Inorganica Chimica Acta, 204 (1993) 73–78

Mononuclear mixed oxosulfidomolybdate(VI) complexes with aminodicarboxylic ligands. Synthesis and spectroscopic characterization by multinulcear magnetic resonance spectroscopy

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(Received May 25, 1992; revised September 11, 1992)

Abstract

Addition of B_2S_3 to a methanolic solution of the $Mo^{VI}O_3L^{2-}$ complex (L = *N,N*-bis(ethanoic acid)-1-amino-2-methylthio-ethane) results in the formation of two different monomeric oxosulfidomolybdate(VI) complexes, $[MoO_2SL]^{2-}$ and $[MoOS_2L]^{2-}$ as indicated by ^1H, ^{13}C, ^{17}O and ^{95}Mo NMR spectroscopy and by the reaction of these two sulfurated species with triphenylphosphine. The temperature dependences of the ^1H NMR spectra indicate exchange processes for both sulfido complexes. Their redox properties are discussed and contrasted with those observed for the parent *fac*-trioxo molybdenum(VI) complex. The primary synthetic route to mixed oxo-sulfido $[MoO_{3-n}S_nL]^{2-}$ complexes described here can be extended to other aminodicarboxylic ligands like iminodiacetic acid.

Introduction

Mononuclear mixed oxo-sulfido Mo(VI) complexes have been subjects of intense spectroscopic studies since the discovery of an Mo(VI) atom with both terminal oxo and terminal sulfido groups in a number of oxomolybdoenzymes [1]. However, only a restricted number and variety of such complexes have been characterized to date [2, 3]. These include the oxothiomolybdate $(MoO_{4-x}S_x)^{2-}$ ($x = 1$–3) and the $MoOS(ONR_2)_2$ and $MoS_2(ONR_2)_2$ ($R = C_2H_5$, C_7H_7) complexes which were prepared by the reaction of H_2S, B_2S_3 or $(Me_3Si)_2S$ with precursor oxo complexes. The progressive conversion of Mo=O to Mo=S results in a lowering of the reduction potential [4], a deshielding of the molybdenum nucleus [5] and a higher fluxional character [3b].

To date, however, it has not been possible to assess the effect of one or two sulfido ligands on the spectroscopic properties of MoO_3L^{2-} complexes because no complex containing such a mixed oxo-sulfido $MoO_{3-n}S_n$ unit has been synthesized. We herein report that B_2S_3 can also be used as a thiation reagent of monomeric trioxomolybdenum(VI) complexes containing a ligand coordinated by a single tridentate iminodiacetate group.

Experimental

Synthesis of N,N-bis(ethanoic acid)-1-amino-2-methylthio-ethane (TIDA)

This synthesis was adapted from the method of Morris *et al.* [8]. A total of 22.1 g (0.20 mol) 2-chloroethylmethylsulfide in 100 ml 50% aqueous methanol was added slowly to a solution containing 26.6 g (0.20 mol) iminodiacetic acid and 21.2 g (0.53 mol) sodium hydroxide in 300 ml 50% aqueous methanol maintained at 60 °C. When half of the above addition had taken place an additional 13.2 g (0.33 mol) sodium hydroxide were added to the mixture. After stirring overnight the methanol was removed *in vacuo* and the remaining aqueous phase acidified to pH 2.5 with concentrated HCl. This last acidification yielded the desired free acid of the ligand as a white solid, which was successively washed with water, methanol and ether and then allowed to air dry (41% yield). ^1H NMR in D_2O: δ, 2.18 (s, 3H, CH_3S–), 2.92 (t, 2H, SCH_2) 3.58 (t, 2H, CH_2N), 4.20 (s, 4H, CH_2CO) ppm.

Synthesis of the complexes

$Na_2[MoO_3(TIDA)]$ (**1**) was synthesized from the reaction of $Na_2MoO_4 \cdot 2H_2O$ (1.21 g, 5 mmol) with the amino acid TIDA (1.04 g, 5 mmol) in 20 ml of methanol. A white solid was obtained on cooling the mixture overnight at 4 °C. The product was filtered off and recrystallized in methanol/acetone (2:1). *Anal.* Calc. for

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$C_7H_{11}MoNNa_2O_7S$: C, 21.2; H, 2.8; N, 3.5; S, 8.1. Found: C, 21.1; H, 2.9; N, 3.4; S, 8.0%.

