Molybdenum(VI)–dioxo complexes with sterically bulky thiocarboxylate ligands. Reactions with aliphatic thiols and electrochemical properties

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(Received April 2, 1991)

Abstract

Under acid conditions, the reaction of $(Bu^n_4N)_2[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]$ with aliphatic thiols yields the monomeric $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ as unique complex product. The experimental pseudo-first order rate constant with respect to the Mo(VI) complex was found to be $K = 6.1 \times 10^{-5}$ s^{-1}. At neutral pH, however, an unstable Mo(IV) species was formed which was also electrochemically detected in a reversible Mo(V,IV) couple. $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ appears to be obtained by the reaction of $[Mo^{IV}O(O_2CC(S)Ph_2)_2]^{2-}$ with unreacted $[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]^{2-}$. Steric features on the ligand (gem-diphenyl groups) explain that the latter reaction does not lead to the expected formation of μ-oxo Mo(V) dimers. $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ undergoes a one-electron reversible reduction on the cyclic voltammogram time scale, being also oxidized by nitrate ions to the starting Mo(VI) complex. The relation of these results to enzymatic systems is briefly discussed.

Introduction

Thiols may be considered physiological reductants acting as endogenous electron donors in reductase reactions of molybdenum hydroxylases [1] which catalyze two-electron oxidation of purines, aldehydes, sulfite and formiate in animals and microorganisms. Reactions between thiols and Mo(VI) complexes are therefore of interest as possible models for such redox process in the enzymes. While it is well known that thiols are readily oxidized to the corresponding disulfide, only dioxo–Mo(VI) complexes containing sulfur-donor atom ligands have been found to show an appreciable reactivity. Namely, only the well-characterized $[MoO_2(S_2CNEt_2)_2]$ [2] and $[MoO_2(LNS_2)]$ (L = 2,6-bis(2,2-diphenyl-2-mercapto-ethyl)pyridine (−2)) [3] complexes have been reported to be cleanly reduced at an appreciable rate by arenethiols whose more acidic character has been assumed to promote the protonation and loss of an oxo ligand to give a MoO(IV) complex. Moreover, when the reaction is carried out in the presence of an oxygen donor such as Me_2SO [3], the Mo(IV) species is reoxidized to the original Mo(VI) complex. The system then operates catalytically but the overall reaction is slow because of the sluggish rate of the MoO_2(VI) complex reduction. Neither reactions with aliphatic thiols nor obtention of stable monomeric Mo(V) complex have been previously reported for these systems.

We have previously reported [4] the preparation and X-ray characterization of the $[MoO_2(O_2CC(S)Ph_2)_2]^{2-}$ complex (**1**), containing the sterically hindered 2,2-diphenyl-2-mercaptoacetic acid (TBA). This ligand appears to be particularly interesting as it is closely related to the thioglycolic acid [5] which seems to form a 1:2 Mo(V)–thioglycolic complex whose EPR parameters ($\langle g \rangle = 1.978$; $\langle A \rangle = 34$ G) have previously been related to several oxomolybdoenzymes. In addition, our recent investigations [6] have demonstrated that the reaction between complex **1** and its own free ligand (TBA) yields dithiodibencilic acid and the monomeric $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ complex (**2**) whose EPR spectrum ($\langle g \rangle = 1.978$ and $\langle A \rangle 38$ G) is completely similar to the above mentioned Mo(V)–thioglycolic species.

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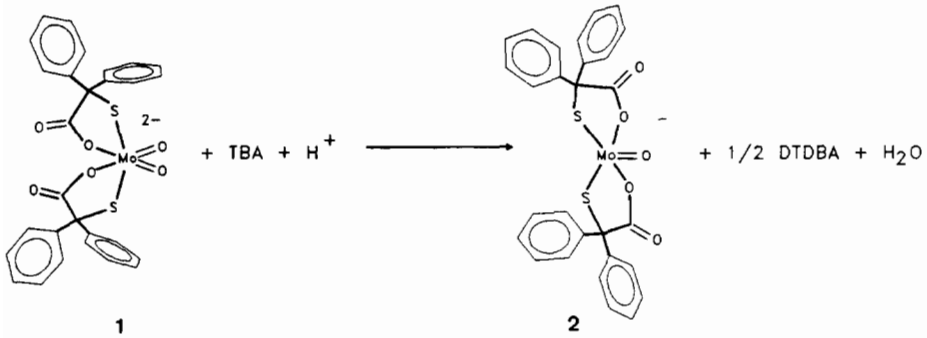

