to presence of the low-energy ligand π* orbitals which allow significant negative charge delocalization.

The electrochemical data indicate that there are several factors which contribute to the stability of mixed oxidation state dimers. Dioxo-bridged compounds appear always to be oxidized and reduced by two-electron processes; hence, the formation of mixed oxidation state compounds is precluded. This leaves mono-oxo-bridged, triply bridged, and disulfido-bridged compounds as possible routes to stabilized mixed oxidation state compounds. Although mixed oxidation state

dimers have not as yet been isolated, the disulfido-bridged compounds have the longest transient lifetime. Because the only disulfido-bridged compounds that have been studied also have sulfur-containing capping ligands, the importance of bridging sulfur alone on the stability of mixed oxidation state dimers cannot be determined. Although ligands with extensive π systems (such as the riboflavin radical anion) can stabilize reduced molybdenum dimers, such ligands are not mandatory for the stabilization of mixed oxidation state dimers. The longest lived Mo(V)-Mo(IV) dimer that has been studied to date, Mo₂O₂S₂(dme)₂²⁻ (dme is the dianion of 1,2-dimercaptoethane),²² contains aliphatic sulfur capping ligands.

Finally, if biological molybdenum is dimeric in the native enzymes, and if it remains dimeric in the presence of substrate, the Mo(V) ESR signals observed in four of the enzymes in the presence of substrate must be due to mixed oxidation state dimers. On the basis of our studies on the redox behavior of bridged binuclear molybdenum systems we conclude that, given these assumptions, biological molybdenum is not dioxo-bridged in the native enzymes because dioxo-bridged species are not capable of undergoing one-electron oxidations or reductions.

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Registry No. Mo₂O₄Q₂(py)₂, 30052-16-5; Mo₂O₃(me)Q₂, 59448-73-6; Mo^VMo^{IV}O₃(me)Q₂⁻, 59574-38-8; Mo^VO₃Q₄, 17979-39-4; Mo^VMo^{IV}O₃Q₄⁻, 59492-68-1; Mo^{IV}O₃Q₄²⁻, 59448-74-7; Mo^VMo^{VI}O₃Q₄⁺, 59492-69-2; Mo^{IV}O₂Qpy⁻, 59448-75-8; Mo^{VI}O₂Qpy⁺, 59448-76-9; (NH₄)₂MoOCl₅, 17927-44-5; pyridine, 110-86-1.

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