Redox Properties of Potassium μ-Thio-bis(hexacyanomolybdate(IV))

NEPAL C. HOWLADER, GILBERT P. HAIGHT, Jr.

School of Chemistry, University of Illinois, Urbana, Ill. 61801, U.S.A.

TREVOR W. HAMBLEY

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide 5001, S.A., Australia

and GEOFFREY A. LAWRANCE

Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra 2600, Australia

Received December 3, 1982

The reactions of thiomolybdenum compounds with cyanide has attracted some interest recently [1–5]. The interest arises in part from the observation that cyanide is an inhibitor of molybdoenzymes [6, 7], except nitrogenase, for which it is a substrate [8]. Further, there has been speculation that formation of soluble cyano complexes by reaction of MoS_2 with CN^- in the prebiotic soup may play a role in the chemical evolution of metalloproteins and enzymes [9]. Studies of the chemistry of molybdenum have been extensive in recent years, and have been reviewed [10].

The μ-thio dimer $[Mo_2(CN)_{12}S]^{6-}$ has been isolated previously [1], and was shown to to be remarkably inert to hydrolysis, a property reportedly common to bridging sulphide in molybdenum complexes [11]. The crystal structure of the double salt of $K_6[Mo_2(CN)_{12}S]$ with $K_2[MoO_4]$ illustrated the single Mo–S–Mo bridge, but displayed a Mo–S–Mo angle of 169.5°. The reasons for this bending were not obvious, but it may arise from O···N contacts in the double salt employed. Infrared spectra of the simple potassium salt suggested a linear Mo–S–Mo in that salt, which is the expected geometry [1].

We have prepared the $K_6[Mo_2(CN)_{12}S]$ complex by a different route, from reaction of aqueous solutions of KCN and $(NH_4)_2Mo_2(S_2)_6 \cdot 2H_2O$ [12] in a 5:1 molar ratio. Upon standing for approximately seven days, large green crystals of the product formed, and were collected by filtration and air dried. The product was spectroscopically analogous to the reported complex [1], and a brief structural analysis of one isolated crystal confirmed the $Mo_2(CN)_{12}S^{6-}$ unit*. Since Mo(IV) is an intermediate oxidation state for molybdenum, we have investigated the redox properties of the complex; in view of the chemical stability of the Mo(IV) dimer, the reactivity of oxidized or reduced forms was of interest.

The voltammetry of the complex was studied in both DMSO and water, using mercury (dropping mercury, DME, or hanging mercury drop, HMDE) electrodes, or gold and platinum billets, as the working electrodes. A platinum coil auxiliary electrode and a saturated (KCl) calomel reference electrode were employed. Solutions were degassed with argon. The electrochemical equipment employed has been described elsewhere [13]. Both oxidation and reduction processes were observed in both solvents, and the results are collected in Table I.

Reduction of the dimer in both DMSO and water occurs at very negative potentials near the solvent limit in each case. The behaviour in the two solvents differs, with a quasireversible couple observed in DMSO at −2.08 V, while the reduction in water is completely irreversible, and occurs at markedly lower potential (−1.46 V). The reduction occurred too near the solvent limit to permit accurate coulometry experiments. However, d.c. waveheight comparisons with a variety of complexes where the couple is well defined support the assignment of a two electron couple per dimer unit. The calculated diffusion coefficient for the quasireversible couple in DMSO assuming $n = 2$ (Table I) is reasonable for an ion of this charge and size. Further, the irreversible reduction in water and the quasireversible reduction in DMSO have similar peak currents in the cyclic voltammograms, and it is reasonable that the totally irreversible process at very negative potential in water proceeds with complete reduction of Mo(IV) to Mo(III). Several oxidation processes of the cleaved and reduced dimer in water are seen at more positive potentials on the reverse scan in the cyclic voltammogram, and these can be assigned to oxidation of the Mo(III) monomer fragments. These waves are absent in DMSO, where integrity of the dimer is preserved on the voltammetric timescale.

The variation with solvent is illustrated clearly in Fig. 1 in the cyclic voltammograms. The irreversible and quasireversible nature of the reduction in water and DMSO respectively are also illustrated in the variable frequency in-phase a.c. polarography, also illustrated in Fig. 1. The behaviour in DMSO is typical of a quasireversible couple [14], while the small and frequency independent a.c. signal observed in water is characteristic of an irreversible process. The variation from DMSO to water clearly implicates water in the mechanism for decomposition of the

---

*The complex crystallized in the orthorhombic space group *Pnma* or *Pn*2_1*a*, *a* 11.754(2), *b* 14.901(7), *c* 18.140(2) Å, *U* 3177.3 Å^3. Refinement was compounded by disorder problems which made choice of space group and full refinement difficult.

0020-1693/83/0000-0000/$03.00

TABLE I. Redox Processes for $K_6[Mo_2(CN)_{12}S]$.

