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SYNTHETIC ASPECTS OF Cu–Mo–S SYSTEMS AND THEIR POSSIBLE RELEVANCE TO COPPER–MOLYBDENUM ANTAGONISM

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A. INTRODUCTION

The role of trace elements in biological systems is well recognised and it is now established that life would not be possible without active participation of these metal ions. There has been a systematic effort to explore the various roles of trace elements [1–5] but the interaction of these elements with themselves has not been studied in detail. Copper may interact with many

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essential trace elements inside the organism. These interactions may result in stimulation or antagonism of each other, e.g. the presence of Cu (present in ceruloplasmin) stimulates the synthesis of haemoglobin and the effect of excess molybdenum results in the depletion of copper for metabolic purposes; this is known as "Cu–Mo antagonism". The first report of such an interaction came in 1938 when the cattle grazing pastures on molybdenum rich soil developed acute diarrhea and debilitation [6]. The disease referred to as "teart" could be cured by spraying the pastures or watering the animals with $CuSO_4$ solution. Evidently, the deficiency of copper induced by excess of molybdenum was supposed to be the reason for the disease [7]. In studies with sheep it was established that sulphate content of the diet is also of crucial importance [8–10].

The relay of this Cu–Mo interaction to various other interactions and the difference in its modus operandi in monogastrics and ruminants has led to a wide range of interests. Unfortunately most of attempts were concerned with administering copper, molybdenum and sulphur compounds to ruminants and monogastrics and thereby speculating upon the mode of interaction on the basis of the concentration of these elements in various parts of the body. Some excellent reviews are available with regard to such studies [11–16], but the chemistry of such interactions has not been reviewed; only some isolated approaches have been made [17–20]. The purpose of this review is therefore to present an up to date and comprehensive account of attempts made to understand the chemistry and nature of this Cu–Mo–S interaction. Since MoS_4^{2-} has been proven to be the greatest antagonist of copper [20] and is involved in this interaction it is necessary to briefly review the incorporation of MoS_4^{2-} in biological systems and the evidence for its formation in vivo. Since the chemistry of the Cu–Mo–S system developed so far is mainly the chemistry of the interaction of Cu^{n+} and MoS_4^{2-} and the poorly soluble complex species formed by the involvement of Cu–MoS_4^{2-} interaction has been held responsible for the depletion of copper for metabolic purposes; the chemistry of MoS_4^{2-} relevant to the Cu–Mo–S interaction has also been outlined.

B. MoS_4^{2-} INCORPORATION IN BIOLOGICAL SYSTEMS

In recent years the chemistry of sulphur containing ligands has gained momentum, probably due to their importance in various metallobiomolecules which are responsible for vital functions like electron transfer, catalytic behaviour and redox reactions.

The relevance of thiomolybdates, $MoS_nO_{4-n}^{2-}$ ($n \doteq 1$–4), and particularly of MoS_4^{2-} in some biological processes has recently been recognised. The isolation of MoS_4^{2-} by the acid/base hydrolysis of Mo–Fe protein of

Clostridium pasteuranim in 1978 by Zumft [21] had particular impact on the fast development of the chemistry of thiometallates in general and of MoS_4^{2-} in particular. Thiomolybdates are also formed in the digestive track of ruminants [17,18,22–24] and are proven to be responsible for the depletion of copper for biological system [20]. They also seem to be associated with some irritations of copper metabolism in man [25] and high molybdenum content of soil has been held responsible for copper deficiency in ruminants [20].

C. EVIDENCE FOR THE FORMATION OF MoS_4^{2-} IN VIVO

Molybdenum is probably absorbed into biological systems as molybdate anion [26]. The levels of Mo in an organism are determined primarily by the available Mo in the soil and/or certain soil structures with low Mo content [28]. Legumes, citrus fruits, broccoli and even grasses and grains planted in such soils show stunted growth and other symptoms which are relieved by the application of fertilisers containing Mo [29]. Plants can incorporate up to several hundred parts per million (ppm) of Mo into their tissues without showing adverse symptoms [30]. However, ruminants which are fed forage from soils with high levels of available Mo develop problems with their Cu metabolism which leads to severe effects [31]. People in the molybdenum-rich Ankavan region of the U.S.S.R., who are estimated to consume 10–15 mg day^{-1} of Mo have an usually high incidence of gout [27]. There are no symptoms clearly identifiable with molybdenum deficiency in animals and humans [31a]. This may reflect the trace quantities of molybdenum required for their essential function which are supplied by the daily dietary intake. However, there are some reports which suggest that molybdenum hydroxylates may be responsible for certain abnormalities in humans [31b].

