

Molybdenum complexes with sterically-hindered thio-carboxylate ligands. Electrochemical properties of the anionic complex bis(2,2-diphenyl-2-mercaptoethanoate)dioxomolybdate(VI) in protic solvents

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Abstract

The electrochemistry of the *cis*-dioxo-Mo(VI) complex $[\text{Mo}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ (**1**), containing two coordinated thiobenzilate ligands, has been investigated in methanol and water by cyclic voltammetry and differential pulse polarography. It undergoes an irreversible proton-assisted reduction at -0.88 V versus SCE which yields two monooxo Mo(IV) species, $[\text{Mo}^{\text{IV}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ and $[\text{Mo}^{\text{IV}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)(\text{Solv})_2]$, which are involved in a ligand dissociation equilibrium. Even in aqueous solution, steric factors on the ligand can stabilize the reduced Mo(IV) monomers thus eliminating their very common reaction with the starting Mo(VI) complex to give monooxo-bridged Mo(V) dimers. The reduced monomeric Mo(IV) species are, in turn, reversibly oxidized at more positive potentials ($[\text{Mo}^{\text{IV}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$, -0.48 V; $[\text{Mo}^{\text{IV}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)(\text{Solv})_2]$, -0.28 V), to yield the corresponding monooxo Mo(V) species. In order to examine chemical and electrochemical differences between Mo-S and Mo-O ligation, we have also studied the electrochemical behaviour of the fully oxygenated benzilate complex, $[\text{Mo}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}(\text{O})\text{Ph}_2)_2]^{2-}$. The bielectronic reduction of the complex occurs at the more negative potential of -1.35 V, indicating a low π -donor interaction of the oxygen atoms on the ligand with the molybdenum d orbital. For both thiobenzilic and benzilic systems, the electrochemical generation of aqueous stable Mo(IV) species, which are reversibly oxidized to stable monomeric Mo(V) complexes, mimics the redox behaviour assumed for molybdenum hydroxylase enzymes.

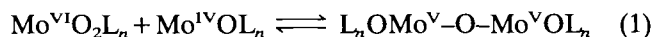
Key words: Electrochemistry; Molybdenum complexes; Oxo complexes; Thiocarboxylato complexes

Introduction

Molybdenum is an essential component in an important number of enzymes that catalyze two-electron oxidation or reduction processes [1]. All oxomolybdo-enzymes possess a common molybdenum co-factor (Mo-co) [2] which cycles among the oxidation states of VI, V and IV during catalytic turnover which leads to the overall reaction [3]: $\text{X} + \text{H}_2\text{O} \rightleftharpoons \text{XO} + 2\text{H}^+ + 2\text{e}^-$. Thus, a second centre such as a heme centre, Fe-S cluster and sometimes flavins serves as an electron acceptor (oxidase) or electron donor (reductase). According to this mechanism, the Mo centre acts as a relay station between a two-electron substrate redox

reaction and two coupled one-electron redox reactions at the other electron-transfer centre.

A vast number of cyclovoltammetric studies on *cis*-dioxo-Mo(VI) complexes is known [4]. They appear to be electrochemically reducible, usually irreversibly, to the IV state but the resulting reduced product is always an oxo-bridged Mo(V) dimer which is formed through the comproportionation reaction (1):



Yet, we must point out that, apparently, tetradentate aminothiols complexes having fully protonated amino groups, $\text{Mo}^{\text{VI}}\text{O}_2(\text{LH}_2)$, can be electrochemically reduced to monomeric $\text{Mo}^{\text{V}}\text{O}$ or $\text{Mo}^{\text{IV}}\text{O}$ species, depending on pH [5]. These unusual redox properties have been based on deprotonation of the coordinated amino groups with elimination of H_2O upon reduction

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$(\text{Mo}^{\text{VI}}\text{O}_2(\text{LH}_2) + 2e^- = \text{Mo}^{\text{IV}}\text{OL}^{2-} + \text{H}_2\text{O})$. In fact, such a stabilization of the $\text{Mo}^{\text{IV}}\text{OL}^{2-}$ complex with respect to dimerization was attributed to the strong σ - and π -donor ability of the amido groups and the imposition of a planar structure on the ligand when trigonal nitrogen replaces tetrahedral nitrogen. Bridging through a *cis* position is thus prevented, while bridging through a *trans* position is highly unfavourable because of the *trans* effect of the terminal oxo group in apical position.