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In excess of TBA, complex **2** is stable exhibiting an UV–Vis spectrum with bands at 312, 400 and 505 nm. Its isolation as the tetra-n-butylammonium salt, affords the first X-ray characterized example of a mononuclear five-coordinated Mo(V) species possessing both coordinated thiolate and carboxylate groups. The structure reveals a square pyramidal arrangement of the ligands with both thiolate and carboxylate groups mutually *cis* on the equatorial plane. The oxo group is in an apical site of the pyramid having a *trans* bonding position empty.

In this investigation, the reactivity of complex **1** has been extended to other simple aliphatic thiols which do not form stable complexes with Mo(VI). The pH-dependence of the reaction and the electrochemical properties for complexes **1** and **2** are also reported.

Experimental

Materials and methods

All reactions were performed under an atmosphere of pure argon with use of dried and deoxygenated solvents. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer with chemical shifts referenced to external TMS. The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer using quartz cells. Cyclic voltammetric measurements were carried out by using a HQ-101 battery-powered potentiostat, a Newtronics 200P triangular wave generator and a Rinken-Denshi F-35 x-y recorder. Potentials were measured versus a methanolic satured calomel reference electrode ($E = 0.00$ V versus aqueous SCE) using 0.1 M tetrabutylammonium hexafluorophosphate solutions as supporting electrolyte.

Preparation of Compounds

$[(n\text{-}C_4H_9)_4N]_2[MoO_2(O_2CC(S)(C_6H_5)_2)_2]$

A solution of $(C_6H_5)_2C(SH)CO_2H$, TBA (0.98 g, 4 mmol) in methanol (10 ml) was slowly added to a stirred solution of $Na_2MoO_4 \cdot 2H_2O$ (0.48 g, 2 mmol) in methanol–water mixture (20–7 ml). To the resulting yellow solution, 1.29 g (4 mmol) of $(n\text{-}C_4H_9)_4NBr$ was added. On cooling to 5 °C, yellow crystals grew from the solution in 24–48 h, yield 72%. *Anal.* Calc. for $C_{60}H_{92}N_2O_6S_2Mo$: C, 65.7; H, 8.4; S, 5.8; N, 2.5. Found: C, 65.9; H, 8.3; S, 5.7; N, 2.3%. IR (KBr pellets, cm^{-1}): 870, 905 (Mo=O).

$[(n\text{-}C_4H_9)_4N][MoO(O_2CC(S)(C_6H_5)_2)_2]$

In a reaction vessel previously deoxygenated, 0.49 g of TBA, 0.16 g of $(n\text{-}C_4H_9)_4NBr$ and 0.12 g of $Na_2MoO_4 \cdot 2H_2O$ were placed. Over these, 6 ml of methanol (previously deoxygenated by bubbling argon 30 min in an ultrasonic bath) were added under argon stream which was maintained for an additional 15 min and then the vessel was flame-sealed. Cooling the solution overnight gave 0.1 g (24%) of green air-sensitive crystals. *Anal.* Calc. for $C_{48}H_{56}NO_5S_2Mo$: C, 63.0; H, 6.7; S, 7.6: N, 1.6. Found: C, 63.5; H, 6.8; S, 7.8; N, 1.5%. IR (KBr pellets, cm^{-1}): 975 (Mo=O). EPR (MeOH): $\langle g \rangle = 1.978$, $A = 38$ G.

Results and discussion

Reactivity

The reaction between the tetrabutylammonium salt of **1** and an excess of n-butanethiol resulted in the formation of disulfide as shown by ^1H and ^{13}C NMR spectroscopy. With 50 mM complex solution and 2 equiv. of butanethiol, the reaction affords one equiv./Mo of $[CH_3(CH_2)_3S]_2$ in 24 h. Although no evidence was found for a Mo complex product from a visible color or absorption band, the above stoichiometric ratio is consistent with the immediate formation of the Mo(IV) complex $[MoO(O_2CC(S)Ph_2)_2]^{2-}$ which seems to be unstable and decomposes giving unidentified species lacking Mo–thiolate ligation.

$$[MoO_2(O_2CC(S)Ph_2)_2]^{2-} + 2HS(CH_2)_3CH_3 \longrightarrow [MoO(O_2CC(S)Ph_2)_2]^{2-} + (S(CH_2)_3CH_3)_2 + H_2O \quad (2)$$

A similar degradation induced by thiol in excess has been also reported to produce gradual decaying in the absorption spectrum of the $Mo^{IV}O(LNS)$ complex [3].