One of the vital roles played by Mo is its involvement in the nitrogen cycle. It was shown to be essential for nitrogen fixation early in the 1930s [32]. Subsequent research has revealed that Mo is a necessary constituent of the enzyme nitrogenase, responsible for catalytic reduction of N_2 to NH_3 [33]. In an isolated approach to the study of the chemistry of MoS_4^{2-} with Fe, it was speculated in 1977 that MoS_4^{2-} may be a constituent of nitrogenase [34]; the subsequent isolation of MoS_4^{2-} from the Mo–Fe protein of *Clostridium pasteuranium* in 1978 by Zumft converted speculation into fact [21]. Since then many research groups have been engaged in finding details of the relevant coordination chemistry and preparing synthetic analogues of nitrogenase which may have similar spectroscopic properties and show reactions similar to those of the enzyme.

Confirmation of thiomolybdate formation in the rumen has been made by identification of the characteristic spectral absorption of MoS_4^{2-} ion in supernatants of in vitro rumen cultures [17,18,35]. The presence of $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$ has been similarly detected. However, Mills et al. estimated that the spectral techniques would only detect MoS_4^{2-} in vivo at dietary Mo concentration above 100 mg kg^{-1} dry matter, i.e. at levels characteristic of non-ruminants rather than ruminant interactions [18]. In non-ruminants, proof is one step further away in that the accumulation of endogenous S^{2-} has not been found [36]. Evidence for MoS_4^{2-} incorporation rests largely on the observation that ruminants respond to preformed MoS_4^{2-} in the same way as they do to dietary $MoO_4^{2-} + SO_4^{2-}$. Moreover, a laboratory experiment showed that addition of $MoO_4^{2-} + SO_4^{2-}$ to the diet markedly increased the fraction of plasma Cu that was extractable with sodium diethyldithiocarbamate and led to the appearance of a non-extractable fraction other than ceruloplasmin [37]. This residual Cu (unlike ceruloplasmin Cu) was not released by treatment with trichloroacetic acid, TCA. The credentials of TCA-insoluble Cu as a measure of plasma Cu distribution in vivo were called into question by other workers, who noted that MoS_4^{2-} given intravenously to sheep caused ceruloplasmin Cu to precipitate quantitatively as TCA-insoluble Cu. But TCA-insoluble Cu must reflect an in vivo interaction because it cannot be induced by MoO_4^{2-} in vitro and its formation in vivo is enhanced by adding SO_4^{2-} as well as MoO_4^{2-} to the diet. TCA-insoluble Cu therefore, reflects a systemic consequence of the MoO_4^{2-} and SO_4^{2-} interaction [15].

D. SYNTHETIC ASPECTS OF Cu–Mo–S SYSTEMS

A few M–Mo–S systems obtained by solid state reaction which are not relevant to our discussion here have been reviewed elsewhere [38]. The synthetic chemistry of the M–Mo–S system developed so far is mainly the chemistry of M^{n+}–MoS_n^{2-} interactions. Although the ion, MoS_4^{2-}, has existed in the literature since 1826 [39] its chemistry has only been explored recently [19,40,41].

Interaction of tetrathiometallate with copper is an important reaction having biorelevance. Cupric ion forms several complexes with sulphur-containing ligands retaining its 2 + oxidation state. Contrary to this, thiometallates react with cupric ion with its immediate reduction to the cuprous state, whereas free sulphide ion leads to the immediate precipitation of CuS. Thus the reducing capability of S^{2-} bound to metal ion in the series $MO_{4-n}S_n^{2-}$ (M = Mo, W) is retained.

In many copper proteins, especially those containing thionein bound copper, the formal oxidation state of copper is believed to be 1 + . Thus the interaction between cupric ion and thiometallate to produce cuprous ion is of biorelevance as it is believed that the metabolic activity of copper is facilitated when present in the cuprous state rather than the cupric [16].

The $Cu^{2+}/MoS_4^{2-}/H_2O$ system produces the insoluble polymeric species of unit $[CuMoS_4]^-$ and X-ray structural characterisation of the corresponding $[NH_4]^+$ salt shows the presence of chains of CuS_4 and MoS_4 tetrahedra connected via edges [42a]. The corresponding tungsten analogue $[CuWS_4]^-$ is also known [42b]. In these systems the MS_4^{2-} ion acts formally as a double bridging ligand. $[CuX_4]$ and MX_4 tetrahedra connected via edges are also present in Cu_3MX_4 (M = V, Nb, Ta; X = S, Se) [19].

In the quest to prevent this polymerisation, and backed by the knowledge of the reactivity of these thiometallates with other metal ions including iron [19,43], some non-aqueous reactions were undertaken. The first phase of this type of reaction started with the use of bulky substituted phosphine ligands which are strongly bound to copper(I) and thus could cause the termination of polymerisation. The substituted phosphine coordinates to copper and the possibility of polymerisation at the copper end is removed. The substituted phosphines were considered to be essential for the formation of discrete Cu–Mo–S systems; all the reactions carried out to synthesise Cu–Mo–S systems and even Ag–Mo–S systems involved various substituted phosphines until 1981 [19]. In all these compounds besides the formation of an S-bridged heterometal centre, the Cu (and Ag where Ag compounds are synthesised) is flanked by substituted phosphines. Recently the necessity for phosphine for the termination of polymerisation and hence the formation of Cu–Mo–S system, has been questioned and compounds have been synthesised which do not contain P-donor ligands. CN^- and some N-donor ligands have been used successfully to synthesise the Cu–Mo–S systems [44,45]. All the compounds synthesised so far are interesting from a structural point of view since they contain doubly, triply, quasi-quadruply and quadruply bridging thiometallate ligands. Moreover, their possible incorporation in biological systems is of particular relevance (see below). Thus the following types of compound have been synthesised.