The complex with iminodiacetic acid, $Na_2[MoO_3(IDA)]\cdot 2H_2O$ (**2**) was synthesized as described by Butcher *et al.* [9]. *Anal.* Calc. for $C_4H_9MoNNa_2O_9$: C, 13.4; H, 2.5; N, 3.9. Found: C, 13.3; H, 2.7; N, 3.7%.

The oxo-sulfido complexes were prepared as follows. 1.186 g (3 mmol) of **1** were dissolved in 30 ml of methanol under an argon stream. To this solution, 0.236 g (6 mmol) of B_2S_3 was slowly added and the mixture stirred for 18–20 h under argon, yielding a brown suspension in a deep red solution. The reaction mixture was filtered and the solution concentrated to precipitate a dark red microcrystalline solid which was recrystallized from MeOH (60% yield). Sulfido derivatives of **2** were prepared in a similar way.

Physical measurements

Multinuclear NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 50.3 (^{13}C), 81.01 (^{31}P), 13.04 (^{95}Mo) and 27.13 (^{17}O) MHz, using as internal reference the solvent signal and as external reference Na_2MoO_4, H_3PO_4 or dioxane. Cyclic voltammetric measurements were carried out using a HQ-101 battery-powdered potentiostat, a Newstronics 200P triangular wave generator and a Rinken-Denshi F-35 x-y recorder. 0.20 M acetic/acetate buffer and 0.5 M KCl as supporting electrolyte were used in electrochemical studies. These were carried out at 25 °C in MeOH–water (30%) previously degasified. A Metrohm AGCH9100 hanging mercury drop electrode (HMDE, $A = 0.014$ cm^2) was employed as a working electrode; a platinum-wire auxiliary electrode and the saturated calomel reference electrode (SCE) completed the standard three-electrode cell.

Results and discussion

Ligands which contain a single iminodiacetic group form stable MoO_3L^{2-} complexes with molybdate ions, as judged by virtually complete conversion of unbound to bound NMR ligand resonances in solutions of 1:1 composition. Their formation equilibria from molybdate and deprotonated ligand can be represented by the following general equilibrium

$$MoO_4^{2-} + L^{2-} + 2H^+ \rightleftharpoons MoO_3L^{2-} + H_2O$$

N,N-Bis(ethanoic acid)-1-amino-2-methylthio-ethane (TIDA) behaves similarly, acting as a tridentate ligand. Unequivocal evidence for the involvement of the nitrogen atom and both carboxylate groups in complexation, without participation of the thioether sulfur atom, arises from multinuclear NMR spectroscopy (see below).

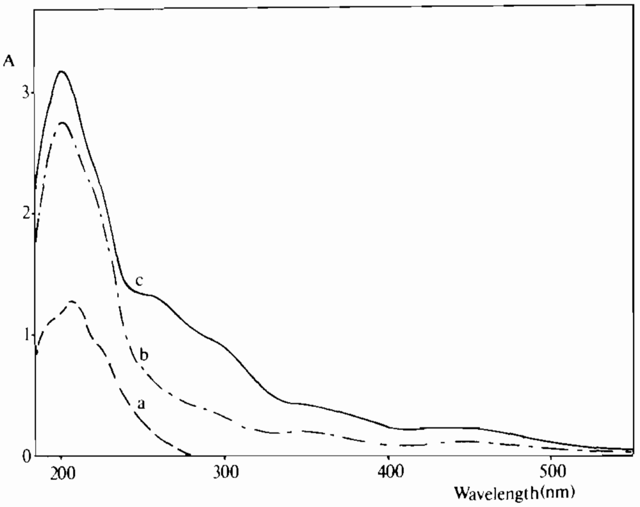

Fig. 1. Effect of B_2S_3 on the UV–Vis spectrum of $MoO_3(TIDA)^{2-}$ (3×10^{-3} M). (a) 0, (b) 2, (c) 3 equiv. of B_2S_3 added.

