The Copper–Molybdenum Antagonism in Ruminants.
III. Reaction of Copper(II) with Tetrathiomolybdate(VI)

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Abstract

The stoichiometry of the reaction between Cu(II) and $MoS_4{}^{2-}$ in neutral aqueous solution was observed to proceed with a 1.5:1 Cu:Mo ratio. The reaction results in the reduction of Cu(II) and the quantitative formation of an insoluble solid. The results contrast with an earlier report of a 1:1 stoichiometric ratio, this latter ratio was, however, observed with Cu^{II}(albumin) as reactant, in this case no precipitate was observed. The insoluble products were examined by a number of spectroscopic techniques and by X-ray power diffraction and elemental analysis. Two products were identified. Solid A is isostructural with the known $(NH_4)Cu^{I}$-$Mo^{VI}S_4$, *i.e.* has the composition $M^{I}CuMoS_4$, M^{I} = $NH_4{}^+$, Na^+ or Et_4N^+. Solid **B** has the approximate composition $CuMoS_4O_x$, x = 2–3 and contains Cu(I) and Mo(V) centres. Formation of compound **B** therefore involves an unusual internal two-electron redox process. The reaction and products are of particular biological significance.

Introduction

In our previous paper [1] we reported preliminary results on the nature of the reaction in aqueous media between various Cu(II) compounds and the tetrathiomolybdate(VI) ion, $MoS_4{}^{2-}$. We now report more detailed studies, particularly on the insoluble solid that forms during the reaction.

This reaction is of special significance to the well documented Cu–Mo antagonism that afflicts ruminants [1–3]. Contrary to a recent claim [4] the reaction between Cu(II) species and $MoS_4{}^{2-}$ (and other oxythiomolybdate(VI) ions) is more facile than that between Cu(II) and S^{2-} ions [1]. Thus, the reaction with thiomolybdate ions, producing an insoluble Cu-containing product, offers a plausible

explanation of how Mo can cause Cu deficiency in ruminants.

Cu^I–Mo–S systems have also attracted considerable attention because of their interesting structural and electronic properties, much of this work, pioneered by Muller [5], has recently been reviewed [4–6]. In these studies non-aqueous solvents, Cu(I) reactants and an organic ligand were generally used so as to produce discrete, isolable, complexes. Although the formation of Cu(I) from the reaction between Cu^{II} and $MoS_4{}^{2-}$ is well known, there has been no detailed investigation on the mechanism of this redox reaction, it is generally assumed, e.g. see [4], that the product still contains the $MoS_4{}^{2-}$ ion. The nature of the redox reaction is also relevant to Fe–Mo–S cluster formation in the enzyme nitrogenase [7]. The results presented here show that an unusual two-electron internal transfer reaction can occur.

Experimental

All chemicals used were of 'AnalaR' or equivalent grade. The ammonium, tetraethylammonium and sodium salts of $MoS_4{}^{2-}$ were prepared according to described methods [8, 9]. $(Et_4N)_2[Mo_2{}^VO_2S_2(S_2)_2]$ was prepared as described by Rittner *et al.* [10].

The stoichiometry of the reaction between Cu(II) and $MoS_4{}^{2-}$ was determined in pH 7.4 phosphate-buffered solutions containing 0.15 mol dm^{-3} NaCl, using bis(glycinato)copper(II) and $(NH_4)_2MoS_4$ as reactants. Concentrations of reactants were of the order 10^{-2}–10^{-4} mol dm^{-3}. After mixing the two reactants the reaction mixture was centrifuged before spectroscopic examination. The presence of chloride ion had no observable effect on the reaction. To obtain the solid products formed during the reaction fresh aqueous solutions of $CuSO_4 \cdot 5H_2O$ and $M_2{}^{I}$-MoS_4 (M^{I} = $NH_4{}^+$, Et_4N^+ or Na^+) were used. The solids were collected by filtration, washed with water, ethanol and ether and then dried in a dessica-

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tor under vacuum. Previous work [11] showed that the solids were readily contaminated with any copper(II) coordinating ligands that were used (e.g. amino acids or peptides), so these were avoided in this work. For elemental analyses the solids were first digested with a bromine–carbon tetrachloride mix followed by several acid digestion–evaporation cycles on a water-bath (to avoid overheating).