(i) Binuclear species

Compounds of the type (a) $(PPh_4)_2[NCCu(MoS_4)]$ and (b) $[(NMe_4)_2]$-$NCCu(MoS_4)CuCN$ were synthesised by the reaction of CuCN and MoS_4^{2-}. It is interesting to note here that use of a particular cation governs the structure of the resulting species. Thus, when $[PPh_4]^+$ is used the monomeric compound (a) is obtained whereas when $[NMe_4]^+$ is used the polymeric compound (b) is obtained. In (b) the MoS_4^{2-} is coordinated to a CuCN molecule as well as to a zig-zag CuCN chain thereby giving a polymeric structure [44]. $(PPh_4)_2[NCSCuMoS_4]$ could be synthesised when CuSCN was allowed to react with one mole of MoS_4^{2-} [45]. Here the effect of different cations to give different species as in the case of CuCN was not observed [46].

The reaction of one mole of each of CuSCN, MoS_4^{2-} and *o*-phen resulted in the formation of $[o\text{-phen–CuMoS}_4]^-$ which could be trapped by use of the $[PPh_4]^+$ cation [45]. This species is particularly interesting because it may be used for the generation of trinuclear species since two S sites of the MoS_4^{2-} are left uncoordinated. The third metal to be coordinated may be Cu (see below). Transferring the methodology to isolate the analogous trimetallic Fe–Mo–Fe systems [45] one could explore the possibility of attaching iron instead of copper at the other end. The redox chemistry of this type of trinuclear species with Cu, Mo, Fe centres would be particularly interesting for modelling various biological redox systems. In all these binuclear species described above, MoS_4^{2-} acts as a bidentate ligand and Cu is coordinated to two sulphur atoms thereby forming Cu–S–Mo bridges, the structural aspects of which are discussed later. Recently the species $[(PhS)CuMoS_4]^{2-}$ was synthesised from the reaction of $[NCCuMoS_4]^{2-}$ and PhSH [47].

(ii) Trinuclear species

Trinuclear species of the composition $L_nM'_2(MS_4)_4$ (where L = PPh_3, $PMePh_2$, $AsPh_3$; M′ = Cu, Ag, Au; M = Mo, W; $n = 2$–4) could be obtained [19,45]. In all these complexes M′ atoms are coordinated via a doubly bridging MS_4^{2-} ligand in a symmetrical fashion. Moreover one or two monodentate ligands L are attached to M′. Thus, when $n = 4$ both atoms are surrounded by a distorted tetrahedron whereas for $n = 2$ both have almost a trigonal planar environment; with $n = 3$ one of the M′ atoms is tetrahedrally coordinated while the other has a trigonal planar environment. For the case of copper the symmetrical species with $n = 4$ could not be achieved with PPh_3 or $AsPh_3$ but was possible when silver was used [19]. The symmetrical species with copper could be obtained when 2 moles of *o*-phen and two moles of CuSCN were allowed to react with one mole of MS_4^{2-} [45,48]. This species having the formula $[(o\text{-phen})_2Cu_2MS_4]$ could also be obtained when the binuclear species $[o\text{-phenCuMoS}_4]^-$ (see above) reacted with one mole of CuSCN and of *o*-phen. All these compounds were characterised by spectroscopic investigation and by X-ray structural determination wherever single crystals could be obtained [45].

From the stoichiometric point of view the compound having the general formula $M'_4M_2S_6(PR_3)X_2$ (where M′ = Cu, Ag; M = Mo, W; X = S, O; $R_3 = Ph_3$, $(C_7H_7)_3$; $MePh_2$) may also be put under this category but the central unit has a new type of cage formally thought to be obtained by the fusion of two $MS_2M'_2S$ rings. Here the MXS_3^{2-} ligand acts as a quasi-quadruple bridging ligand [49].

The existence of two six membered rings has been established by isolating a compound consisting of the half structure of the cage. When reacted in solution for a longer time this changes to produce the more stable cage compound by a pseudo-dimerisation process [50]

$$\begin{array}{ll} MoOS_3^{2-} \xrightarrow{Cu/PPh_3} & 2[MoOS_3Cu_2(PPh_3)_3] \\ & \quad\quad\quad\downarrow \\ & Mo_2O_2S_6Cu_4(PPh_3)_4 + 2\ PPh_3 \end{array}$$

Recently the species $[(PhS)_2Cu_2MoS_4]^{2-}$ was synthesised and an equilibrium with the binulcear species $[(PhS)CuMoS_4]^{2-}$ was established using ^{95}Mo NMR as follows [47]

$$2\ [(PhS)CuS_2MoS_2]^{2-} \rightleftharpoons [(PhS)CuS_2MoS_2Cu(SPh)]^2 + MoS_4^{2-}$$