As described in 'Experimental', complex $[MoO_3(TIDA)]^{2-}$ (**1**) was isolated in the solid state. Its high solubility and stability in MeOH prompted us to investigate its reaction with B_2S_3. The UV–Vis spectrum for **1** in methanol consists of an intense band $\lambda_{max} = 206$ nm ($\epsilon = 8900$ M^{-1} cm^{-1}). Small changes in the spectrum (Fig. 1) are observed on addition of increasing the amount of B_2S_3 from 1 to 3 equiv., after 8 h. The main feature of interest in the final spectrum is the appearance of weak low-energy bands centered around 300 and 450 nm with $\epsilon < 3000$ M^{-1} cm^{-1}. Such a spectrophotometric behavior is rather more related to that observed for the above-mentioned $MoOS(ONR_2)_2$ and $MoS_2(ONR_2)_2$ complexes [10] than to the formation of μ-oxo or μ-sulfido Mo(V) dimers. In fact, a distinctive feature in the electronic spectra of such dimers is the presence of an intense transition around $\lambda = 470$ nm for μ-oxo species [11] and around 400 nm for μ-sulfido species [12], both with ϵ higher than 9000 M^{-1} cm^{-1}.

The present paper describes our efforts in characterizing these sulfurated species using techniques of NMR spectroscopy and cyclic voltammetry.

NMR spectroscopy

Redissolution of **1** in D_2O affords a set of ^1H and ^{13}C NMR resonances which are clearly different from those obtained for the free ligand (see 'Experimental'). The ^1H NMR spectrum (Fig. 2(a)) exhibits, in addition to an AB-type quartet signal (δ_A 9.63, δ_B 3.33 ppm, $J = -16.3$ Hz), a singlet signal due to the methyl protons ($\delta = 2.0$ ppm) and an AA'BB' spin system ($\delta_A = \delta_{A'} = 3.53$ ppm and $\delta_B = \delta_{B'} = 2.76$ ppm) which arises from the protons of the ethylene carbon chain linking the sulfur and nitrogen atoms. Compared to the free ligand, the

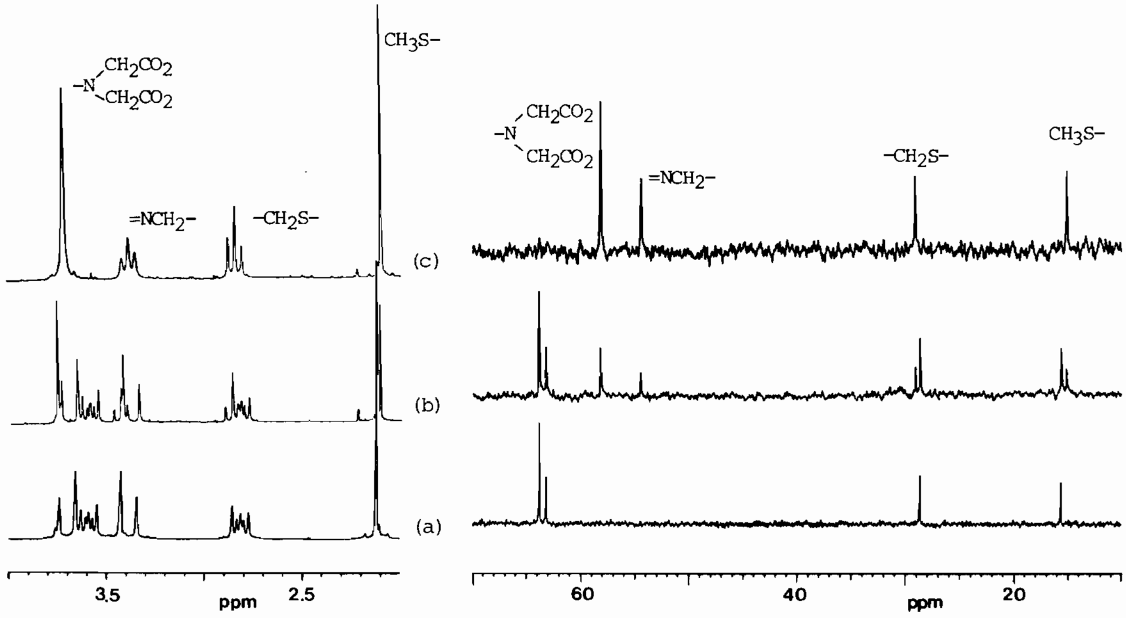

Fig. 2. ${}^1H$ and ${}^{13}C$ NMR spectra at r.t. of samples obtained by using an increasing amount of B_2S_3 on $MoO_3(TIDA)^{2-}$ complex; (a) 0 equiv.; (b) 1 equiv. of B_2S_3; (c) excess of B_2S_3.

