Redox Properties of Mononuclear and Triply-bridged Binuclear Thiolato Anions of Oxomolybdenum(V)

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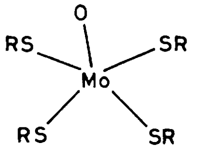
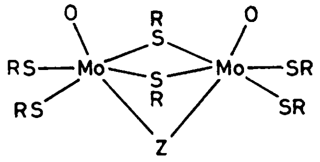
Summary Interconversion of mononuclear $[Mo^{V}O(SR)_4]^-$ (**1**; R = aryl or alkyl) and triply-bridged, binuclear $[Mo^{V}_2O_2(SR)_6Z]^-$ (**2**; Z = OMe, OEt, or SCH_2Ph) anions occurs *via* redox processes involving both the molybdenum and ligand thiolate centres.

THE paramagnetic mononuclear anions $[Mo^VO(SR)_4]^-$ (**1**)[1,2] exhibit a $(4d_{xy})^1$-based ground state and, for R = aryl, are kinetically stable. However, they convert into the spin-coupled anions (**2**)[3] when a ligand capable of occupying the unique bridging position Z is available and this prevents isolation of (**1**; R = alkyl) at room temperature.



(1)



(2)

Both the metal and ligand centres in such species are electroactive and a thorough investigation of the electrochemistry of the free thiols HSR, salts $Et_4N[SR]$, and disulphides RSSR (R = Ph, *p*-tolyl, or benzyl) at Pt electrodes in MeCN and dimethylformamide (dmf) has been completed.† A knowledge of these free ligand processes is essential to assign the metal anion electrode processes and to identify free ligand species produced either by chemical reactions following electron transfer or by non-redox phenomena (see Figure 1, for example).

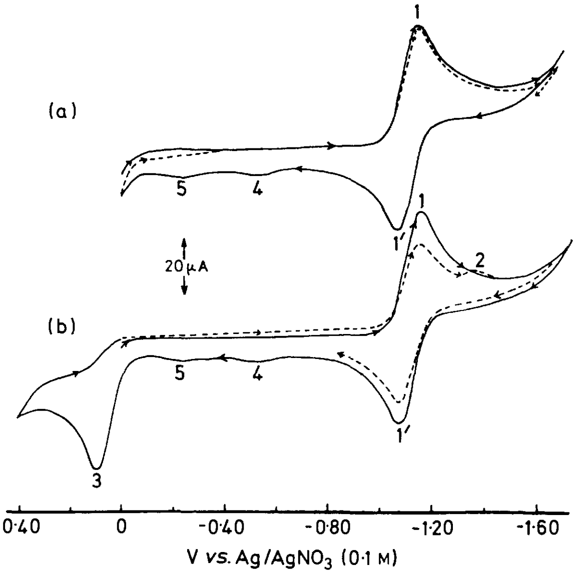


FIGURE 1. Cyclic voltammograms of 8×10^{-3} M solutions of $Et_4N[MoO(SPh)_4]$ in MeCN at 25 °C and a scan rate of 200 mV s^{-1}. (a) Cathodic scans from 0·0 V. (b) Cathodic scans from 0·0 V including peak 3. Species (**1**) are rather sensitive to traces of dioxygen and/or protonic impurities in solution which can lead to the presence of low concentrations of free ligand species in solution.

Peaks 4 and 5 are due to: $2[SPh]^- + H_2 \xrightarrow{4} 2HSPh + 2e^-$ and $2[SPh]^- \xrightarrow{5} PhSSPh + 2e^-$.