(iii) Tetranuclear species

Tetranuclear species of the composition $Cu_3MS_3ClL_3X$ (M = Mo, W; X = S, O; L = PPh_3, $AsPh_3$) are reported from the reaction of stoichiometric amounts of constituents [19]. The MXS_3^{2-} ligand is triply bridging. Three copper atoms, Mo, three S atoms and Cl are supposed to be formally located on the eight corners of the distorted cubic unit formed. The fourth atom attached to Mo namely X, projects out of the cube and so do the L_3 ligands each attached to a copper centre. Hence, the coordination polyhedra of the three Cu centres are not equivalent. One Cu has a distorted tetrahedral environment while the other two are in a trigonal planar environment. Some of these compounds have also been characterised by X-ray structural analysis.

From the stoichiometric point of view the compound $[(CuCl)_3MoS_4]^{2-}$ may be put in this category but its structure is quite different and is particularly fascinating in that it has a chair configuration confirmed by X-ray structural investigation [51]. The tungsten analogue $[(CuCl)_3WS_4]^{2-}$ has also recently been synthesised and structurally characterised [52].

(iv) Pentanuclear species

Pentanuclear species of general formula $L_4Cu_4(SCN)_2MS_4$ (where L = py or γ-pic; M = Mo, W) were obtained by the reaction of CuSCN, MS_4^{2-} and L in appropriate stoichiometry [45]. These compounds were synthesised only recently and have particular impact on the chemistry of MoS_4^{2-} because in them all four S atoms of the MoS_4^{2-} unit are symmetrically coordinated to four copper atoms. The coordination environment of copper is not equivalent in this case because two of the Cu atoms are tetrahedrally coordinated (2S and MoS_4^{2-} and 2L) while the other two have trigonal planar coordination (2S of MoS_4^{2-} and SCN^-). The structural resemblance of these units with homonuclear copper species is particularly interesting (see below). None of these compounds could be structurally characterised by X-ray analysis because of the lack of suitable single crystals, but the compounds were characterised by various spectroscopic techniques (see below) [45].

E. STRUCTURAL ASPECTS OF Cu–Mo–S SYSTEMS

Preliminary structural characterisation of Cu–Mo–S complexes is achieved by high intensity absorption bands in the UV/visible region and by IR and Raman spectroscopy. The strong S → Mo charge transfer band and characteristic IR and Raman bands of MoS_4^{2-} are significantly affected by coordination of MoS_4^{2-} to metals [53]. The effect, however, depends on the coordination environment around MoS_4^{2-}. Splitting and shifting of one or more bands of the three prominent transitions ν_1 $(t_1 \rightarrow 2e)$, ν_2 $(3t_2 \rightarrow 2e)$

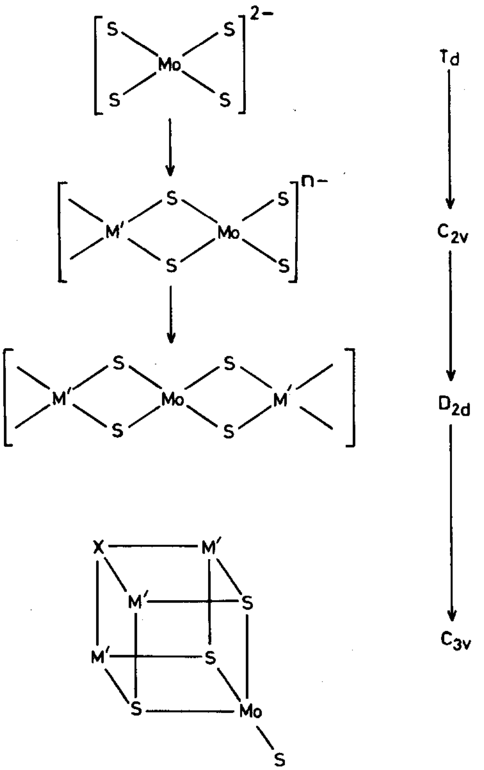


Fig. 1. Symmetry of coordination environments of MoS_4^{2-}.

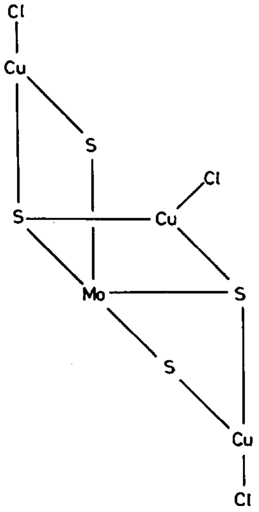


Fig. 2. Structure of $[(CuCl)_3MoS_4]^{2-}$.

