

First Characterization of a Tetrathiomolybdate(v) Derivative by EPR, UV-VIS and IR Spectroelectrochemistry

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The trinuclear complex ion $[(\text{NC})(\text{OC})_3\text{Re}(\text{MoS}_4)\text{Re}(\text{CO})_3(\text{CN})]^{2-}$ 1^{2-} is reversibly reduced to a Mo^V containing trianion 1^{3-} , which exhibits hypsochromically shifted charge-transfer bands, bathochromically shifted CN, CO and MoS stretching frequencies and an axial EPR signal with $g_{\parallel} > g_{\perp}$.

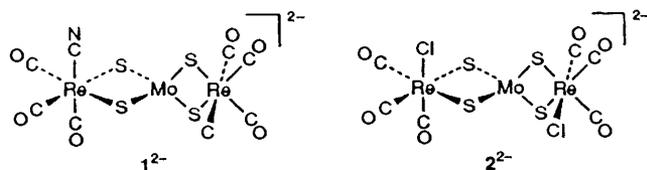
Four- or five-coordinate Mo^V complexes involving a mixed O/S donor atom set have been much studied¹ with regard to their biological relevance, *e.g.* in the semireduced molybdopterin cofactor.² The reduction of stable tetrathiomolybdate(vi), MoS₄²⁻, however, requires a very negative reduction potential³ of -2.94 V *vs.* Fe(C₅H₅)₂^{0/+} in DMF (dimethyl formamide) although the molybdenum 4d orbitals are easily populated optically in relatively low-lying ligand-to-metal charge-transfer excited states.⁴ In our efforts to characterize d¹ tetrathiomolybdates³ we have now used the twofold coordination of neutral but strongly polarizing low-spin d⁶ fragments Re(CO)₃(CN) to MoS₄ⁿ⁻ in order to effect a reversible Mo^{VI}/Mo^V transition at moderately negative potentials. Complexes of MoS₄³⁻ may have been involved in electrochemical processes of (L_nM)₂(μ-MoS₄), L_nM = (bpy)₂Ru²⁺,⁵ Mo(CO)₄,^{6a} CuCN;^{6b} we now report the first characterization of such species by spectroelectrochemical techniques.

The trinuclear complex ion $[(\text{NC})(\text{OC})_3\text{Re}(\text{MoS}_4)\text{Re}(\text{CO})_3(\text{CN})]^{2-}$ 1^{2-} was obtained as the bis(tetraethylammonium) salt by treatment of $[\text{Cl}(\text{OC})_3\text{Re}(\text{MoS}_4)\text{Re}(\text{CO})_3\text{Cl}]^{2-}$ 2^{2-} with NEt₄CN in acetonitrile. † (NEt₄)₂(**2**) was prepared‡ from Re(CO)₅Cl and (NEt₄)₂MoS₄ in acetonitrile and showed irreversible reduction at -1.76 V cathodic peak potential, on the other hand, (NEt₄)₂(**1**) is reversibly reduced at -1.62 V *vs.* Fe(C₅H₅)₂^{0/+} in MeCN-0.1 mol dm⁻³ Bu₄NPF₆.

Spectroelectrochemical reduction of the Mo^{VI} species 1^{2-} in an optically transparent thin layer electrolytic (OTTLE) cell^{3,7}

† Dark-blue compound [λ_{max} 16 890, 20 200(sh) and 27 320 cm⁻¹ in acetonitrile], satisfactory elemental analysis (C, H, N).