For other complex systems, different to aminothiols, recent works have demonstrated that reaction (1) can be suppressed by using sterically bulky ligands, which hinder the required approximation between the $\text{MoO}_2(\text{VI})$ and $\text{MoO}(\text{IV})$ species [6]. Thus, these types of complexes have been proven to sustain clean oxidations of a variety of substrates without formation of inert μ -oxo $\text{Mo}(\text{V})$ dimers ($\text{Mo}^{\text{VI}}\text{O}_2\text{L} + \text{X} \rightleftharpoons \text{XO} + \text{Mo}^{\text{IV}}\text{OL}$).

Within this assumption, we have previously reported [7] the synthesis of $[\text{Mo}^{\text{VI}}\text{O}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ (**1**), $(\text{HO}_2\text{CC}(\text{SH})\text{Ph}_2)$ being the sterically hindered 2,2-diphenyl-2-mercaptoethanoic acid, thiobenzilic acid) which is the first dioxo-molybdenum(VI) complex capable of oxidizing aliphatic thiols under homogeneous conditions. We first demonstrated this capacity in the reaction of **1** with its own free ligand present in excess [8]. Such a reaction led to oxidation of thiobenzilic acid to the disulfide $(\text{O}_2\text{CCPh}_2\text{S})_2^{2-}$, while **1** was, in turn, reduced to the monomeric $[\text{Mo}^{\text{V}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^-$ complex (**2**). Complexes **1** [7] and **2** [8] contain two coordinated carboxylate groups each, as revealed by single crystal X-ray structural studies. Atomic parameters for **1** and **2** correlate well with those determined from EXAFS data for Mo-enzyme systems in the oxidized and reduced forms, respectively [9].

Finally, it is necessary to recognize that most of the electrochemical studies on $\text{Mo}(\text{VI})\text{O}_2$ complexes reported so far are limited to neutral pH using organic solvents like DMF, THF, CH_3CN , etc. Considering that Mo enzymes act in aqueous living media, electrochemical studies at more acidic conditions, using water or methanol as solvents, should complement the above studies. The present paper is directed toward the electrochemical properties of **1** in the protic solvents water and methanol, under neutral and acidic conditions. Preliminary aspects of this investigation have been previously described [7] in a brief communication in which some thiolate ligand redox processes were misinterpreted.

Experimental

A three-electrode potentiostat (CR 2000) with a Newtronics 200P wave generator was used for cyclic voltammetric experiments. CVs were recorded on a

Riken-Denshi X-Y recorder. The cell was equipped with a Metrohm 9100 hanging mercury drop electrode (HMDE), a platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE). Kalousek polarograms were recorded by means of a Metrohm Polarecord E-506 (Stand 505). Pulse polarograms were obtained using a Metrohm 646 VA Processor (Stand VA 647). Potentials were referenced versus Ag/AgCl , $\text{KCl}(\text{s})$ electrode. Potentiostatic reduction was made by a computerized Wenking High Power Potentiostat Bank-88 connected to a voltage integrator Bank EVI 80. All electrochemical experiments were carried out in a thermostated cell under argon atmosphere.

$(\text{NH}_4)_2[\text{MoO}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]$ (**1**) was synthesized and characterized according to procedures described earlier [7]. Doubly distilled water and methanol were used. KCl (Merck), sodium acetate (C. Erba) and acetic acid (C. Erba), all of analytical grade were used without further purification. Tetrabutylammonium hexafluorophosphate (Aldrich) was used as supporting electrolyte in MeOH.

Results and discussion

The cyclic voltammetric pattern of **1** is quite sensitive to both the electrode and the nature of the medium (solvent, pH and electrolyte). As shown in Fig. 1, the cyclic voltammogram (CV) displays two cathodic peaks at -0.27 (a) and -0.88 (b) V, versus the saturated calomel reference electrode (SCE), in unbuffered aqueous solutions (pH=4.9) and using a hanging mercury drop electrode (HMDE). Reversal of the voltage-scan direction results in anodic peaks at -0.23 (a') and -0.35 (b') V. Peak potential separation indicates that waves a and a' are reversibly coupled, but peaks b and b' must be irreversibly associated since anodic scans beginning at a potential just slightly more positive than the second reduction peak b do not show the oxidation peak b'. For the free thiobenzilic acid ligand only one reversible couple was observed under the same experimental conditions (Fig. 1(b)), the morphology and peak potentials being closely related to the above a/a' couple found for the complex **1**. Therefore, the first cathodic peak for the complex must be assigned to a ligand-centred process while the other b/b' couple can be attributable to the reduction of the molybdenum centre.