and ν_3 ($= t_2 \rightarrow 4t_2$) electronic transitions are observed but no generalisation has yet been made regarding the nature of perturbation with respect to a particular coordination environment. This is also the case for other M–Mo–S systems. IR and Raman techniques [19,43] are however quite helpful and predictive. Thus, the T_d symmetry of MoS_4^{2-} is lowered to C_{2v} when binuclear complexes (see Fig. 1) are formed and to D_{2d} when trinuclear complexes are formed (Fig. 1). This local microsymmetry of MoS_4^{2-} may not be very clear in some of the complexes of type $[(CuCl)_3MoS_4]^{2-}$ (see Fig. 2), but for the tetranuclear species (see Fig. 1) and the pentanuclear species a rough approach to C_{3v} and T_d may be considered. Based on these the splitting of IR and Raman bands may be summarised as follows:

T_d	$\rightarrow D_{2d}$	$\rightarrow C_{2v}$
A_1(R)	– A_1(R)	– A_1(IR, R)
T_2(IR, R) <	B_2(IR, R) –	A_1(IR, R)
		B_1(IR, R)
	E(IR, R) <	B_2(IR, R)

Thus, the $\nu_1(A_1)$ vibration of the free MoS_4^{2-} ion retains its totally symmetric nature even after coordination and the asymmetric vibration splits in different ways depending on the local symmetry of the coordinated MoS_4^{2-} group.

(i) Electronic spectra

The electronic spectra (Table 1) of Cu–Mo–S complexes show characteristic absorption bands whose positions are roughly comparable to those of free MoS_4^{2-}. Since Cu^+ contains a closed *d*-shell configuration the spectra are much simpler than those involving an open *d*-shell configuration where the spectra become more complex and the possibility that *d–d* transitions may be obscured in the envelope of strong charge-transfer S–Mo bands cannot be ignored. In the spectra of the closed *d*-shell $[NCCuMoS_4]^{2-}$ and $[Zn(MoS_4)]^{2-}$, the ν_1 and ν_3 bands are shifted while the ν_2 band remains practically unchanged suggesting that the t_1 orbital of the MoS_4^{2-} ligand is more strongly disturbed than the $3t_2$, $2e$ and $4t_2$ molecular orbitals [44,53]. However some recent observations suggest a shift in the ν_2 bands indicative of the fact that the situation is not so simple [45,47]. The electronic spectra (Table 1) show that the intensities of two lowest energy bands are reduced and the ν_2 band position is bathochromically shifted. This shift is more pronounced in trinuclear species. However, the solid state spectra of some of the representative species agree with those of the solution spectra regarding the band maxima of these complexes. Thus, the reflectance spectra of $[(PPh_3)_3Cu_2MoS_4]$ shows the appearance of a ν_2 band at about 370 nm [54]

TABLE 1

Electronic spectra of synthesised complexes (nm)

Compound	Electronic transitions			Ref.
	ν_1	ν_2	ν_3	
$(NH_4)_2MoS_4$	467	318	242, 207	56
$(PPh_4)[(o\text{-phen})CuS_2MoS_2]$	495	338	260, 242	45
$(PPh_4)_2[NCSCuS_2MoS_2]$	495	338	258, 242	45
$(NMe_4)[NCCuS_2MoS_2]$	472	451, 318	247, 224	19
$[(o\text{-phen})CuS_2MoS_2Cu(o\text{-phen})]$	495	375	258, 242	45
$[(PPh_3)_3CuMoS_4]$	490	370		54
$[(\gamma\text{-pic})_4Cu_4(SCN)_2MoS_4]$	490	370	245, 210	45
$[(py)_4Cu_4(SCN)_2MoS_4]$	490	370	245, 210	45
$(NH_4)_2WS_4$	386	217		19
$(PPh)_4[o\text{-phen})CuS_2WS_2]$	407	298	266, 260, 252	45
$[(o\text{-phen})CuS_2WS_2Cu(o\text{-phen})]$	405	340	250, 240	45
$[(\gamma\text{-pic})_4Cu_4(SCN)_2WS_4]$	405	335	242	45
$[(py)_4Cu_4(SCN)_2WS_4]$	408	335	255, 252	45
$[PhSCuS_2MoS_2]^{2-}$ [a]	480	350, 328 [b]	286, 240	47
$[PhSCuS_2MoS_2CuPhS]^{2-}$ [a]	495	370, 342 [b]	284, 245	47

[a] PPh_4^+ salt. [b] CT (PhS–Cu).

in close agreement with the position of ν_2 bands shown in Table 1 and obtained in solution.

A striking feature of the solid state reflectance spectra of complexes with a Cu–Mo–S system is the appearance of a shoulder (720 ± 10 nm) assigned to a d^{10} (Cu)—MoS_4^{2-} transition. The assignment of this band as shown in Fig. 3 was made recently by analogy with similar shoulders obtained in solid state reflectance spectra of $AgCrO_4$ complexes which are unambiguously assigned to a d^{10} (Ag)—CrO_4^{2-} transition [55]. This observation has been of immense importance in determining the delocalisation of charge around Cu, Mo and S centres, details of which are discussed under XPS studies.

