Separation and Unusual Stability of the Sulphur-bridged Ion $Mo_2S_2O_2^{2+}$

By BRUCE SPIVACK and ZVI DORI*

(*Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel*)

Summary The sulphur-bridged ion, $Mo_2S_2O_2^{2+}$, which has been separated from the parent compound, $Na_2Mo_2O_2S_2$-(cysteine)$_2$, is stable towards acids and does not dissociate to a paramagnetic monomeric species, as does its oxo-bridged analogue, $Mo_2O_4^{2+}$, even in very concentrated acidic solutions.

IT is now well recognized that in certain molybdo-enzymes, the molybdenum atom at the active site is bound, at least in part, to sulphur ligands, either as a thiol group from a cysteine residue, or as sulphide ions.[1] In this connection, sulphido-bridged complexes of Mo^V are of interest, and recently several such complexes have been synthesized, characterized, and their structures determined by three-dimensional *X*-ray diffraction techniques.[2] We now report the separation and unusual stability of the sulphur-bridged ion, $Mo_2S_2O_2^{2+}$.

A solution of $Mo_2S_2O_2^{2+}$ has been prepared by dissolving the complex di-μ-sulphido-bis[oxo-(cysteinato)molybdenum(V)], $[Mo_2S_2O_2(cysteine)_2]^{2-}$ in 1N-HCl and running the solution through Sephadex G-10[3] to remove the liberated cysteine. The effluent solution is diamagnetic and has the absorption spectrum shown in the Figure. Addition of cysteine and neutralization to pH 6 regenerates the parent complex. Thus, we suggest that the absorbing species which gives rise to the observed electronic spectrum is the aquo-ion (I). This structure is analogous to that of the known oxo-bridged dimer, $Mo_2O_4^{2+}$.[4]

Of particular interest is the stability of this ion towards strong acids. It is well known that in many cases the S^{2-} ligand can be easily removed as H_2S from the co-ordination sphere of metal ions upon treatment with acids. For

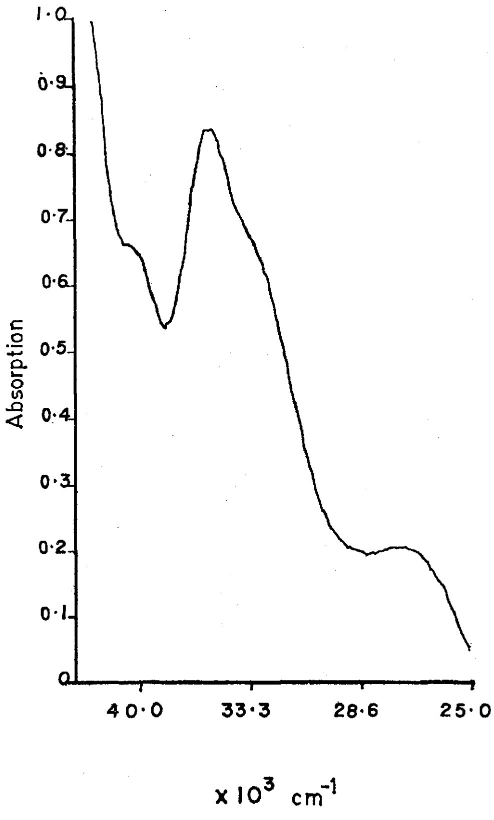
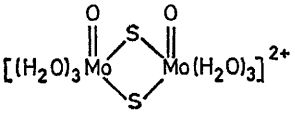


FIGURE.

example, HCl liberates hydrogen sulphide from ferredoxins.[5] Similarly, MoS_4^{2-} reacts with HCl to produce H_2S and insoluble sulphides.[6] Thus, it was unexpected to find that the electronic absorption spectrum of the $Mo_2S_2O_2^{2+}$ ion shows only a slight red shift (probably due to substitution of Cl^- for co-ordinated water) as the acid concentration is increased to 10N. Furthermore, the solution remains diamagnetic and no evolution of H_2S is observed even after several weeks. These results are unexpected in view of the fact that the analogous oxo-bridged ion is known to dissociate into paramagnetic monomeric species even at much lower acid concentrations.[7]



(I)

Structural investigations[2] have shown that the Mo–Mo distance in sulphido-bridged complexes of Mo^{V} is longer than that found in the oxo-bridged analogues by *ca.* 0·3 Å. It is therefore reasonable to suggest that the Mo–Mo interaction (*i.e.* direct Mo–Mo overlap) is probably not the major factor influencing the stability of the bridge towards dissociation. Since concentrated acid does not split the bridge with liberation of H_2S, it is suggested that the nucleophilic character of the S^{2-} ligand in this ion is greatly reduced by a strong Mo–S interaction. Consequently, the sulphide ion is less susceptible to protonation, which we believe, is necessarily the first step in the formation of monomeric, paramagnetic species.

We thank Dr. G. Schmuckler for helpful discussions.

(*Received*, 16*th July* 1973; *Com.* 1006.)

---

[1] R. C. Bray and J. C. Swann, *Structure and Bonding*, 1972, **11**, 107.

[2] B. Spivack and Z. Dori, *J.C.S. Dalton*, 1973, **1173** and refs. therein.

[3] The separation and purification of transition-metal complexes by chromatography on Sephadex G-10 will be published shortly, G. Schmuckler, personal communication.

[4] M. Ardon, L. Halicz, and A. Pernick, Abstracts of 42nd Meeting, Israel Chemical Society, 1972, p. 76.

[5] J. C. Rabinowitz, *Adv. Chem.*, 1971, **100**, 322.

[6] G. Kruss, *Annalen*, 1881, **225**, 29.

[7] C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 831.