${}^1H$ and ${}^{13}C$ chemical shift variations decrease on going from the nitrogen atom to the methyl group. This observation clearly indicates that the CH_3–S–CH_2–CH_2– arm must be uncoordinated and the expected facial tridentate coordination is achieved by coordination of the nitrogen atom and both carboxylate groups on the acetate arms of the TIDA ligand. Such a coordination is strongly supported by both the magnetic inequivalence of the methylene protons of the iminodiacetate arms and the large downfield shift of carboxylate groups in the ${}^{13}C$ NMR spectrum.

The absence of any ${}^1H$ or ${}^{13}C$ signal corresponding to the free ligand reasonably suggests that no appreciable dissociation of this complex species occurs in D_2O or MeOH. In support of this proposition, only one peak of bound molybdenum could be observed in the ${}^{95}Mo$ NMR spectrum for a D_2O solution of this complex species (Fig. 3(a)). This peak lies at 62 ppm higher frequency relative to the signal of $MoO_4{}^{2-}(aq)$ as external reference.

The molecular geometry of this complex can be further evidenced by ${}^{17}O$ NMR spectroscopy (Fig. 4) which has been utilized to glean structural and bonding information from oxomolybdenum complexes [13]. Tripodal ligands have inequivalent oxygen atoms and indeed each displays a 2:1 doublet in the terminal oxo region. Therefore, from the ${}^{17}O$ NMR spectrum shown in Fig. 4, the obvious assignment attributes the 668.6 and 709.4 ppm peaks to the terminal Mo=O bonds (1:2 ratio, respectively) while the single peak appearing at 299.4 ppm downfield from H_2O may be assigned to the coordinated oxygen from both carboxylate ligand groups (around 255 ppm for the free carboxylic group).

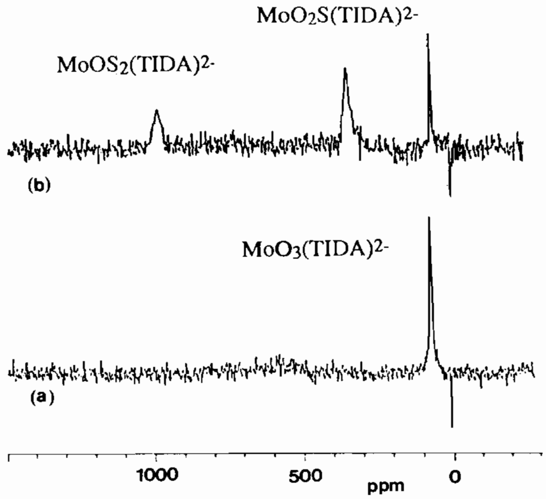

Fig. 3. ${}^{95}Mo$ NMR spectrum for the $MoO_3(TIDA)^{2-}$ complex before (a) and after (b) treatment with 1 equiv. of B_2S_3.

Addition of a variable amount of B_2S_3 (1–4 equiv.) to a methanolic solution of the above trioxo molybdenum complex yields a beautiful deep-red solution from which a crude solid was isolated according to the procedure given in 'Experimental'. This solid material appears to be stable in air but slow oxidation occurs in D_2O or MeOH solutions. Its elemental analysis indicates that the Mo/S mole ratio depends on the amount of B_2S_3 added.

We, therefore, have examined in detail, by ${}^1H$ and ${}^{13}C$ NMR spectroscopy, the product distribution re-

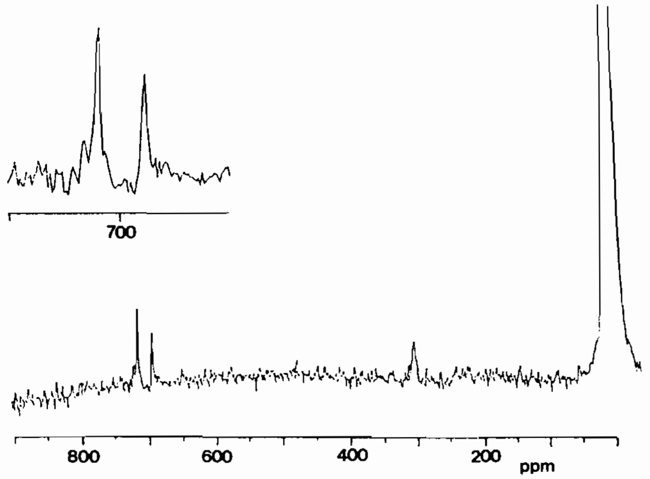

Fig. 4. ^{17}O NMR spectrum at r.t. of $MoO_3(TIDA)^{2-}$.