The present result is in strong contrast to that which has been yielded by using TBA as substrate instead of butanethiol. In fact, as previously reported [6], the reaction between complex **1** and an excess of TBA does not lead to the obtention of Mo(IV) species but to the monomeric Mo(V) complex $[MoO(O_2CC(S)Ph_2)_2]^-$ (**2**).

It is not at all evident why complex **1** reacts in such a way with TBA while with butanethiol it does not, but there is no doubt that protons from the carboxylic group of TBA stabilize the Mo(VI)/Mo(V) conversion. To demonstrate this supposition the spectrophotometric course of the reaction with butanethiol (RSH/Mo = 8), in the presence of benzoic acid ($C_6H_5CO_2H$/Mo = 4) as a proton source, was recorded (Fig. 1). As the spectrum of the Mo(VI) complex, with a maximum at 370 nm, diminishes with time, tight isosbestic points at 455 and 345 nm are detected, and the final spectrum is identical with that, and demonstrates quantitative formation, of $[MoO(O_2CC(S)Ph_2)_2]^-$. In a parallel experiment, no reaction was observed between benzoic acid and butanethiol at room temperature for at least 24 h.

The amount of butanethiol reacting with a known amount of complex **1** at acid pH was also determined by ^1H NMR spectroscopy. Compared to the result obtained at neutral pH, one-half of the butanethiol reactant is now consumed and so stoichiometric data are consistent with the proposed stoichiometries for reactions (1) and (2).

By following the disappearance of **1** at 370 nm or the appearance of **2** at 505 nm, the spectrophotometric data on Fig. 1 permit also the kinetic study of the reaction between complex **1** and butanethiol. For both wavelengths we obtained lineal logarithmic variations of the absorbance versus time to $\geq 90\%$ reaction, from which a pseudo-first order constant with respect to complex **1** of $K_{obs} = 6.1 \times 10^{-5}$ s^{-1}, $T = 25$ °C, was determined by a least-squares analysis (Fig.2). The foregoing result demonstrates that this reaction is much faster than that reported between the $MoO_2(LNS_2)$ complex (15 mM) and PhSH (2.5 equiv.), which was only 63% complete after 62 h [3].

Lastly, considering that complex **1** and **2** have identical stoichiometry except for the additional oxo ligand in **1**, an oxidation of **2**, involving the removal of an oxygen atom from a substrate, would interconvert these complexes an produce the catalytic oxidation of the thiol. A substrate of biological interest is the nitrate ions. Reductions of nitrate by hexacoordinated Mo(V) complexes with complicated kinetics have been previously reported [7]. As recognized earlier [8], efficient electron transfer requires binding to an oxo–molybdenum(V) species, with subsequent electron transfer, loss of NO_2 and disproportion of the latter to yield NO_2^- and NO_3^-.

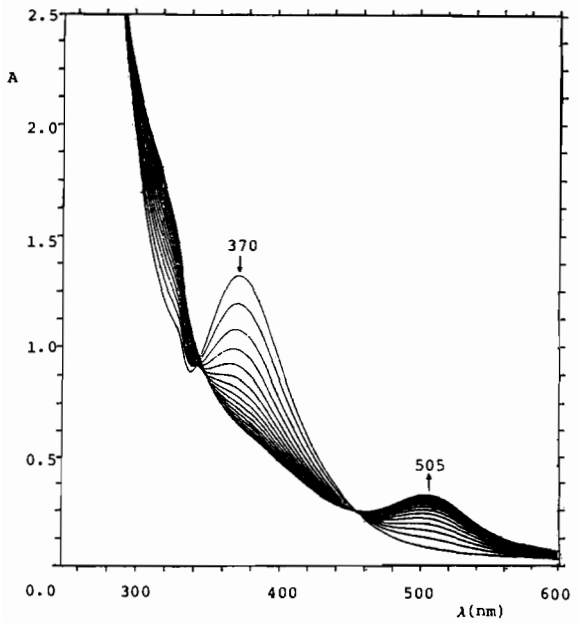

Fig. 1. Spectral changes in the reaction of 0.23 mM **1**, 8 equiv. of C_4H_9SH and 4 equiv. of benzoic acid in methanol solution at 25 °C. Spectra were recorded every hour at a scan rate of 120 nm min^{-1}.