Solvent[a]	Process	d.c. (V)	a.c. (V)	Elec.[b]	Cyclic d.c.				n (Coulometry)
					E_{pf} (V)	E_{pb} (V)	ΔE (mV)	$E_{1/2}$ (V)	
DMSO	$Mo^{IV} \rightarrow Mo^{V}$	~ +0.1[c]	−0.07, +0.09[d]	Hg[e]	+0.22	−0.10	–	–	
				Au[f]	$+0.14_5$	-0.04_5	190	+0.05	
				Pt[g]	+0.20	−0.16	360	+0.02	2.1
	$Mo^{IV} \rightarrow Mo^{III}$	−2.08[h]	−2.08[i]	Hg[g]	-2.15_3	-2.06_6	87	−2.11	
				Au[f]	~ −2.2	abst[j]	–	–	
water	$Mo^{IV} \rightarrow Mo^{V}$	+0.22, +0.31[k]	$+0.21_5$, +0.30[l]	Hg[e]	+0.34	−0.08	–	–	
				Au[m]	+0.33	+0.16	170	$+0.24_5$	
				Pt[m]	+0.35	+0.15	200	+0.25	1.9
	$Mo^{IV} \rightarrow Mo^{III}$	−1.46[n]	−1.50[o]	Hg	−1.60[p]	abst.	–	–	

[a] 0.1*M* $(Bu_4N)(BF_4)$ electrolyte; ambient temperature; complex concentrations 0.66 and 0.82 m*M* in DMSO and water respectively. [b] Stationary HMDE, or Au and Pt button electrodes. [c] Broad wave near solvent limit at the DME; $i_d \sim 3.6$ μA. [d] Double wave, complicated by adsorption component of the more negative signal; ω 100 hz. [e] 500 mV/s scan rate; wave complicated by adsorption. [f] 50 mV/s scan rate. [g] 100 mV/s scan rate. [h] $i_d = 3.94$ μA; $E_{1/4} - E_{3/4} = 62$ mV; $D = 2.5 \times 10^{-6}$ cm^2 s^{-1} with n = 2. [i] ω 100 Hz. [j] Wave near solvent limit and not well resolved. [k] Two distinct steps observed; total $i_d \sim 5$ μA, since near solvent limit. [l] Preceded by a clearly characterized adsorption shoulder, defined from phase-sensitive a.c. polarography, at +0.13 V; ω 40 Hz. [m] 200 mV/s. [n] Simple wave near solvent limit; $i_d \sim 6$ μA; $E_{1/4} - E_{3/4}$ 70 mV. [o] ω 40 Hz. [p] Oxidation (back) waves seen at −0.72 V and −0.27 V; reduction waves occur at −0.36 V and −0.74 V on the second scan.

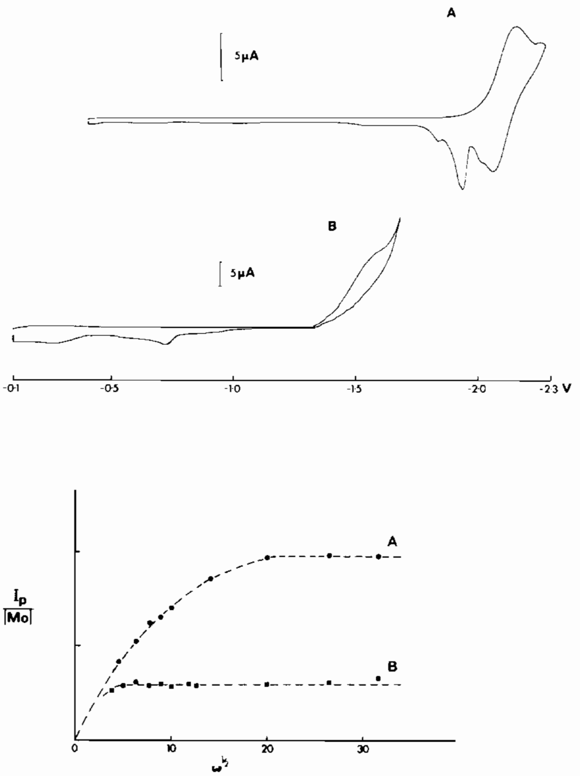

Fig. 1. Electrochemical reduction of $K_6[Mo_2(CN)_{12}S]$ in (A) DMSO, and (B) water. Top: cyclic voltammetry at the HMDE (scan rate 200 mV/s). Bottom: frequency dependence (I_p/[Mo] versus $\omega^{1/2}$, Hz) of the in-phase a.c. peak current.

reduced dimer, probably by rapid hydrolysis of the μ-thio bridge.