Differential pulse polarograms (dpp) confirm these considerations concerning the separation between ligand- and metal-centred processes (see Fig. 2). In acid media (acetic/acetate buffer) where dpp recorded for complex **1** and the free ligands become more differentiated, four well-defined cathodic waves (A, B, C and D) appear for a solution of **1** whereas for the free

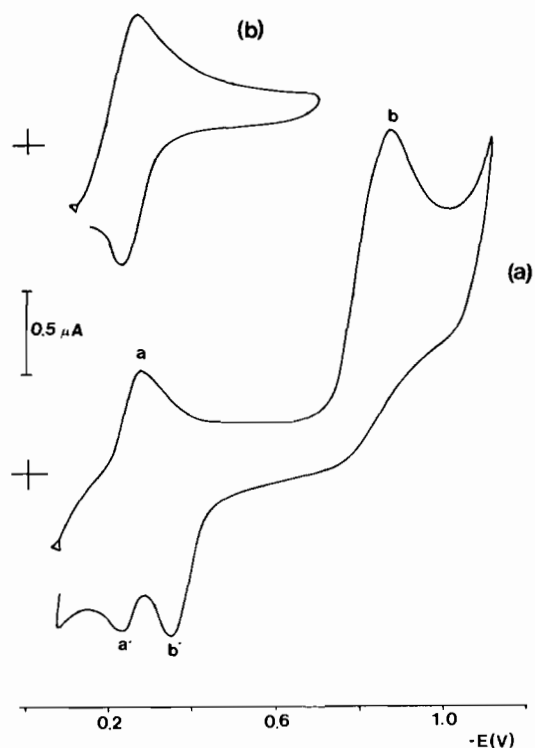


Fig. 1. HMDE cyclic voltammogram for an aqueous solution of **1** (10^{-3} M) in KCl 1 M: (a) potential range from 0.0 to -1.4 V vs. SCE, (b) potential range restricted from 0.0 to -0.75 V vs. SCE.

thiobenzilic acid only the second dpp wave B can be observed (Fig. 2(b)).

Characterization of the ligand-centred reductions

CVs for unbuffered solutions of uncomplexed thiobenzilic acid only show the *a/a'* couple (Fig. 1(b)) which is preceded by a prominent anodic current. The electrochemical parameters, ΔE_p (30 mV) and i_{pc}/i_{pa} ($=1$), suggest that two electrons are involved in this reversible reduction. Furthermore, peak potentials are cathodically shifted by increasing the solution pH from 4.0 to 7.0, giving a linear $E_p=f(\text{pH})$ plot whose slope (*c.* 60 mV/pH) indicates that two protons are involved in the electrochemical process (transferred protons/transferred electrons ratio is equal to unity). Similar features, related with the reversibility and proton and electron stoichiometry, characterize the *a/a'* couple displayed by an aqueous solution of **1** under the same experimental conditions.

To further corroborate the two-electron stoichiometry of this ligand-centred process, Kalousek polarograms [10], based on the superposition of negative pulses (K_4 method), or positive pulses (K_3 method) to a linear potential sweep were performed for the dpp waves A and B. The height of these waves increases monotonically with the square root of the pulse frequency (see Fig. 3), and their shapes fit well to the theoretical curves