Cu and Mo analyses were carried out by atomic absorption on an IL 151 instrument. Some of the Mo analyses were also determined by the University of Manchester Microanalytical Service, as were the C, H, N and S analyses. Na was determined by flame photometry with a Corning 400 photometer. UV–Vis spectra were recorded with a Perkin-Elmer 555 spectrophotometer using a thermostatted cell-block. IR spectra were measured on a Perkin-Elmer 683 instrument with KBr disc samples. ESR spectra were recorded with a Bruker ER-200D spectrometer using liquid N_2 frozen samples. X-ray powder diffraction patterns (XRD) were recorded using Ni-filtered Cu radiation from a Philips PW 1010 generator and a Debye–Scherrer camera. The powder patterns obtained were indexed and compared with known patterns in the literature [12]. X-ray photoelectron spectra (XPS) were recorded at the University of Loughborough.

Results

Stoichiometry of the Reaction between Cu^{II} and $MoS_4{}^{2-}$

As noted earlier [1], on mixing aqueous solutions containing Cu(II) and $MoS_4{}^{2-}$ reactants there was an immediate reduction in the UV–Vis spectrum of both reactants and of the ESR spectrum of Cu(II). The reaction was also accompanied by the formation of a red–brown fine precipitate. The formation of this solid was evident even at 10^{-4} mol dm^{-3} reactant levels, indicating its insolubility.

The stoichiometry for complete removal of the UV–Vis (see Fig. 1) and ESR spectra of the reactants required a 1.5:1 Cu:Mo ratio, and not 1:1 as claimed earlier [1]. However, with bovine serum albumin as the Cu(II) ligand a 1:1 ratio was required for the same UV–Vis and ESR changes. In this latter case no precipitate was observed. In all cases only the ESR spectrum of the initial Cu(II) species was observed during the course of the reaction.

Attempted Characterisation of the Solid Products

The product precipitates were collected from solutions with Cu:Mo reactant ratios varying from 1:1 to 2:1. $(NH_4)_2MoS_4$, $(Et_4N)_2MoS_4$ and $Na_2MoS_4 \cdot 3.5H_2O$ were all used as sources of $MoS_4{}^{2-}$ ion. Difficulties were encountered in obtaining consistent analytical results, especially for Mo and S.
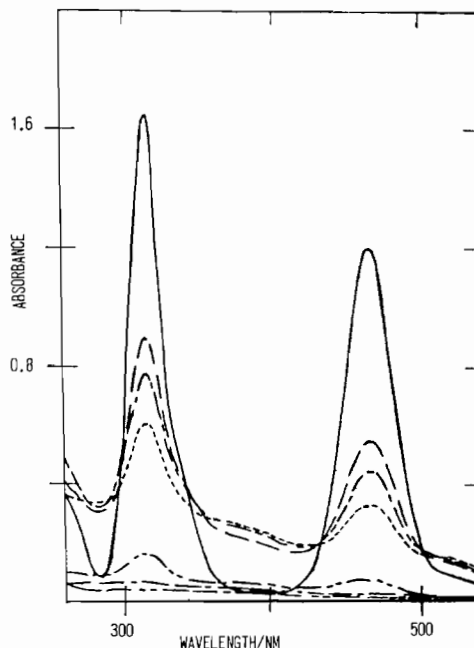

Fig. 1. UV–Vis spectra of aqueous solutions of $(NH_4)_2$-MoS_4 (1×10^{-4} mol dm^{-3}) and $[Cu(GlyO)_2]$. Mo:Cu, 1:0 ——; 1:0.8 — —; 1:0.96 – · –; 1:1.12 – – –; 1:1.28 – · · –; 1:1.44 — — · — —; 1:1.60 — — · ·.

In all cases small amounts (1–2%) of the cation from the starting $MoS_4{}^{2-}$ salts were evident. The total analytical figures added up to *ca.* 89% for any of the solids, typical results are shown in Table I. The analytical figures taken together with the XRD patterns, some of which are given in Table II, suggest the presence of two compounds. Compound **A**, from the XRD results is microcrystalline, dominates the XRD photographs of the solids produced from 1:1 Cu:Mo solutions, and is isostructural with the known $(NH_4)CuMoS_4$ [13], *i.e.* has the composition $M^ICu^IMo^{VI}S_4$, the lack of any ESR signal from the ammonium compound confirming the metal oxidation states of I and VI. From the composition and X-ray structural analysis [13] all S atoms are present as sulphide.