(ii) Vibrational spectroscopy (Tables 2 and 3)

Structural aspects of the Cu–Mo–S systems can be determined reasonably using IR and Raman spectroscopy. The terminal Mo–S groups are characterised by one or two vibrational frequencies between 480–510 cm^{-1} and the bridging Mo–S groups by frequencies between 430 and 460 cm^{-1} [53]. The expected trend of splitting is observed in binuclear and trinuclear

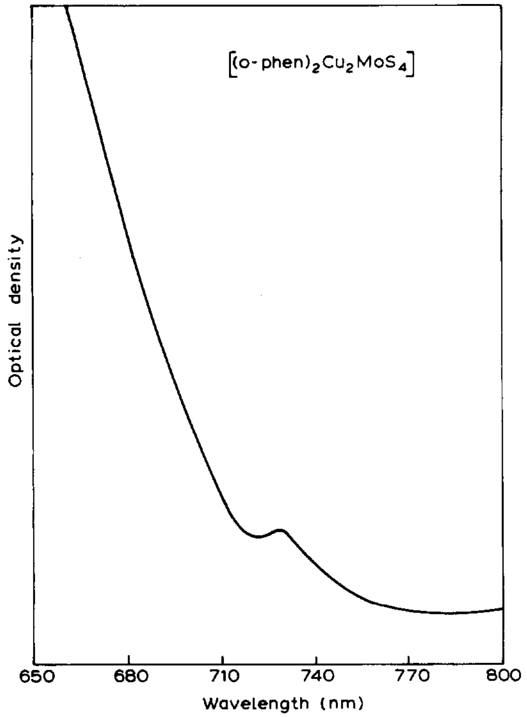


Fig. 3. Reflectance spectrum of $[(o\text{-phen})_2Cu_2MoS_4]$.

TABLE 2

Assignment of Mo–S and Mo–O vibrations in complexes derived from $[MoO_{4-n}S_n]^{2-}$ anions (cm^{-1})

Compound	$\nu(Mo–S)_{br}$	$\nu(Mo–S)_{term}$	$\nu(Mo–O)_{term}$	Ref.
$(NH_4)_2MoS_4$		472		19
$(PPh_4)[(o\text{-phen})CuMoS_4]$	425, 448	488, 499		45
$(PPh_4)_2[NCSCuMoS_4]$	440, 450	485, 495		45
$(PPh_4)_2[NCCuMoS_4]$	447, 416	500, 486		19
$[(o\text{-phen})_2Cu_2MoS_4]$	460			45
$[(PPh_3)_3Cu_2MoS_4]\cdot0.8CH_2Cl_2$	465			57
$[AsPh_3)_3Cu_2MoS_4]$				45
$[Cu_3(PPh_3)_3ClMoS_4]$	447, 441			57
$[Cu_3(AsPh_3)_3ClMoS_4]$		510		45
$[Cu_3(PPh_3)_3ClMoOS_3]$	451, 444		923, 908	57
$[Cu_3(AsPh_3)_3ClMoOS_3]$			910	45
$[(\gamma\text{-pic})_4Cu_4(SCN)_2MoS_4]$	450			45
$[(\gamma\text{-pic})_4Cu_4Cl_2MoS_4]$	450			45
$[(py)_4Cu_4(SCN)_2MoS_4]$	450			45
$[(py)_4Cu_4Cl_2MoS_4]$	450			45
$[PhSCuS_2MoS_4]^{2-}$ [a]	479, 440	491		47
$[PhSCuS_2MoS_2CuSPh]^{2-}$ [a]	470, 462			47

[a] PPh_4^+ salt.

TABLE 3

Assignment of W–S and W–O vibrations in complexes derived from $[WO_{4-n}S_n]^{2-}$ anions (cm^{-1})

Compound	$\nu(W–S)_{br}$	$\nu(W–S)_{term}$	$\nu(W–O)_{term}$	Ref.
$(NH_4)_2WS_4$		455		19
$(PPh_4)[(o\text{-phen})CuWS_4]$	448	495		45
$(PPh_4)_2[NCSCuWS_4]$	440, 460	490		45
$[(o\text{-phen})_2Cu_2WS_4]$	450			45
$[(PPh_3)_3Cu_2WS_4]\cdot CH_2Cl_2$	455, 451			57
$[(AsPh_3)_3Cu_2WS_4]$				45
$[Cu_3(PPh_3)_3ClWS_4]$	436, 430			57
$[Cu_3(AsPh_3)_3ClWS_4]$		515		45
$[Cu_3(PPh_3)_3ClWOS_3]$	436, 430		928, 922	57
$[Cu_3(AsPh_3)_3ClWOS_3]$			920	45
$[(\gamma\text{-pic})_4Cu_4(SCN)_2WS_4]$	432			45
$[(\gamma\text{-pic})_4Cu_4Cl_2WS_4]$	432			45
$[(py)_4Cu_4(SCN)_2WS_4]$	430			45
$[(py)_4Cu_4Cl_2WS_4]$	430			45

species. Raman spectral assignments represented in Table 4 are also in agreement, and Cu–S stretching vibrations are also assigned. For complexes of the type $[(AsPh_3)_3Cu_3S_3MXCl]$ (X = O, S; M = Mo, W) and $[(AsPh_3)_3Cu_3MS_4]$ the important M–S could not be located due to the presence of strong $AsPh_3$ ligand vibrations around 460 cm^{-1}. The characterisation of the arsine derivatives has been made by comparing the X-ray powder diffractogram of these complexes with those of the corresponding phosphine complexes [45].