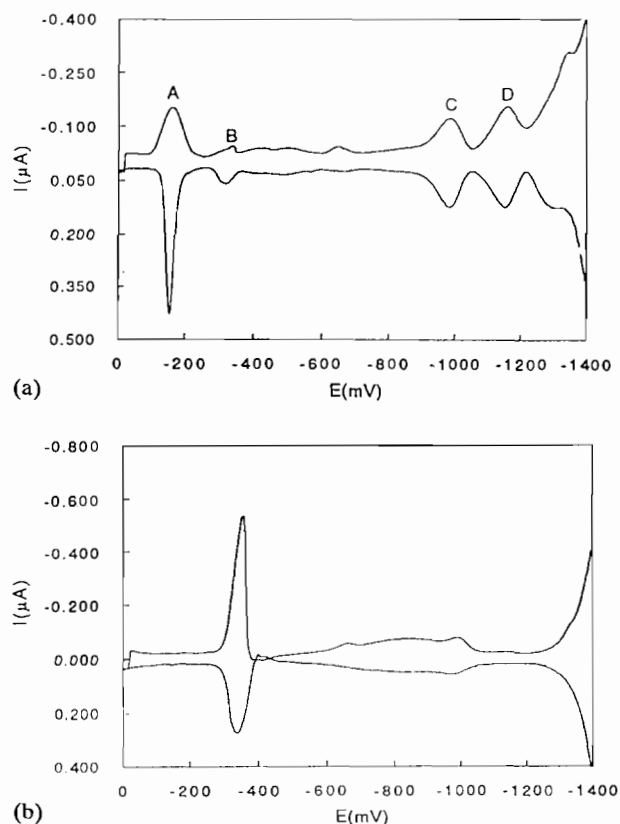


Fig. 2. Dpp in acetic/acetate buffer at pH 3.1, $\Delta E = \pm 50$ mV, $t = 2$ s: (a) solution of **1**, 2.63×10^{-6} M; (b) solution of thiobenzilic acid, 2.8×10^{-5} M.

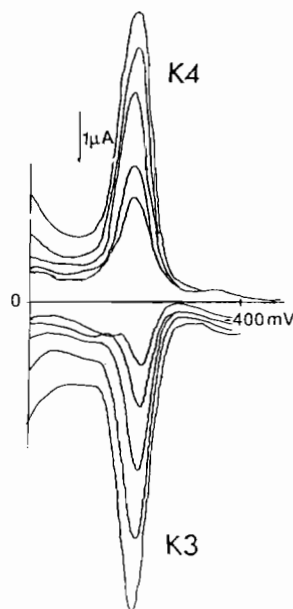
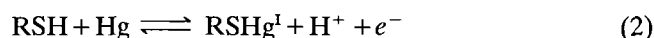


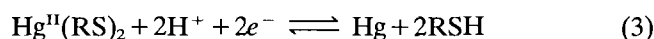
Fig. 3. K3 and K4 polarograms for the ligand-centred wave A recorded on a 4×10^{-4} M solution of **1** in acetic/acetate buffer at pH 4.0, $t = 0.6$ s, $j = 4 \times 10^{-8}$ A/mm; $f_k = 50, 75, 150, 300, 600$ Hz.

for reversible diffusion-controlled processes [10]. As expected, the half-height width is equal to the limiting value for a two-electron reversible process as pulse amplitude approaches zero.

This electrochemical response for free or coordinated thiobenzilic acid can be contrasted with those previously reported for other sulfur derivatives. Specifically, electrochemical behaviour of alkylthiols at the HMDE in aqueous solution has been the subject of several polarographic investigations [11]. An oxidation wave is observed as a result of mercurous thiolate complex formation which involves oxidation of the mercury electrode rather than thiol oxidation to a disulfide:



However, as reported for alkyl disulfides [11], dithiocarbamates [12] and dithiothreitol [13], our present findings suggest that thiobenzilic acid induces a further oxidation of the mercury electrode to a mercury(II) thiolate species that in turn can be reversibly reduced. The cyclic voltammetric *a/a'* couple is then represented by eqn. (3), which also accounts for the dpp waves A (complexed) and B (uncomplexed) thiolate groups of the thiobenzilic acid ligand.



Couples A and B were further characterized by a series of dpp experiments at variable temperature (see Fig. 4). Wave A is enhanced by increasing the temperature from 278 to 303 K, reaching a maximum constant intensity at this latter temperature. Linear plots of $\ln i_p$ versus $1/T$ led to an apparent activation energy of *c.* 25 kJ mol⁻¹. As expected, this value is much higher than that obtained for the uncomplexed thiobenzilic acid ligand (wave B), at the same buffered pH of 3.1, which was found to be 2.3 kJ mol⁻¹ (278 < *T* < 323 K).