Compound **B**, from the XRD results is amorphous and dominates the XRD photographs when higher aqueous Cu:Mo ratios were used. The elemental analyses are consistent with a stoichiometry for **B** close to $CuMoS_4O_x$ ($x = 2–3$), the oxygen content being deduced from the *ca.* 11% deficiency in the elemental analyses. Both the elemental analyses and thermogravimetric analyses confirm the absence of 0 in the form of H_2O. This compound displays a distinctive ESR signal (Fig. 2) which from its *g* values and form can be attributed to the presence of monomeric Mo(V) centres. Interestingly, if the solid reaction product was not thoroughly washed then an extra ESR signal was evident which was

TABLE I. Typical Percentage Elemental Compositions of the Insoluble Reaction Products

Reactant ratio Cu(II):$M^I_2MoS_4$	M^I	Percentage composition							Total
		Cu	Mo	S	M^I	C	H	N	
1:1	NH_4	20.3	26.7	39.7	–	0.5	0.5	1.2	88.9
1.5:1	NH_4	21.7	27.1	38.3	–	0.6	0.5	1.1	89.3
2:1	NH_4	21.5	25.5	35.2	–	0.8	0.3	0.4	83.7
1:1	Na	20.5	27.8	38.7	2.1	0.4	0.5	0	90.0

TABLE II. XRD Data for the Copper Thiomolybdate Solids: d-Spacings (10^{-10} m) and Relative Intensities in Parentheses

1:1 solid[a]	1.5:1 solid[b]	1:1 solid[c]	$(NH_4)CuMoS_4$
5.67(100s)			5.67(100s)
5.29(10d)	5.3(100d)	5.3(100d)	
4.00(15s)			4.01(25s)
	3.1(10d)	3.10(10d)	
2.98(25s)			2.99(30s)
2.84(5s)			2.83(12s)
2.52(1s)			2.53(8s)
2.43(5s)			2.44(18s)
	2.35(5d)	2.40(10d)	
2.25(5s)			2.24(20s)
1.84(10s)	1.89(15s)	1.90(10s)	1.85(20s)
1.79(1s)			1.79(12s)

[a]Using $(NH_4)_2MoS_4$ at a 1:1 Cu:Mo ratio. [b]Using $(NH_4)_2$-MoS_4 at a 1.5:1 ratio. [c]Using $Na_2MoS_4 3.5H_2O$ at a 1:1 ratio; s = sharp, d = diffuse.

typical of Cu^{II} ions in tetrahedral sites ($g_{11} = 2.41$, $A_{11} = 128$ G). Power saturation measurements of the ESR spectrum showed that the three resonances saturated at the same power level, suggesting that this signal arises from just one paramagnetic centre. The observation of the three g features is as expected for an anisotropic Mo(V) system of low symmetry.

XPS of **B** confirms Cu^I to be present and not Cu(II), since no 'satellite lines' typical of the Cu(II) state [14] were observed. The spectrum shows the Mo atoms to be in the same environment (sharp $Mo_{3d5/2}$ and Mo_{3p} peaks) and also shows 0 to be present at amounts above that expected from just surface contamination. Some of the results are summarized in Table III. The nature of the spectrum also suggests considerable electron delocalisation to be present, this is also evident from the fact that many other S-ligand systems give Mo electron-binding energies that are insensitive to the nature of the Mo oxidation-state.

The IR spectrum of **B** shows two sharp peaks at *ca.* 460 and 910 cm^{-1} which can be assigned to ν(Mo–S) and ν(Mo–O) transitions respectively. No absorptions, however, were observed in the 500–520 cm^{-1} region where the ν(S–S) mode of the persulphide (S_2^{2-}) ion would be expected. Apart
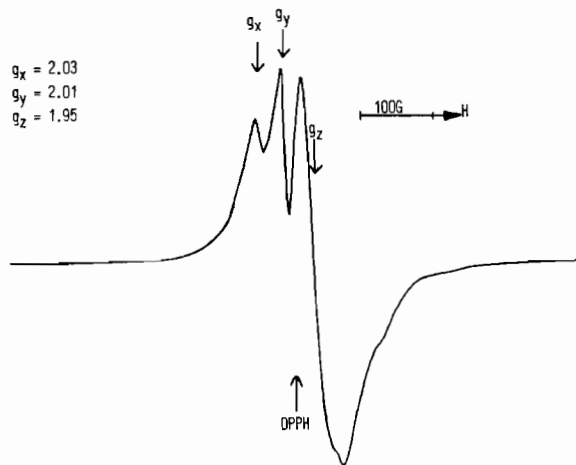

Fig. 2. ESR spectrum of the solid at 120 K obtained from a 1:1 Cu(II):MoS_4^{2-} reaction solution (DPPH = 2,2-diphenyl-picrylhydrazyl calibrant).