(iii) Resonance Raman spectra

Using this technique the influence of the nearest and next-nearest neighbours on the vibrations of the ligand chromophore can be investigated [58]. The intensities of bands due to the totally symmetric vibration of the thiomolybdate ligand were strongly enhanced using the 488 nm line of an Ar^+ laser which falls within the ν_1 absorption frequency of the internal charge transfer transition of the MoS_4^{2-} chromophore. Recently, this technique has been exploited to investigate the influence of next-nearest neighbours whereby a distinction can be made between unsymmetrically and symmetrically substituted M′ complexes containing trinuclear species. When it is unsymmetrically substituted the deviation from D_{2d} symmetry can clearly be recognised by observing the overtones originated from the combination bands of the type $n\,\nu_1(A) + \nu_1^*(A)$ (assuming C_{2v} symmetry for the fragment $P_2M'S_2MoS_2M'P$). This type of combination band appears as a weak feature on the high energy side of the bands of the different $n\,\nu_1$ overtones. When symmetrically substituted M′ is present this type of feature is not expected and only the $n\,\nu_1$ overtones are observed [58].

Compounds containing symmetrically substituted M′ have been subjected to this type of analysis. Among these $[(FeCl_2)_2MoS_4]^{2-}$ has been structurally characterised by X-ray crystallography, whereas suitable single crystals

TABLE 4

Raman spectral data (cm^{-1})

Compound	ν_s(M–S)	ν_{as}(M–S)	ν(M′–S)	$\delta(MS_2)$	Ref.
$[(PPh_3)_3Cu_2MoS_4]$	446	470	267, 303	154	57
$[(PPh_3)_3Cu_2WS_4]$	469	459	257	163	57
$[(PPh_3)_4Ag_2MoS_4]$	462	447	235	167	57
$[(PPh_3)_4Ag_2WS_4]$	441	463	235	162	57
$[(o\text{-phen})_2Cu_2MoS_4]$	441	458	258	161	45
$[(o\text{-phen})_2Cu_2WS_4]$	460	450	255	161	45

for crystal structure determination of the silver complex $[(PPh_3)_2AgS_2MoS_2Ag(PPh_3)_2]$ could not be obtained [58]. The complex [(*o*-phen)-CuS_2MoS_2Cu(*o*-phen)] also shows similar resonance Raman spectra compared to the symmetrical iron and silver complexes cited above [45]. It is evident that these three complexes are symmetrically substituted on the M′ metal. A remarkable feature of these spectra is the appearance of combination bands of the type $n\,\nu_1 + \nu(\text{M}'\text{–S})A_1$ which suggests strong electronic interaction between M′(Ag^+, Cu^+) and MoS_4^{2-} [45]. This observation supports the previous discussion regarding electronic interaction between d^{10}(Cu) and MoS_4^{2-} centres resulting in shifts of the charge transfer bands in the electronic spectra.

(iv) XPS studies

The determination of the binding energy of core electrons makes it possible to deduce the chemical environment of an atom. When similar structural environments are present in a series of complexes, the change in binding energy which reflects the electron density of an atom may be helpful in assigning the formal oxidation state of an atom. Sometimes complications do arise and these may even be helpful in extracting certain information. Thus an inner-shell vacancy induced by photoionisation can make a sudden change in the central potential. The relaxation energy of the outer electron under adiabatic conditions is imparted to the ejected photoelectron. The sudden perturbation of the screening of the remaining electrons may induce a “shake up” transition involving the excitation of a valence electron to a higher unoccupied orbital [59]. This “shake up” process occurring simultaneously with the core electron photoejection results in satellite lines on the higher binding energy side of the main peak [60]. Selection rules of the sudden approximation suggest that compounds with completely filled *d* shells, for example Cu(I), do not have satellite lines [61,62]. Thus, copper when present in the cupric state does have satellite peaks in the 2*p* electron level whereas in Cu(I) these are absent.

In Table 5 some representative examples of the binding energies of the copper core electrons are presented. The relevant information one might get from these data are as follows:

(i) In CuCN the metal-to-ligand back-bonding causes a shift of electron density from filled *d* orbitals of copper to empty antibonding orbitals of the cyano ligand. No satellite peaks can be seen in its spectrum [61]. The decrease in the electron density at copper results in a high binding energy of the Cu(2*p*) electrons.