Finally, from the slope of linear $E_p = f(T)$ representations, the variation of entropy associated to both A and B reduction waves was calculated as $\Delta S = nF(\Delta E_p / \Delta T)$. The value obtained for the two-electron reduction of the complexed ligand (220 ± 20 J mol⁻¹ K⁻¹) was,

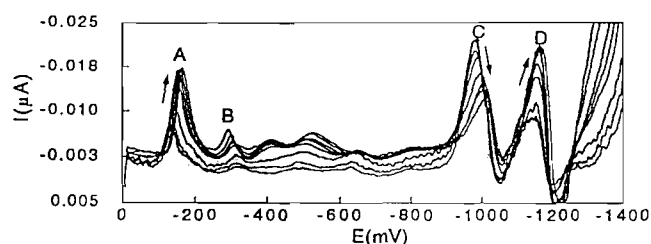


Fig. 4. Temperature effect on dpp waves for a 5.8×10^{-6} M solution of **1** in acetic/acetate buffer at pH=3.1, $\Delta E = -10$ mV, $t = 0.5$ s. Temperatures varied from 10 to 50 °C.

as expected, significantly higher than that obtained for the uncomplexed ligand (155 ± 10 J mol⁻¹ K⁻¹).

Characterization of the metal-centred processes

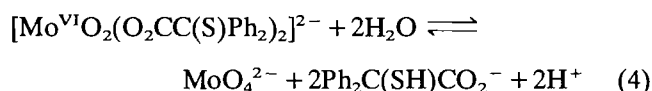
According to the CV in Fig. 1, the redox behaviour of complex **1** in aqueous acetate buffered solutions exhibits a reduction process centred at -0.88 V (b). The anodic scan shows that this process is coupled to the oxidation wave appearing at -0.35 V (b'). The clear irreversibility of this first reduction step is a feature generally observed for most of the dioxo-Mo(VI) complexes studied, and it has been attributed to a rearrangement of the Mo coordination sphere accompanying oxo loss.

The pH dependence of wave (b) indicates an uptake of protons associated with the electron transfer, while its large current function $I_{pc} = 1000$ A cm mol⁻¹ s^{1/2} V^{-1/2} ($I_{pc} = i_{pc}/cAV^{1/2}$) is quite compatible with a two-electron reduction. In fact, monoelectronic reductions of other dianionic monomeric Mo(VI) complexes in aqueous media have been reported [14] to give I_{pc} values of *c.* 500 A cm mol⁻¹ s^{1/2} V^{-1/2}, while two-electron reductions provide I_{pc} values ranging from 1000 to 1500 A cm mol⁻¹ s^{1/2} V^{-1/2} [15]. However, attempts at coulometry on the ammonium salt of complex **1** at platinum or mercury pool electrodes failed to give satisfactory results because of proton discharge from ammonium ions and adsorption processes involving the ligand species, respectively. In addition, attempted coulometry on a graphite electrode at potentials more negative than $E_{pc}(b)$ gave continuous coulomb counts indicating the existence of unidentified chemical reactions following the electrode process b.

Assuming that two electrons are involved in the initial reduction of **1**, the foregoing results do not differentiate between a single two-electron transfer and two separate one-electron transfer steps. In this regard, it is worth noting that the CV data for Mo^{VI}O₂ complexes with aromatic tetradentate N₂S₂ ligands [5b] in THF solutions show a different behaviour depending on pH. Thus, under acidic condition (HCl) or in the presence of *N*-methylimidazole acting as a nucleophilic species, the CV includes two separate one-electron reductions to give first the $[\text{Mo}^{\text{VO}}(\text{N}_2\text{S}_2)]^-$ species and then the further reduced $[\text{Mo}^{\text{IVO}}(\text{N}_2\text{S}_2)]^{2-}$. At neutral conditions, however, these complexes undergo a single two-electron reduction.

For the present system, the cathodic peak b shifts anodically when pH decreases but no change in the voltammetric pattern or appearance of new peaks was evident in the CVs obtained at the lowest tested pH (pH=3.0). The only observed variation was an increase in the intensity of the ligand-centred reduction process *a/a'* at the expense of the metal-centred reduction b when the

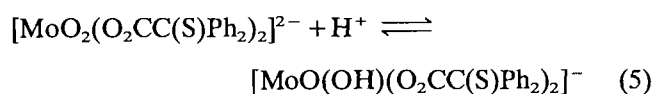
pH increased because of the expected progressive dissociation of **1** (eqn. (4)).



Nevertheless, from pH 6.5 and below, peak b reached a maximum constant intensity indicating that all Mo(VI) present in the solution could be assumed to be coordinated. In this pH interval (4.0 to 6.5), plots of $E_p = f(\text{pH})$ are straight lines from whose slopes one can deduce that the initial reduction of **1** is preceded by capture of one mole of protons per mole of transferred electrons.