The electrochemistry of anions (**1**) and (**2**) was studied by d.c. polarography, cyclic voltammetry (c.v.) at Pt, and controlled potential electrolysis coupled with coulometry and d.c. polarographic monitoring of the products of electrolysis. The initial cathodic process for (**1**; R = Ph or *p*-tolyl; see Table and Figure 1a) satisfies the criteria[4] for a quasi-reversible one-electron charge transfer process where the current is controlled by a mixture of diffusion and electron transfer kinetics.‡ The total data confirm a chemically reversible couple [equation (1)].

$$[Mo^VO(SR)_4]^- + e^- \underset{1'}{\overset{1}{\rightleftharpoons}} [Mo^{IV}O(SR)_4]^{2-} \qquad (1)$$

A typical cathodic c.v. scan for (**2**; R = Ph or *p*-tolyl; Z = OMe, OEt, or NEt_2) at 25 °C and a scan rate of 500 mV s^{-1} in MeCN is shown in Figure 2a. It features a primary irreversible process 2 associated with an overall two-electron reduction step.§ Secondary peaks 1′ and 1

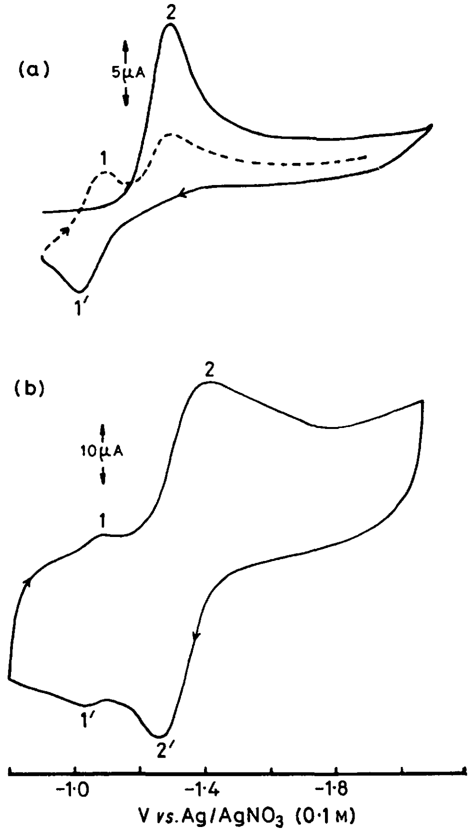


FIGURE 2. Cyclic voltammograms for 10^{-3} M solutions of $Et_4N[Mo_2O_2(SPh)_6(OMe)]$ in MeCN at a Pt electrode with supporting electrolyte, $Et_4N[PF_6]$ (0·1 M) at (a) scan rate 500 mV s^{-1} at 25 °C, (b) scan rate, 20,000 mV s^{-1} at −39 °C; this is a steady state voltammogram.

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† Seven redox processes involving these species have been detected at Pt in MeCN [*vs.* $Ag/AgNO_3$ (0·1 M) reference electrode] and dmf (*vs.* S.C.E.). The results are essentially in agreement with reported studies of HSPh–PhSSPh in dmf [(a) F. Magno, G. Bontempelli, and G. Pilloni, *J. Electroanalyt. Chem.*, 1971, **30**, 375] and of PhSSPh in MeCN [(b) G. Bontempelli, F. Magno, and G. Mazzocchiri, *J. Electroanalyt. Chem.*, 1973, **42**, 57], except that the absorption-controlled analogue of the reduction of PhSH in dmf observed previously [see ref. (a) above] was not detected in the present study.

‡ The charge transfer step is, in fact, nearly reversible on the c.v. time scale as the c.v. response remains visually unaltered with respect to peak separation for scan rates from 5–20,000 mV s^{-1}.

§ Confirmed by controlled potential electrolysis at process 2 and the ratio of polarographic peak currents for equimolar solutions of (**1**) and (**2**).

are identified with the couple in equation (1). In fact, d.c. polarograms of the products of electrolysis of (**2**) at peak 2 are typical of the mononuclear species (**1**) (Table) but the peak current is half that expected for formation of two molecules of (**1**) from one molecule of (**2**).