$g_x = 2.03$
$g_y = 2.01$
$g_z = 1.95$

TABLE III. XPS Data for Thiomolybdates: Binding Energies (eV), Resolution ±0.2 eV

Sample	S(2p)	$Mo(3d_{5/2})$	$Cu(2p_{3/2})$
$(NH_4)_2MoS_4$	162.3	229.9	
CuCN			934.1
$(NH_4)CuMoS_4$	161.6	229.7	932.5
$(Et_4N)_2[Mo_2O_2S_2(S_2)_2]$		230.5[a]	
CuMoS (1.5:1)[b]	163.2	230.5	934.4

[a]Taken from ref. 10. [b]Solid from a 1.5:1 Cu:MoS_4^{2-} solution.

from this latter difference the IR and XPS (Mo_{3d}) results for **B** and for the anion $[Mo_2^VO_2S_2(S_2)_2]^{2-}$, reported by Rittner *et al.* [10], are very similar.

Conclusions

The spectroscopic results clearly show that the stoichiometry of the reaction between Cu(II) and MoS_4^{2-} proceeds with a 1.5:1 Cu:Mo ratio. This contrasts with our earlier report of a 1:1 stoichiometry for low molecular mass Cu(II) complexes [1].

That this latter result is erroneous is clearly evident from a comparison of the UV–Vis spectra in Fig. 1 with those given earlier [1]. The latter were complicated by scattering due to the presence of increasing amounts of suspended solids as the Cu:Mo ratio increased (as noted by the authors). In the present work this was avoided by careful centrifugation of the reaction mixtures. Cu–albumin, however, was still observed to react with a 1:1 ratio and in contrast to the low molecular mass Cu(II) reactants, no precipitate was observed to form.

The formation of the highly insoluble, probably polymeric, solids is highly significant to the Cu–Mo antagonism. At the 1.5:1 Cu:Mo reactant ratio virtually all the Mo is precipitated in the forms of compounds **A** and **B**, solid **A** is clearly isostructural with the known $(NH_4)CuMoS_4$ compound [13] which contains Cu^I, Mo^{VI} and S^{2-}. Solid **B** is of particular interest since the results show that both metal centres have undergone a one-electron reduction. The interesting and biologically important redox reactions of Mo–S systems have been highlighted by Stiefel [15]. The ability of both Mo and S centres to change oxidation states can lead to internal redox processes that are induced by external oxidants, e.g. by organic disulphides [16]:

$$RSSR + 2MoS_4{}^{2-} \longrightarrow 2RS^- + Mo_2{}^V S_4(S_2)_2{}^{2-}$$
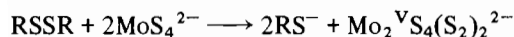
In this example an internal two-electron transfer process has occurred induced by the disulphide, resulting in a dimeric Mo(V)–persulphide complex which is the thiol analogue of the anion $[Mo_2{}^V O_2$-$S_2(S_2)_2]^{2-}$ mentioned earlier. By analogy Cu(II) is the external oxidant in the formation of compound **B**, the first example of a Cu(I)–Mo(V)–S complex. We would therefore, by comparison, expect a formulation $Cu^I Mo^V S_2(S_2)$. However, our elemental analyses, supported by the IR and XPS results, are more consistent with the empirical formula $CuMo$-S_4O_3, which clearly gives an imbalance of electronic charge. Although the IR spectra did not show any evidence for the presence of persulphide ion there appears to be a close spectroscopic similarity between **B** and the anion $[Mo_2{}^V O_2 S_2(S_2)_2]^{2-}$ in terms of the environments of the Mo(V) centres. At this stage we are unable to comment further on the nature of **B** or on the significance of the 1.5:1 reaction stoichiometry. In the future we hope to carry out EXAFS measurements which should delineate the nature of the Cu and Mo environments.

The tungsten analogue, $WS_4{}^{2-}$, appears to undergo a similar reaction with Cu(II) with a 1.5:1 Cu(II): $WS_4{}^{2-}$ stoichiometric ratio [17]. However, the solids formed showed no evidence of oxygen being present and neither was there ESR evidence for a

W(V) state. This latter difference to the Mo system could reflect the generally easier reduction of Mo as compared to W. In agreement with this $MoS_4{}^{2-}$ was found to undergo a reversible one-electron reduction by cyclic voltametry at *ca.* −2.5 V (relative to the standard calomel electrode), in DMF solutions, whilst no reduction could be observed for $WS_4{}^{2-}$ (*i.e.* not below −3 V). The surprisingly large reduction potential for $MoS_4{}^{2-}$ can be explained in terms of the observed extensive electron delocalisation stabilising the metal centre towards reduction and shows perhaps why cooperative redox processes are observed for this ion.

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