On the other hand, dpp experiments indicated in Fig. 2(a) show that there are two waves, C and D, associated to the metal-centred cyclovoltammetric reduction process b. Both waves are heavily influenced by buffered medium. In acetate buffer (pH=3.1), they appear well defined but in a phosphate buffer (pH>3.1) they collapse to a single wave. Their observed half-wave width is consistent, independent of pH, with the two-electron stoichiometry deduced from the above CV peak current data.

Another pertinent observation based on variable temperature dpp is that the intensity of wave D increased at the expense of wave C (see Fig. 4), the apparent Arrhenius activation energy being c. 25 kJ mol⁻¹. Such a result can be interpreted in terms of the existence of a chemical equilibrium involving two Mo(VI) complexes at acidic pH. Since formation of dimeric species is sterically hindered, the existence of a protonation equilibrium affecting the oxomolybdenum core seems to be the most probable assumption. This is supported by the fact that both the C and D waves exhibit the same variation of the peak potential with temperature which implies that the variation in entropy associated with such an equilibrium is negligible. Consequently, in agreement with the presumed protonation nature of this equilibrium, no significant structural changes occur and dpp waves C and D can be assigned to the two-electron reduction of each one of the molybdenum(VI) complexes involved in the equilibrium described by eqn. (5).



The peculiarity of such an initial two-electron reduction is based on its comparison with previous electrochemical studies reported for other sterically hindered Mo^{VI}O₂ complexes which act as models for the molybdenum binding site of the molybdenum co-factor [4g]. As far as we know, most of them are neutral charged complexes only soluble in aprotic solvents in

which they display irreversible monoelectronic reductions to Mo^{VO} or Mo^{VO}(OH) species. It has been suggested that these types of species are unstable on the cyclic voltammetry scale, the most likely mode of decomposition being the interaction with unreduced Mo(VI)O₂ complex. Such a lack of stability has been attributed to solvent and protonation effects which are obviously different in DMF than in aqueous solution where native enzymes display reversible couples [4g].

To elucidate the importance of solvent effects and electrode nature in the redox behaviour of **1**, we have re-examined its electrochemical response under experimental conditions more similar to those used in the previously investigated MoO₂ model complex systems. The CV of the tetrabutylammonium salt of **1** in DMF or CH₃CN at the platinum electrode does not show any reduction peak in the +0.75 to -1.50 V potential range. For the ammonium salt, which can also act as a proton source, the only observed cathodic peak at -1.1 V corresponds to the reduction of H⁺ ions to H₂ and moreover, as expected, the replacement of the Pt electrode by a glassy-carbon electrode (GCE) causes the disappearance of this peak. Therefore, the conclusion is that complex **1** exhibits an inert electrochemical character in these aprotic solvents and potential ranges studied.

This result led us to examine the electrochemistry of **1** in a more water-related solvent like methanol. As is depicted in Fig. 5, the CV at the GCE for the ammonium salt of **1** exhibits a prominent irreversible reduction peak at -1.35 V (b) accompanied, when the scan is reversed, by anodic peaks at -0.48 and -0.28 V (peaks c and d, respectively). In the second and successive scans, cathodic peaks at -0.38 and -0.65 V (c' and d') were developed. The intensity of the initial reduction peak (b) tends decisively towards a two-electron process which clearly resembles the above described reduction peak b of **1** in aqueous solution and at the HMDE (Fig. 1(a)).

Oxidation peaks c' and d' are associated with this two-electron reduction peak b. In principle, they could be ascribed to two successive oxidation processes of the initially formed Mo(IV) product (Mo(IV) $\xrightarrow{c'}$ Mo(V) $\xrightarrow{d'}$ Mo(VI)). However, this assumption appears to be improbable based on their total intensity which approaches half of the intensity of peak b. Such a 2:1 intensity ratio ($i_b/(i_{c'} + i_{d'})$) provides a reasonable indication of the formation of two different Mo(IV) species which each undergo a reversible one-electron oxidation at c' (-0.48 V) and d' (-0.28 V) to give two Mo(V) species.