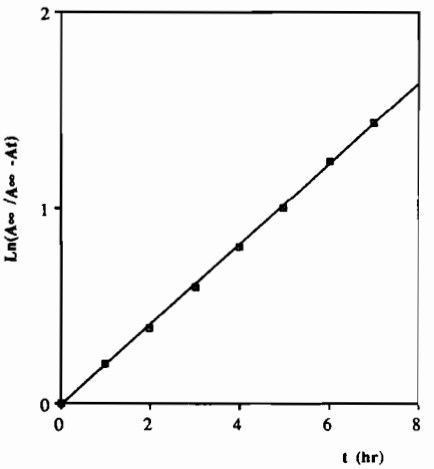

Fig. 2. Plot of Ln $(A_\infty/A_\infty - A_t)$ vs. time at 25 °C for the spectral changes registred in Fig. 1 at 505 nm. The solid line is a least-squares fit to the points.

Reduction of nitrate by oxo–molybdenum(IV) complexes avoids the NO_2 intermediate since a two-electron transfer from Mo(IV) to NO_3^- has been invoked to occur [9]. In both of these cases it has been stressed that nitrate must be bound in a position *cis* to the oxo ligand for electron transfer to occur and therefore, in some cases, after nitrate binding and before electron transfer, isomerization to the *cis* configuration may be required.

Just because conversion of complex **1** to **2** gives rises to a rearrangement of the thiocarboxylate ligands and leaves a vacant position *trans* to the remaining terminal oxygen group (reaction (1)), the reaction between complex **2** and nitrate ions can be supposed to be rapid as well as favorable. In fact, spectrophotometric examination of the reaction between complex **2** and nitrate ions showed that the dioxo Mo(VI) complex was quickly formed. However, the final solution was found to undergo a rapid reaction of degradation, leading initially to a pale yellow solution followed by a complete fade. Because the Mo(VI,V) complexes were destroyed, nitrite or nitrogen dioxide identification was not attempted in the final solution.

A similar degradation of the $MoO(LNS_2)$ complex by nitrite ions has been observed [10] but, for this system, addition of sulfamic acid avoids the ulterior bleaching reactions of Mo(IV,VI) complexes by scavenging nitrite ions [9]. For the present system detailed studies directed toward the development of such catalytic processes are under way and will be reported later.

Reaction mechanism

While the reduction of complex **1** to a Mo(IV) species in the reaction with a thiol is not surprising, the ability to form a stable monomeric Mo(V)–oxo complex is unexpected. Indeed, no complexes exhibiting such a behaviour have been previously reported in reactions with thiols or tertiary organophosphines which are so considered to be two-electron processes [11]. Therefore, it appears from our results that $[MoO(O_2CC(S)Ph_2)_2]^-$ is produced through the reaction between the nascent Mo(IV) species and unreacted $[MoO_2(O_2CC(S)Ph_2)_2]^{2-}$, according to eqn. (3), which would also explain why protons stabilize the Mo(VI)/Mo(V) conversion.

$$[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]^{2-} + [Mo^{IV}O(O_2CC(S)Ph_2)_2]^{2-} + 2H^+ \longrightarrow 2[Mo^{V}O(O_2CC(S)Ph_2)_2]^- + H_2O \quad (3)$$

It is presently accepted, as a general feature, that reduction of Mo(VI) dioxo complexes is accompanied, unless it is sterically prevented, by the reaction between Mo(VI) and Mo(IV) oxo complexes but the product is always the oxo-bridged Mo(V) dimer [11]. The only exception to this generalization is supported by the electrochemical results reported for $Mo^{VI}O_2L$ complexes (L = tetradentate amino thiol ligands) [12] which can be reduced to stable monomeric $Mo^{V}OL^-$ species. The formation of such species bode well for our reactivity scheme since this unusual behaviour has been attributed to deprotonation of the amino groups with elimination of H_2O upon reduction. Further, it was observed that when MoO_2LH_2 is reduced coulometrically to the IV oxidation state and an equivalent amount of MoO_2LH_2 is added, $MoOL^-$ was rapidly formed in high yield, according to eqn. (4), which parallels eqn. (3) we propose here.

