Sulphur-bridged Complexes of Mo^{V} and Mo^{VI} Containing the Ligands Ethylenediaminetetra-acetic Acid, Cysteine, and Histidine

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Summary The synthesis of characterization of several sulphur-bridged complexes of Mo^{V} and Mo^{VI} containing edta, cysteine, and histidine are reported.

IT is now well established that molybdenum has an essential function in a number of sulphydryl enzymes such as xantine oxidase,[1] aldehyde oxidase,[2] nitrate reductase,[3] and nitrogenase.[4] The importance of molybdenum–sulphur binding in these systems has been suggested by several workers on the basis of e.s.r. measurements, and it has also been suggested that at the active site the molybdenum is bound, at least in part, to a cysteine residue.[1,2] However, Spence has pointed out[5] that the possibility of the existence of sulphur-bridged species in molybdenum enzymes should not be ruled out. This type of bridging is known to play a vital role in non-heme iron proteins such as ferrodoxin.

We have prepared sulphur-bridged complexes of Mo^{V} and Mo^{VI} containing ligands such as ethylenediaminetetra-acetic acid, cysteine, and histidine, chosen because of their relevance to biological systems.

The reaction of K_2MoS_4 with H_2K_2(edta) in aqueous solution at pH 6·0 has led to the isolation of a light-red crystalline material whose elemental analysis agrees well with the formula $K_2Mo_2O_4S$(edta),H_2O. The complex is a 2 : 1 electrolyte in water and its electronic absorption spectrum consists of bands at 21,000(sh), 31,400 (ϵ 6000) and 35,000 (8100) cm^{-1}. The compound crystallizes in space group *Ima*2 (or *Imam*) of the orthorhombic system with a cell of dimensions $a = 7{\cdot}26 \pm 0{\cdot}02$, $b = 19{\cdot}31 \pm 0{\cdot}02$, $c = 14{\cdot}12 \pm 0{\cdot}02$ Å, $V = 1979$ Å^3, $D_m = 2{\cdot}23 \pm 0{\cdot}02$, $D_c = 2{\cdot}24$ g/cm^3 for $Z = 4$. The i.r. spectra indicate that all four carboxyl groups are bound,[6] and the absence of a strong band at the 490—500 cm^{-1} region[7] suggests that the complex does not contain the thiomolybdenyl group. The same compound can also be prepared by bubbling H_2S through a water solution containing the known Mo^{VI}–edta complex[8] at pH 7·0—8·0.

The ^1H n.m.r. spectra of the edta complexes of Mo^{V} and Mo^{VI} have been reported by Sawyer.[9,10] Both complexes exhibit a quartet assigned to the methylene protons and a singlet assigned to the ethylene protons (for Mo^{VI}–edta: centre of quartet at 3·70, J 17 Hz; singlet at 3·87; for Mo^{V}–edta: centre of quartet at 3·40, J 17 Hz; singlet at 2·67)† The large upfield shift of the Mo^{V}–edta singlet has been attributed to the shielding of the ethylenic protons by the bridging oxygen atoms.[10]

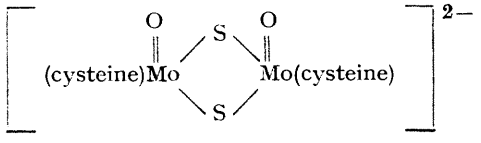
The n.m.r. spectrum of the complex $K_2Mo_2O_4S$(edta) is more complicated, consisting of two singlets at 3·50 and 2·60

† Chemical shifts in p.p.m. relative to sodium 2,2-dimethyl-2-silapentane-5-sulphonate.

and an overlapping pattern of three quartets which are centred between 3·30 and 3·50. The appearance of the two singlets might suggest the existence of an equilibrium between a closed form (structure similar to the Mo^V–edta complex) in which the sulphur atom bridges the two molybdenum atoms, and an open form (a structure similar to that of the Mo^{VI}–edta complex)[11] in which the vacant co-ordination site on one of the molybdenum atoms is occupied by a water molecule. In support of the sulphur-bridged structure, we note the existence of a band of medium intensity at 470 cm^{-1} in the i.r. spectrum which may be associated with the Mo–S–Mo moiety.[12]