sulting from the reaction with B_2S_3. Redissolution in methanol of the solid obtained with less than 2 equiv. of B_2S_3 produces a solution whose ^1H and ^{13}C NMR spectra exhibit the signals for the MoO_3L^{2-} complex as well as a set of new resonances which resemble those observed for the free ligand in which methylene protons of the acetate arms appear as a singlet (Fig. 2(b)). An analogous result was obtained for the solid product obtained when more than 2 equiv. of B_2S_3 were added, but it was also found that an increase in the thiation reagent concentration causes the complete loss of the MoO_3L^{2-} peaks and a corresponding increase in the new peaks (Fig. 2(c)). The foregoing spectroscopic results may be rationalized if it is considered that only a mixed oxo-sulfido species $[MoS_xO_{3-x}(TIDA)]^{2-}$ is isolated as product which has a fluxional character as demonstrated by variable temperature experiments. Stereochemical non-rigidity has also been observed for $MoOS(ONR_2)_2$ and $MoS_2(ONR_2)_2$ complexes [3b] but not for dimeric Mo(V) species containing sulfur or oxygen bridging linkages.

Figure 5 collects the ^1H NMR spectra over as wide a temperature range as possible, namely 310–193 K, the lower limit being determined by the solvent. As the temperature of the sample decreases, the initial spectrum first broadens and then sharpens to give a set of new broad resonances that seems to result from the superposition of two individual species. In fact, the methyl group signal collapses at about 253 K and below, appearing as a doublet whose intensity ratio is *c*. 5:2. Simultaneously, new broad AB patterns associated with the methylene protons begin to appear but, unfortunately, at the lowest temperature conveniently accessible with this solvent they are not sharp enough to be assigned.

Therefore, under these experimental conditions, the foregoing ^1H and ^{13}C NMR results clearly indicate that B_2S_3 only acts as a thiation reagent showing no ability to reduce the starting tri-oxo Mo(VI) complex to Mo(V) μ-oxo or μ-sulfido dimers. Chemical support for this spectroscopic conclusion, and thus for the terminal character of all the sulfur atoms coordinated to the molybdenum, comes from the reaction between the sulfurated complex and a tertiary organo phosphine like PPh_3. If the Mo=S unit can be generated it should be quite reactive. As indicated by ^{31}P NMR spectroscopy such a reaction led to the immediate formation of $SPPh_3$ (49 ppm referred to free PPh_3) and an essentially colorless solution denoting the formation of unidentified molybdenum species lacking Mo–S ligation. Again, this result would seem to rule against the presence of dimeric species which, under similar conditions, are inert to PPh_3 because of a lower electron density on the bridged sulfur atom.