‡ Dark-blue compound [λ_{max} 17 180, 20 920(sh) and 27 750 cm⁻¹ in acetonitrile], $\tilde{\nu}(\text{CO})$ 2010, 1945 and 1905 cm⁻¹ (MeCN), satisfactory elemental analysis (C,H,N).



in the above electrolyte showed a clean electron-transfer equilibrium with isosbestic points and low-energy shifts of the weak CN ($2118 \rightarrow 2109 \text{ cm}^{-1}$) and of the more intense CO stretching bands [$2027(\text{w}) \rightarrow 1997(\text{w})$, $2009 \rightarrow 1985$, $1935(\text{br}) \rightarrow 1888(\text{br}) \text{ cm}^{-1}$, Fig. 1]. The *facial* substitution pattern at the tricarbonylrhenium(I) centre should produce three IR detectable CO stretching bands. The characteristic $\nu_{\text{as}}(\text{Mo-S})$ vibration of the tetrathiomolybdate core⁴ shows an expected³ low-energy shift on reduction from 460 to 440 cm^{-1} .

Whereas the low-energy shifts of the vibrational bands reflect the occupation of an antibonding orbital in the trianion 1^{3-} , the electronic absorption energies, in particular the two major allowed LMCT transitions $t_1 \rightarrow e$ and $t_2 \rightarrow e$ (spectroscopic T_d symmetry),⁴ show a characteristic intensity loss and a distinct high energy shift on reduction ($1^{2-} \rightarrow 1^{3-}$), *i.e.* from 16890 to 20240 cm^{-1} and from 27320 to $32800(\text{sh}) \text{ cm}^{-1}$. These shifts are larger than those of the only other previously reported $d^0 \rightarrow d^1$ tetrathiomolybdate system, *viz.*, the ReS_4^{-2-} species.³ The lowering of the metal oxidation state results in a relative destabilization of the metal d levels and in an increase of the energy of transitions to those orbitals. A weaker band, attributed to a less symmetry-favoured LMCT transition from one of the sulfur p orbital combinations (t_1), is observed for the Mo^{V} complex 3^{3-} at 17480 cm^{-1} . Intense metal-to-metal charge-transfer bands are not expected owing to poor orbital overlap.^{3b} Weak ligand-field transitions of the $4d^1$ system 1^{3-} lie at *ca.* $7500(\text{br,sh})$ and 9830 cm^{-1} and thus further in the near-IR region than those of the $5d^1$ ion ReS_4^{2-} ($11500\text{--}9500 \text{ cm}^{-1}$).³

The Mo^{V} trianion 1^{3-} as obtained by electrochemical reduction in $\text{Me}_2\text{CO}-0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NClO}_4$ shows an EPR signal only at temperatures below 10 K . The axial spectrum is broadened by a relatively small superhyperfine coupling from two $^{185,187}\text{Re}$ isotopes ($I = 5/2$, $a_{\parallel} = 3.2 \text{ mT}$),⁸ the ratio $g_{\parallel} = 2.019 > g_{\perp} = 1.965$ has been similarly reported recently for pentacoordinated Mo^{V} anions $\text{MoO}(\text{Sar})_4^{-}$.^{1a}

While the EPR results for the MoS_4^{3-} derivative thus agree with previously obtained values for Mo^{V} centres in a sulfur-rich environment, the new optical and IR data may be useful in obtaining EPR-independent information on the occurrence of such centres in biology^{1,2} or catalysis.⁹

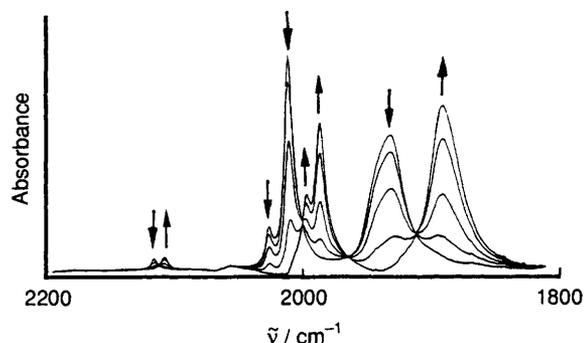


Fig. 1 IR absorption spectra in the CN/CO-stretching region from reductive spectroelectrochemistry of $1^{2-} \rightarrow 1^{3-}$ in acetonitrile $-0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6$

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