TABLE. D.c. polarography[a] of species (**1**) and (**2**) in MeCN

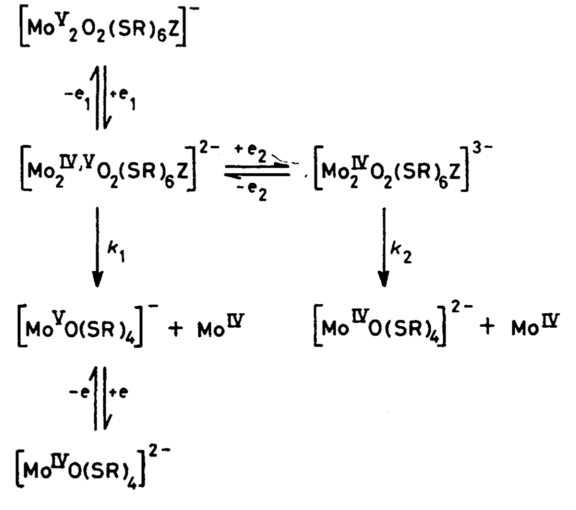
Anion[b]	$E_{\frac{1}{2}}$/V	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$[c]/mV
$[\mathrm{MoO(SPh)_4}]^-$	−1·13	71
$[\mathrm{MoO(S}\text{-}p\text{-tolyl})_4]^-$	−1·18	58
$[\mathrm{MoO(SCH_2Ph)_4}]^-$[d]	−1·23	
$[\mathrm{Mo_2O_2(SPh)_6(OMe)}]^-$	−1·26	62
$[\mathrm{Mo_2O_2(S}\text{-}p\text{-tolyl})_6\mathrm{(OMe)}]^-$	−1·34	54
$[\mathrm{Mo_2O_2(SCH_2Ph)_7}]^-$	−1·34	58

[a] 25 °C; drop time 0·5 s; Ag/AgNO$_3$ (0·1 M) reference electrode; Et$_4$N[PF$_6$] (0·1 M) supporting electrolyte. [b] 10^{-3} M solutions of the Et$_4$N$^+$ salts. [c] Standard deviation of 3 mV. [d] Calculated as the potential at 0·8517 I_p^1 in the c.v. at 25 °C (R. S. Nicholson, *Analyt. Chem.*, 1966, **38**, 1406).

At c.v. scan rates > 1000 mV s^{-1}, an anodic process 2′ (Figure 2b) associated with 2 can just be detected at 25 °C. However at −39 °C and fast scan rates, processes 2 and 2′ dominate (Figure 2b) and the total data are consistent with a two-electron process occurring *via* two one-electron transfer steps with similar E^0 values[5] (*i.e.*, $E_1^0 \sim E_2^0$) [equations (2) and (3)]. The above observations for anions (**2**) at 25 and −39 °C show that chemical reactions occur subsequent to electron transfer and a likely interpretation is given in the Scheme.

$$\mathrm{Mo_2^V} + e^-_1 \rightleftharpoons \mathrm{Mo_2^{IV,V}} \quad E_1^0 \tag{2}$$

$$\mathrm{Mo_2^{IV,V}} + e^-_2 \rightleftharpoons \mathrm{Mo_2^{IV}} \quad E_2^0 \tag{3}$$



SCHEME 1

The contribution of each pathway to the overall process under a given set of conditions will be governed by the relative magnitudes of the chemical rate constants k_1 and k_2 (Scheme 1) for the decomposition of the $\mathrm{Mo_2^{IV,V}}$ and $\mathrm{Mo_2^{IV}}$ species. Note that both chemical reactions lead to the production of one mole of $[\mathrm{Mo^{IV}O(SR)_4}]^{2-}$ per mole of $[\mathrm{Mo_2^VO_2(SR)_6Z}]^-$. Electroactive species are not formed from the other Mo atom and its fate is unknown.