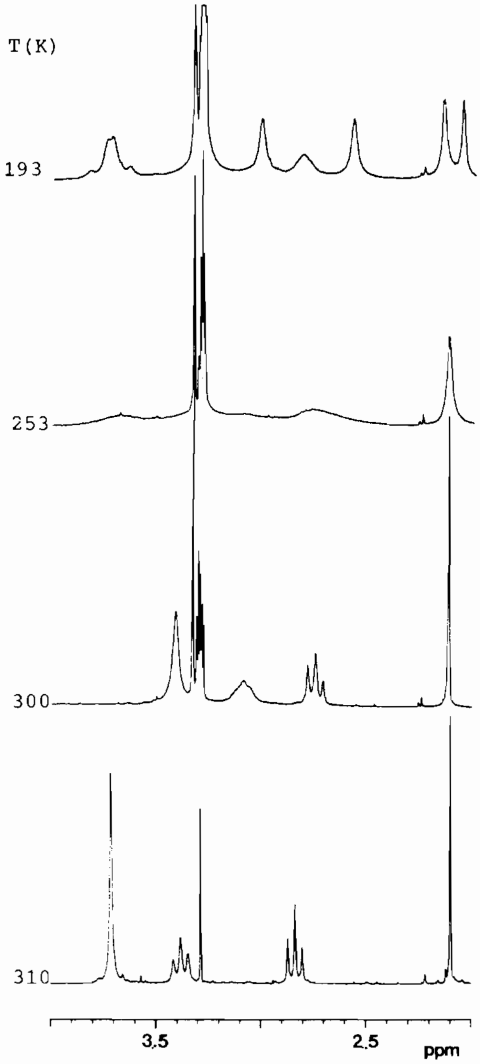

Fig. 5. Temperature-dependent ^1H NMR spectra in CD_3OD for a sample of the complex products obtained upon treatment with 2 equiv. of B_2S_3.

On the other hand, ^{95}Mo NMR spectroscopy has proven useful in distinguishing dioxo, oxo-sulfido, and disulfido Mo(VI) complexes [5]. Figure 3(b) shows the 13.04 MHz ^{95}Mo NMR spectrum in CD_3OD of a sample obtained by adding to **1** one equivalent of B_2S_3. Besides the signal at 62 ppm arising from $[MoO_3(TIDA)]^{2-}$, two well separated resonances of different intensity are observed at 343 and 990 ppm. This result shows that the two new molybdenum centers have very different chemical environments which strongly supports that the isolated solid is most likely a mixture of two monomeric Mo(VI) complexes formulated as MoO_2SL^{2-} and $MoOS_2L^{2-}$. For *cis*-dioxo Mo(VI) complexes, replacement of one terminal oxo group by a sulfido group causes a deshielding of the molybdenum center of about 700 ppm while replacement of both oxygens generates a deshielding of over 1200 ppm [5]. In our case, the lower value of the molybdenum shifts must be related to the molybdenum atomic charges, that should be higher in $MoO_{3-x}S_x$ ($x=1$ or 2) complexes because there is an additional oxo group bonded to molybdenum [14]. We have not observed any spectroscopic evidence for the formation of a trisulfido substituted MoS_3L^{2-} species in our reaction system which seems to point out that the lability towards oxygen replacement decreases with the degree of sulfuration, as previously reported for other *cis*-dioxomolybdenum(VI) complex systems [15].

Evidence for the monomeric character of these complexes was also obtained from ^{17}O NMR spectra which show a single broad resonance at 740 ppm. This signal is clearly in the range observed for terminal oxo groups (700–900 ppm) and not in the bridged oxo group range (530 and 612 ppm) [16].

Finally, we should remark that a similar reaction with B_2S_3 has been proved effective in converting the Mo=O bond to the Mo=S bond when instead of TIDA the ligand is iminodiacetic acid (IDA). Addition of an excess of B_2S_3 to a methanolic solution of this complex led to the formation of similar dark red solutions from which a solid product could also be isolated. Redissolution of this crude product gives the same ^{1}H NMR spectrum as that observed for the free ligand. Therefore, instead of the AB-type quartet signal (δ_A 3.36, δ_B 2.73 ppm, $J_{AB}=-17.3$ Hz) displayed by the trioxo complex $MoO_3(IDA)^{2-}$, only a singlet signal at 3.09 ppm, present in the free ligand spectrum, could be observed. As shown in the comparative Table 1, the spectroscopic characterization of these $MoO_3(IDA)^{2-}$ sulfurated derivatives by ^{17}O and ^{95}Mo NMR spectroscopy supports the same conclusions concerning their oxo-sulfido mixed nature, $MoO_{3-x}S_x(IDA)^{2-}$ ($x=1$ or 2), as those described above for the TIDA complex system.

Cyclic voltammetry

An earlier electrochemical study [17] demonstrated that MoO_3L^{2-} is reduced in two irreversible proton-assisted steps to give an oxo-bridged Mo(V) species ($E_p=-0.75$ V) and then to a Mo(III) dimer species ($E_p=-1.12$ V). Redissolution of the sulfurated crude material isolated after the addition of more than 2 equiv. of B_2S_3 to a methanolic solution of the $MoO_3L_2{}^{2-}$ complex, gives rise to a similar cyclovoltammetric pattern in which both peaks appear splitted and move toward less negative values of potential (Fig. 6).