The formation of two Mo(IV) species is firmly supported by a previous work [17] on chemical and electrochemical properties of a complex **1** analogue containing two thioglycolate ligands, [Mo^{VI}O₂(SCH₂-

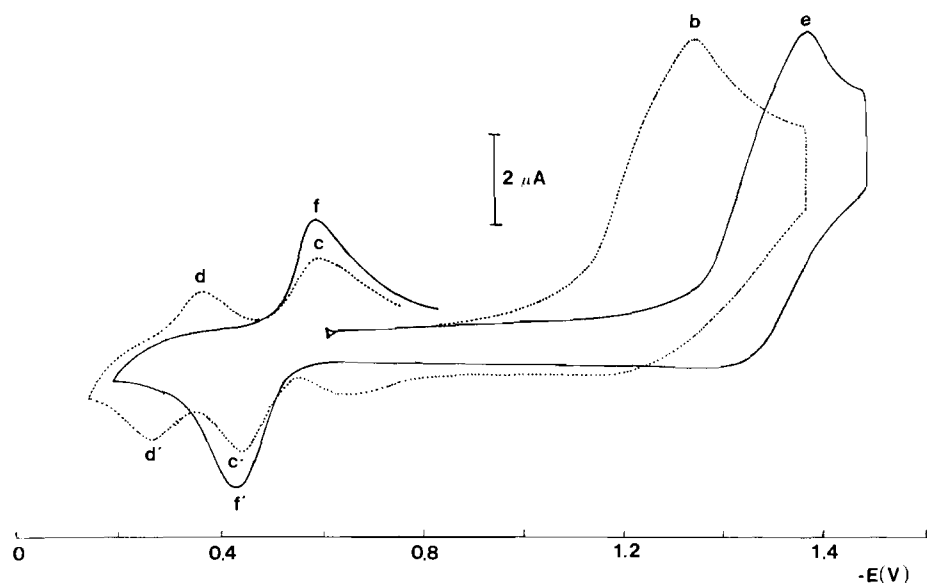
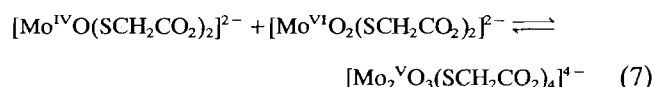
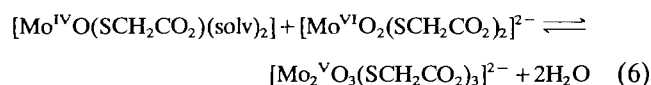


Fig. 5. CV at the GCE recorded on a methanolic solution (0.1 M (TBA)PF₆) of the ammonium salts of [Mo^{VI}O₂L₂]²⁻ complexes with L=benzilic acid (continuous line) and thiobenzilic acid (broken line). Scan rate 0.25 V s⁻¹.

CO₂)₂]²⁻, a thiobenzilate derivative in which *gem*-diphenyl groups have been replaced by hydrogen atoms. Chemical or electrochemical reduction of this non-sterically hindered complex implies the initial loss of one terminal oxo group with the consequent formation of the Mo(IV) complex [Mo^{IV}O(SCH₂CO₂)₂]²⁻, which partially dissociates to give a free thioglycolate ligand ion and an Mo(IV)-thioglycolate complex, [Mo^{IV}O(SCH₂CO₂)(solv)₂], of stoichiometry 1:1. The comproportionation reaction of each one of these Mo(IV) complexes with unreduced [Mo^{VI}O₂(SCH₂CO₂)₂]²⁻ complex yields two different μ -oxo Mo(V) dimers as stable final products (eqns. (6) and (7)).