Oxidation in both DMSO and water at mercury electrodes is complicated severely by adsorption processes (Fig. 2); at platinum and gold electrodes, the adsorption phenomena are not apparent, and a single but broad and quasireversible cyclic voltammogram is observed in each solvent. Comparison of waveheights for oxidation in the d.c. polarography and cyclic voltammograms in both solvents with waveheights for reduction indicate that the same number of electrons are involved in each process, *i.e.* oxidation is a two electron per dimer unit process. The d.c. process in water indicates a stepwise process may occur, and two signals are clearly observed in the a.c. polarogram. Variable frequency and phase-sensitive a.c. polarography indicates both a.c. processes are electron transfer in nature, supporting the concept of stepwise one electron oxidations. The two steps are not resolved in the cyclic voltammetry at solid electrodes, while the results at the HMDE are severely complicated by adsorption phenomena. Coulometry at a controlled potential 200 mV above the $E_{1/2}$ value using a platinum basket working electrode showed a two electron per dimer oxidation in both water and DMSO, although the oxidation was irreversible on the coulometric timescale, with molybdenum(V) monomer units being formed. Voltammetry of the products confirmed the irreversible nature of the coulometric oxidation, since the initial waves were absent in the final product.

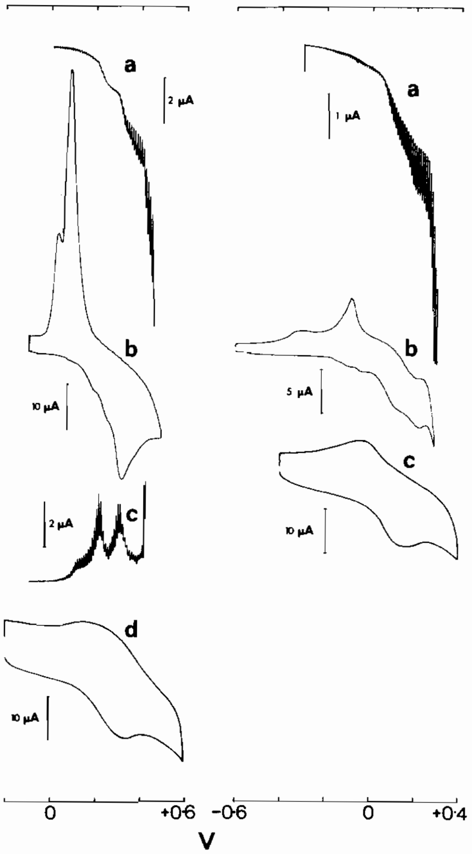

Fig. 2. Electrochemical oxidation of $K_6[Mo_2(CN)_{12}S]$. Left (in water): (a) d.c. polarogram; (b) cyclic voltammetry at the HMDE (scan rate 200 mV/s); (c) a.c. polarogram, ω 60 Hz; (d) cyclic voltammetry at stationary Au (scan rate 200 mV/s). Right (in DMSO): (a) d.c. polarogram; (b) cyclic voltammetry at the HMDE (scan rate 200 mV/s); (c) cyclic voltammetry at stationary Au (scan rate 50 mV/s).

The integrity of the dimer is preserved on the voltammetric timescale upon oxidation to Mo(V) and reduction to Mo(III) in DMSO, although the products are not stable on the coulometric timescale. The quasireversible Mo(IV)/Mo(V) couple observed near +0.2 V in both water and DMSO suggests that with the appropriate choice of ligands and solvent, multinuclear Mo(V) complexes may be synthetically accessible from the Mo(IV) precursors.

References

1 M. G. B. Drew, P. C. H. Mitchell and C. F. Pygall, *J. Chem. Soc., Dalton Trans.*, 1213 (1979).

2 M. G. B. Drew, P. C. H. Mitchell and C. F. Pygall, *Angew. Chem., Internat. Ed., Engl., 15,* 784 (1976).

3 A. Müller and P. Christophliemk, *Angew. Chem., Internat. Ed., Engl., 8,* 753 (1969).

4 E. Crepaz, *Gazzetta, 58,* 391 (1928).

5 P. C. H. Mitchell and C. F. Pygall, *J. Inorg. Biochem., 11,* 25 (1979).

6 R. C. Bray in 'Proc. 2nd. Internat. Conf. Chem. Uses Molybdenum', P. C. H. Mitchell (ed.), Climax Molybdenum Co., London, (1977), p. 26.

7 V. Massey and D. Edmonson, *J. Biol. Chem.*, 245, 6595 (1970).

8 R. W. F. Hardy and E. Knight, *Biochim. Biophys. Acta, 139,* 69 (1967).

9 M. T. Beck and J. Ling, *Naturwiss., 64,* 91 (1977).

10 E. J. Steifel, *Progr. Inorg. Chem., 22,* 1 (1977).

11 P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 110 (1975).

12 A. Müller, R. G. Bhattacharyya and B. Pfefferkorn, *Chem. Ber., 112,* 778 (1979).

13 N. C. Howlader, G. P. Haight Jr., T. W. Hambley, M. R. Snow and G. A. Lawrance, *Inorg. Chem.*, submitted.

14 D. E. Smith in 'Electroanalytical Chemistry', Vol. 1, A. J. Bard (ed.), Marcel Dekker, New York (1966), p. 1.