TABLE 1. ^{95}Mo and ^{17}O NMR chemical shifts and linewidths for $MoO_{3-x}S_xL^{2-}$ complexes (relative intensities are given in parentheses)

Complex	^{95}Mo		^{17}O	
	δ (ppm)	$w_{1/2}$ (Hz)	δ (ppm)	$w_{1/2}$ (Hz)
$MoO_3(TIDA)^{2-}$	61.5	100	299.4 688.6 (1) 709.4 (2)	400 160 160
$MoO_2S(TIDA)^{2-}$	343.0	350		
$MoOS_2(TIDA)^{2-}$	990.0	500	740.0	250
$MoO_3(IDA)^{2-}$	63.2	130	702.3	180
$MoO_2S(IDA)^{2-}$	344.0	250		
$MoOS_2(IDA)^{2-}$	926.0	350	735.0	250

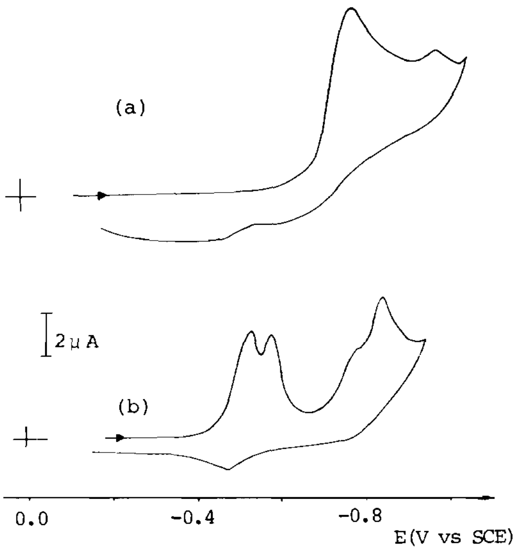

Fig. 6. Cyclic voltammograms at the HMDE corresponding to 1 mM solutions of $MoO_3(TIDA)^{2-}$ (a) and $MoOS_2(TIDA)^{2-}$ (b) in acetic/acetate buffer; pH=5.0; scan rate 0.12 V s^{-1}.

Specifically, the cyclic voltammogram of this sulfurated material exhibits two closely separated cathodic peaks at -0.520 and -0.590 V, followed by two other overlapped reduction peaks at -0.740 and -0.800 V. The first electrode process was described as a two-electron reduction to a transient Mo(IV) monomer which subsequently reacts with the remaining Mo(VI) complex to form a dimeric Mo(V) complex. The latter Mo(V) species can be further reduced at a more negative potential in an irreversible four-electron step to an Mo(III) dimer.

Therefore, this electrochemical behavior also supports the conclusion that the sulfurated crude material is a mixture of the MoO_2SL^{2-} and $MoOS_2L^{2-}$ species. Dimeric di-μ-oxo, μ-oxo-μ-sulfido and di-μ-sulfido complexes of Mo(V) with EDTA, an aminocarboxylic ligand also, lacking Mo=S bonds reduce at a higher potential and show a very different electrochemical behavior [18]. In fact, it is well-known that upon increasing oxo-substitution of Mo=S containing species the cathodic reduction potentials shift in the positive direction enhancing the ease of reduction of the molybdenum center [19]. Thus, in contrast with what is observed for MoO_3L^{2-} complexes, it is clear that the lower potentials of their sulfido containing derivatives explain their higher ability to react with PPh_3 giving $SPPh_3$.

Interestingly enough, there seems to be little difference in the peak potentials of the mono- and disulfido products. Detailed studies of this and other redox reactions as well as purification of the complexes by fractional crystallization are presently underway.

Conclusions

This study has demonstrated by ^{95}Mo and variable temperature ^{1}H NMR spectroscopy that two different products can be obtained when an excess of B_2S_3 was added to a methanolic solution of an aminodicarboxylic trioxomolybdate(VI) complex at room temperature. Their UV–Vis and electrochemical characterization as well as their fluxionality and reactivity with triphenylphosphine clearly indicate an oxo-sulfido mixed nature for both species, which can play a very important role in molybdoenzymes.

Acknowledgement

We thank DGICYT (Grant PB89–0417) for financial support of this research.

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