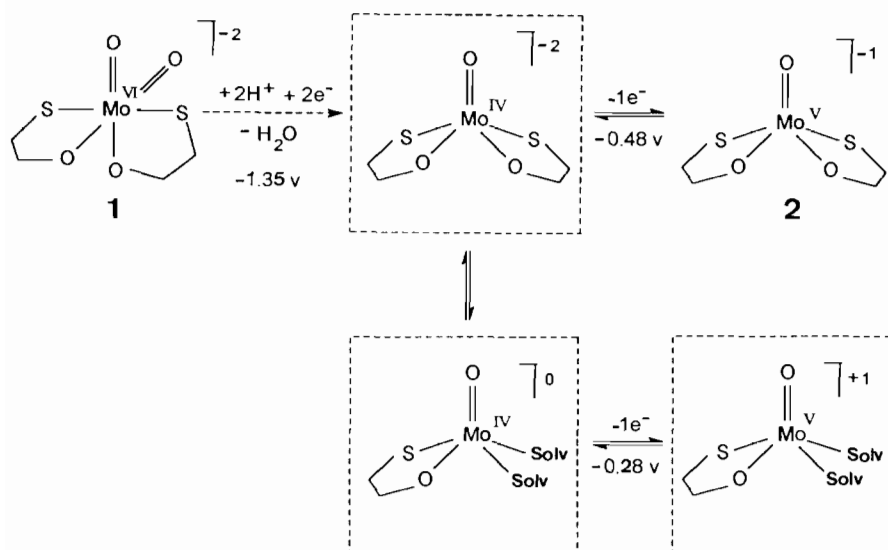


The dimeric Mo(V) complex [Mo₂^VO₃(SCH₂CO₂)₃]⁴⁻, predominantly formed, has been previously isolated and structurally characterized by X-ray diffraction [16]. In addition, it has been previously detected by spectrophotometric methods that Mo(IV) interacts with thioglycolic acid forming a neutral 1:1 Mo(IV)-thioglycolic acid complex in aqueous solutions. This can also be isolated as a solid material whose composition is in agreement with the formula [Mo^{IV}O(SCH₂CO₂)(H₂O)₂] [17].

For the present complex **1**, it appears reasonable, and electrochemically supported herein, to assume a similar reduction mechanism and hence the formation

of two Mo(IV) species containing one or two thiobenzilate ligands. However, owing to the sterically encumbering nature of thiobenzilate ligands, comproportionation reactions (6) and (7) do not occur and, therefore, both Mo(IV) species must now be the stable final reduction products. Attempts to isolate such Mo(IV) complexes have been unsuccessful but one of the voltammetrically observed Mo(V) oxidation products (the one containing two thiobenzilate ligands [Mo^VO(O₂CC(S)Ph₂)₂]⁻), has been previously characterized by X-ray crystallography and cyclic voltammetry [8, 18]. Its structure reveals a square pyramidal arrangement in which both thiobenzilate ligands are fully deprotonated in the equatorial plane and both thiolate groups are *trans* to carboxylate groups. Only one oxo group is coordinated to the Mo(V) atom in the apical site of the pyramid having a *trans* bonding position empty. Such a structure demonstrates the above assumed change in the coordination sphere of the starting *cis*-dioxo-Mo(VI) complex upon reduction.

Scheme 1 summarizes the foregoing redox mechanism derived for complex **1**. This scheme was further supported by examining the cyclic voltammetric behaviour of the ammonium salt of the *cis*-dioxo-molybdenum(VI) complex, [Mo^{VI}O₂(O₂CC(O)Ph₂)₂]²⁻, in which benzilate replaces thiobenzilate ligands in **1**. As presented in Fig. 5, the CV shows an initial two-electron reduction step *e* which is followed by only one reversible oxidation process (*f/f'* couple, formal potential -0.44 V versus SCE). Therefore, the absence of electrochemical complications associated with a partial ligand dissociation in the initially formed [Mo^{IV}O(O₂CC(O)Ph₂)₂]²⁻ complex could be detected. To justify such behaviour, we



Scheme 1.

can invoke differences in π -bonding donor interaction between alkoxide and thiolate groups. For reduced thiocarboxylate complexes $[\text{Mo}^{\text{IV}}\text{O}(\text{O}_2\text{CC}(\text{S})\text{R}_2)_2]^{2-}$ ($\text{R} = \text{Ph}$ or H), thiolate groups on the ligands compete with the terminal oxo group for the same metal d orbitals, and therefore, it is not unrealistic to imagine that the loss of one thiocarboxylate ligand may stabilize the π -bonding $\text{Mo}=\text{O}$ interaction. In contrast, for the Mo^{IV} -benzilate complex the effect of a π -bonding $\text{Mo}=\text{O}$ stabilization upon dissociation of a ligand molecule appears to be small given the much lower π -donor ability of alkoxide groups. Experimental work supporting these π -bonding effects comes from photoelectron spectra obtained for oxo-molybdenum(IV) complexes containing diolato or alkoxide ligands [19]. According to these spectra the interaction between $p\pi$ -electrons of oxygen atoms in the alkoxide groups and the $d\pi$ -electron of the $\text{Mo}(\text{V})$ atom is a purely electrostatic repulsion.

Lastly, we must note that the initial cathodic peak potential, $E_p = -1.57$ V, for the two-electron reduction of the $\text{Mo}(\text{VI})\text{O}_2$ -benzilate complex is 0.22 V more negative than that observed for the thiobenzilic analogue complex under the same experimental conditions. This result is consistent with the effect of O/S substitution on the potentials of $\text{Mo}(\text{VI})\text{O}_2$ complexes containing otherwise identical ligands [20].

Acknowledgement

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