Mo^V complexes with cysteine‡ and histidine are well known[13] and the crystal structure of the cysteine complex[14] has been reported. When a water solution containing the Mo^V–cysteine complex is treated with H_2S a dark red solution results. From this solution, a red-orange crystalline material having the formula $Na_2Mo_2O_2S_2$(cysteine)$_2$, $4H_2O$ (I) has been isolated. It crystallizes in the monoclinic system, space group $P2_1$ (or $P2_1/m$) with a cell of dimension $a = 6{\cdot}69 \pm 0{\cdot}02$, $b = 14{\cdot}95 \pm 0{\cdot}02$, $c = 9{\cdot}62 \pm 0{\cdot}02$ Å, $\beta = 92{\cdot}0 \pm 0{\cdot}1°$, $V = 962$ Å^3, $D_m = 2{\cdot}30 \pm 0{\cdot}02$ cm^3, $D_c = 2{\cdot}29$ g/cm^3 for $Z = 2$.

The i.r. spectra of (I) and of the complex $[Mo_2O_4$(cysteine)$_2]^{2-}$ in the 700—1000 cm^{-1} region are shown in the Figure. The absence of the Mo–O–Mo–O band[15] at 740 cm^{-1} in the spectrum of (I) is apparent. In addition, (I) is diamagnetic and its ^1H n.m.r. spectrum is essentially the same as the one observed for $[Mo_2O_4$(cysteine)$_2]^{2-}$. Thus, we suggest the following structure for complex (I):



The electronic absorption spectrum of (I) consists of bands at 30,300(sh), 35,200(ε10,000), and 44,000(25,000) cm^{-1}, and the spectrum is unchanged in the pH range 5·0—8·5. However, at higher pH, the spectrum undergoes an irreversible change and we are currently trying to isolate the resulting product.

The known Mo^V–histidine complex $(Mo_2O_4$(histidine)$_2]^{2-}$ also reacts with H_2S at pH 8·0 to yield a red-brown diamagnetic crystalline material of composition $Na_2Mo_2O_2S_2$-(histidine)$_2$,H_2O (II). The i.r. spectrum of (II) is shown in the Figure. The absence of the Mo–O–Mo–O band suggests that the structure of (II) is similar to the structure of complex (I). By analogy with the Mo^V-histidine complex,[16] (II) is only sparingly soluble in water and at acidic pH exhibits electronic absorption bands at 27,000(sh), 32,200(sh), 35,800(ε8000), and 40,000(sh). Because of solubility problems we were not able to obtain the ^1H n.m.r. spectrum of this complex.

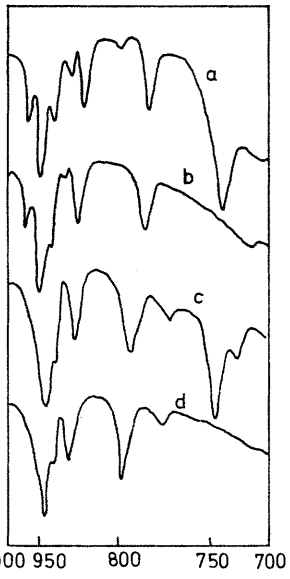


FIGURE. *The solid-state i.r. spectra in the* 700—1000 cm^{-1} *region of*: (a) $Na_2Mo_2O_4$(cysteine)$_2$,$5H_2O$; (b) $Na_2Mo_2O_2S_2$-(cysteine)$_2$,$5H_2O$; (c) $Na_2Mo_2O_4$(histidine)$_2$,$5H_2O$; *and* Na_2Mo_2-O_2S_2 (histidine)$_2$,$5H_2O$.

We thank Dr. David Dalton for his help in the n.m.r. measurements, and the Department of Chemistry for financial support.

(*Received, October 20th*, 1970; *Com.* 1814.)

‡ Several sulphur bridged complexes of Mo^V, including the cysteine complex reported here, have recently been isolated [A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421].

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