$$MoO_2(LH_2) + MoO(IV) \longrightarrow 2MoOL^- + H_2O \quad (4)$$

A conclusion that can be drawn from all these results is that oxo bridging formation may be avoided as a result of steric factors, gem-diphenyl groups on TBA ligand, or geometrical restraints as in the case of aminothiol ligands. The imposition of a planar structure on the coordinated ligand when trigonal nitrogen replaces tetrahedral nitrogen upon deprotonation prevents oxo bridging formation through a *cis* position, while bridging through a *trans* position is highly unfavorable because of *trans* effect of the oxo group [12b]. It should be also noted, however, that although these geometrical restraints prevent dimerization of the $Mo^{V}O$–aminothiol complexes they have been also assumed to obstruct the reaction with similar substrates like nitrate ions which requires bonding of nitrate at *cis* position for electron transfer to occur [12].

Finally, a further comment is necessary concerning the possibility that an intermediate Mo(IV) species can be formed in thiol oxidation reaction produced by complex **1**. This consideration is that the appearance of isosbestic points in the spectral traces obtained under acid conditions (Fig. 1) does not rule out the possibility that other short-lived absorbing species may also be present at a rapidly equilibrated concentration [13].

Electrochemistry

The above scheme of reactivity led us to examine the electrochemistry of complexes **1** and **2**. Dioxo Mo(VI) complexes appear to be electrochemically reducible to the IV oxidation state but not, in general, to the V state while monomeric Mo(V) oxo complexes that have been studied are not electrochemically oxidable to the VI state.

The cyclic voltammogram of the n-tetrabutylammonium salt of complex **1** in DMF does not exhibit a detectable reduction peak in the +0.5 to –1.5 V

range, but its ammonium salt showed a reduction peak at -1.05 V as well as a poorly marked oxidation peak at -0.67 V, coupled to the latter, when scanned in the anodic direction (Fig. 3). From the observed differences between these two salts it can be inferred that coupled proton/electron transfer occurs in this reduction process. The large peak current ($I_p = 950$ A cm^2 mol^{-1} V$^{-1/2}$ s$^{1/2}$) appears to involve the transfer of 2 mol of electrons/Mo and, therefore, the reduction product was presumed to be $[MoO(O_2CC(S)Ph_2)_2]^{2-}$. The ultimate loss of an oxo group is evidenced by the irreversible nature of the cyclic voltammogram.

$$[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]^{2-} + 2H^+ + 2e^- \longrightarrow [Mo^{IV}O(O_2CC(S)Ph_2)_2]^{2-} + H_2O \quad (5)$$

The Mo(IV) complex formed is subsequently reoxidized at -0.67 V to give the $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ species (*vide infra*).

On the other hand, the cyclic voltammograms of complex **2** were found to be reversible so indicating simple electron transfer without ligand modification. The formal potential of reduction is -0.480 V in methanol and -0.650 V in DMF, versus SCE (Fig. 3). Peak potential difference (65–70 mV) and current function (400 A cm^2 mol^{-1} V$^{-1/2}$ s$^{1/2}$) indicate that one electron transfer reaction occurs in this reversible process. Scan to higher potentials revealed a further irreversible oxidation wave at $E_{pc} = +0.400$ V which appears to be due to the formation of an unstable Mo(VI) complex.

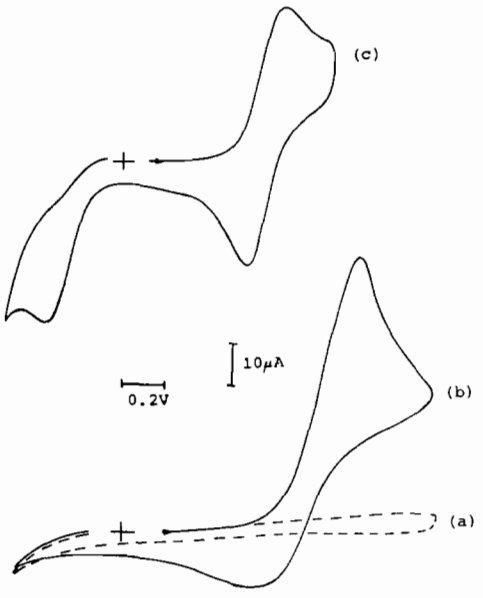

Fig. 3. Cyclic voltammogram for 1.2 mM $[(n\text{-}C_4H_9)_4N]_2[MoO_2(O_2CC(S)(C_6H_5)_2)_2]$ (a), $[H_4N]_2[MoO_2(O_2CC(S)(C_6H_5)_2)_2]$ (b) and $[(n\text{-}C_4H_9)_4N][MoO(O_2CC(S)(C_6H_5)_2)_2]$ (c) in 0.1 M $(Bu_4N)(PF_6)$/DMF. Platinum working electrode. Scan rate 0.15 V s^{-1}.