The anions (**1**; R = alkyl) were not isolated previously as they spontaneously convert into (**2**)[3] at 25 °C. Cathodic scans at 25 °C for (**2**; R = alkyl), *e.g.*, $[\mathrm{Mo_2O_2(SCH_2Ph)_7}]^-$, are qualitatively similar to Figure 2a and are also interpreted in terms of Scheme 1. The mononuclear Mo$^{\mathrm{IV}}$ species $[\mathrm{MoO(SR)_4}]^{2-}$ [presumably exhibiting a $(4d_{xy})^2$-based ground state] appear to be indefinitely stable while the Mo$^{\mathrm{V}}$ analogues, (**1**; R = alkyl), are sufficiently stable to be observed on the c.v. time scale. In addition, species (**1**; R = alkyl) can be generated in low temperature solvent glasses and observed by e.s.r. spectroscopy.[6] The e.s.r. and electrochemical parameters indicate that the electronic state of the molybdenum atom in anions (**1**) is essentially unaffected by the substitution of alkane- for arene-thiolato ligands.

A primary oxidation process 3 (Figure 1b) is exhibited by anions (**1**), but not by (**2**). It is irreversible under all conditions examined and is assigned to the oxidation of ligand thiolate consistent with the overall process shown in equation (4). RSSR is observed electrochemically as is the

$$2[\mathrm{Mo^VO(SR)_4}]^- \xrightarrow{\text{MeCN}} [\mathrm{Mo_2^VO_2(SR)_6(MeCN)}] + \mathrm{RSSR} + 2e^- \tag{4}$$

secondary process 2 (Figure 1b) which, as described above, is characteristic¶ of the two-electron reduction of species (**2**). The data indicate that, in this case, the production of (**2**) is a kinetically controlled process of second or higher order. A mechanism consistent with the available data is presented in equations (5)—(8).** A similar oxidation

$$[\mathrm{Mo^VO(SR)_4}]^- \xrightarrow{\text{MeCN}} [\mathrm{Mo^VO(SR)_3(MeCN)}] + \mathrm{SR}\cdot + e^- \tag{5}$$

$$[\mathrm{Mo^VO(SR)_3(MeCN)}] + [\mathrm{Mo^VO(SR)_4}]^- \xrightarrow{\text{slow}} [\mathrm{Mo_2^VO_2(SR)_6(MeCN)}] + \mathrm{SR}^- \tag{6}$$

$$\mathrm{SR}^- \longrightarrow \mathrm{SR}\cdot + e^- \tag{7}$$

$$2\mathrm{SR}\cdot \longrightarrow \mathrm{RSSR} \tag{8}$$

occurs chemically when FeCl$_3$ reacts[3] with (**1**) [equation (9)].

$$2[\mathrm{Mo^VO(SR)_4}]^- + \mathrm{Fe^{III}Cl_3} \xrightarrow{\text{MeCN}} [\mathrm{Mo_2O_2(SR)_6Cl}]^- + \mathrm{Fe^{II}Cl_2} + \tfrac{1}{2}\mathrm{RSSR} + \mathrm{RS}^- \tag{9}$$

Oxidation and removal of one of the ligands apparently deprives (**1**; R = aryl) of its sterically-controlled kinetic stability.

Oxidation processes which are common to (**1**) and (**2**) occur at more positive potentials. These involve ligand thiolate oxidation from species (**2**). Oxidation of Mo$^{\mathrm{V}}$ to Mo$^{\mathrm{VI}}$ has not been detected in the present systems. The behaviour parallels that[7] of other mononuclear oxomolybdenum(v) species and is not surprising in view of the lack of

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¶ Existing data indicate that the half-wave potentials of (**2**) are essentially independent of the nature of the unique bridging ligand Z.

** The binuclear product is formulated with MeCN co-ordinated in the unique bridging position as benzene thiolate cannot occupy that position [see ref. 3].

thermodynamically stable mononuclear compounds [Mo^{VI}-OL_n]. However, the formal oxidation potential of Mo^{V} would also be expected to be ligand-dependent and may well be shifted negatively in other systems. In addition, ligand cysteinate redox processes might be considered in detailed examinations of the electron transfer mechanisms of molybdoenzymes.

(*Received, 5th July* 1979; *Com.* 728.)

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