The potential of this reversible couple provides an opportunity to investigate the effect of ligand variations on the reduction potentials of mononuclear oxomolybdenum(V) centers and so it must be contrasted with those found for other Mo(V)/Mo(IV) couples such as $MoO(SR)_4^{1-/2-}$ (R = Ph, $E_{1/2} = -0.75$ V in MeCN) [14] and $MoO(mae)^{1-/2-}$ ($E_{1/2} = -0.96$ V in DMF) [12] which contain S_4 and N_2S_2 ligand sets, respectively. The latter complex has not been structurally characterized, the former showing, however, a structure completely comparable to that obtained for complex **2**, being the difference that it possesses four thiolate instead of two and two carboxylate groups on the basal plane.

There is a general agreement that the Mo=O bonding so dominates the ligand field at the molybdenum that the $4d^1$ electron is located in an orbital which is in the plane (*xy*) perpendicular to the oxo group. This half-occupied orbital (HOMO) is considered to accept an electron in electrochemical reduction. Increasing its $d\pi$–$p\pi$ interaction with ligands that lie in the *xy* plane will raise the energy of the HOMO, which is $d\pi$–$p\pi$ antibonding, and makes the complex more difficult to reduce [15]. The reduction potential of complexes presented here indicate that substitution of two thiolate or amido groups by a weaker π-bonding donor oxygen atom of carboxylate groups [16] leads to a change in the potential over 0.2 V so facilitating its reduction to a IV oxidation state.

Conclusions

The $[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]^{2-}$ complex is reduced by aliphatic thiols to the stable monomeric Mo(V) complex $[Mo^{V}O(O_2CC(S)Ph_2)_2]^-$ in an acidic medium, while at neutral pH, the stoichiometry of the reaction indicates that an unstable Mo(IV) is being formed. The former reaction is quantitative and much faster than those reported for other $Mo^{VI}O_2$ complexes which are always reduced to $Mo^{IV}O$ species.

The pH dependence observed for this reaction is supported by eqn. (3) which, with no need of protons, has always been related to the formation of μ-oxo Mo(V) dimers in oxo-transfer reactions.

The claim that MoO_2-tetradentate aminothiols complexes can be electrolytically reduced to $Mo^{V}OL^-$ species is the only reported precedent to the above equation. For this last system, the $Mo^{V}OL^-$ stability appears to be a consequence of deprotonation of amino groups and the imposition of a planar structure on the ligand when trigonal nitrogen replaces tetrahedral nitrogen. However, the present results clearly show that this stabilization may be also attained by using sterically bulky ligands and lowering

the solution pH. Under these conditions, the reactivity of the $[Mo^{VI}O_2(O_2CC(S)Ph_2)_2]^{2-}$ complex in its reaction with thiols is unique and may be closely related to that observed for certain molybdo-enzymes. In fact, an overall chemical reaction cycle for oxo–molybdenum centers of such enzymes involves two-electron irreversible reduction of the Mo(VI) center to Mo(IV), followed by two one-electron reoxidations [17]. The EPR active site concentration of Mo(V) obtained upon reduction of the enzyme with substrate or dithionite is in equilibrium with both Mo(VI) and Mo(IV) concentration and it is also pH dependent [18].

Coupled proton/electron transfer occurs in all electrochemical reactions of these complexes, a mechanism proposed for molybdo-enzymes [19]. The MoO_2(VI)/MoO(IV) couple is clearly irreversible while the MoO(V)/MoO(IV) couple is electrochemically reversible. The occurrence of this reversible couple in the electrochemical results of the Mo(V)–oxo complex is indicative of the stability of the reduced Mo(IV)–oxo species at the time scale used. Thus, monomeric oxomolybdenum complexes in all biological relevant oxidation states of molybdenum are accessible which is an important criterion for modeling a molybdo-enzyme.

Acknowledgement

This research was supported by CICYT Grant No. PB89-0417.

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