(ii) The S(2*p*) binding energy in CuSCN suggests that in CuSCN there is reduced electron density in the S(2*p*) level. Such is the case with the thiourea

TABLE 5

XPS data for some copper compounds (eV)

Compound	$Cu(2p_{3/2})$			$S(2p)$	Ref.
	Satellite		Main peak		
CuO	943.8		935.7		62
Cu–phthalocyanine		943.2	934.2		62
CuCN			934.1		62
CuSCN			933.1	164.3	62
$Cu(SCN_2N_4)_3Cl$			932.5	162.2	62
$Cu(HCOO)_2$	944.6	940.7	936.4		62
Cu–cystine		943.6	934.3	163.7	62
Cu–cysteine			932.3	162.7, 167.8 [a]	62
Cu–penicillamine			933.3	163.2	62
Cu- -mercaptopropionylglycine			933.6	163.7	62

[a] Due to sulphate impurity.

complex where the $S(2p)$ electrons shift 1.1 eV to higher binding energy compared to that of the free ligand. This reduction in electron density is reflected in the $Cu(2p_{3/2})$ binding energy in these compounds.

This type of charge flow can interpret the actual nature of charge transfer. The influence of the relative binding energy with the oxidation state can also be demonstrated easily. For sulphur, unit change in the oxidation state of sulphur results in a shift of about 0.8 eV binding energy [64]. However, a redetermined value for Na_2S shows the $S(2p)$ binding energy at 162.0 eV [64] contrary to 160.8 eV reported earlier [63]. This is due to the difference in the standardisation procedure but the trend in the difference in oxidation state can be seen.

The binding energies of constituent atoms of the Cu–Mo–S system complexes are presented in Table 6. In the anionic complexes the normal trend of the charge present in the complexes is observed compared to the neutral species. The most interesting observation of importance is to understand the electron density on the Cu, Mo/W, S atoms in these systems. The $Mo(3p_{3/2})$ and $Mo(3d_{3/2})$ signals suggest little difference in the electronic charge distribution around molybdenum in its coordinated and uncoordinated form. However, the $S(2p)$ binding energy appears low compared to that found for the uncoordinated MS_4^{2-} ion. This low value in binding energy reflects an increase in the electron density on sulphur. The lowest binding energy observed for sulphur in these complexes is with the symmetrical trinuclear species, $[(o\text{-phen})CuS_2MoS_2Cu(o\text{-phen})]$; correspondingly,

TABLE 6

Binding energies (in eV, standard C(1*s*))

Compound	Cu($2p_{3/2}$)	Mo($3p_{3/2}$)	Mo($3d_{5/2}$)	Mo($3d_{3/2}$)	W($4f_{7/2}$)	W($4f_{5/2}$)	S($2p$)	N($1s$)	S($2s$)	Ref.
$(PPh_4)_2[NCSCuMoS_4]$	933.5	396.3	230.4	233.4			162.1	399.1	225.8	45
$(PPh_4)[(o\text{-phen})CuMoS_4]$	933.5	395.9	230.1	233.1			161.9	399.3	226.2	45
$[(o\text{-phen})_2Cu_2MoS_4]$	933.3	395.6	229.7	232.8			161.6	399.4	225.7	45
$[(\gamma\text{-pic})_4Cu_4(SCN)_2MoS_4$	933.1	396.4	230.4	233.6			162.9	399.1	227.2	45
$[(py)_4Cu_4(SCN)_2MoS_4]$	933.0	396.3	230.2	233.8			162.8	399.1	226.2	45
$(PPh_4)_2[NCSCuWS_4]$	933.5				34.0	36.2	162.6	399.2		45
$(PPh_4)[(o\text{-phen})CuWS_4]$	933.5				33.7	35.9	162.4	399.3		45
$[(o\text{-phen})_2Cu_2WS_4]$	933.3				33.4	35.6	162.2	399.7		45
$[(\gamma\text{-pic})_4Cu_4(SCN)_2WS_4]$	933.0				34.0	36.0	162.7	398.7		45
$[(py)_4Cu_4(SCN)_2WS_4]$	933.0				34.1	36.2	162.8	399.0		45

the increase in the binding energy for Cu($2p_{3/2}$) in this complex compared to that in the free CuSCN is suggestive of a reduction in electron density at the copper in this complex. These two observations together substantiate an electron flow from copper to the sulphur of the MoS_4^{2-} group. This result is in accord with the results obtained through resonance Raman and electronic spectral studies (see above).

(v) X-Ray diffraction studies

What is the nature of any M′–M interaction in these systems? It has been observed with Fe–Mo–S systems that if the separation of the two metals is ca. 2.8 Å considerable overlap can occur between metal *d* orbitals of appropriate symmetry. Unambiguous information regarding this bonding interaction cannot be obtained in a straightforward manner by the use of crystallographic data only. The M′–M separation is very much dependent on the M′–S–M angle which remains relatively invariant in most of the structures comprising complexes with Fe with variation of other substituent groups as ligands coordinated to Fe [43]. Thus X-ray structural parameters do not lead to a conclusive decision regarding the possibility of a metal–metal bond in these systems.

F. MULTINUCLEAR COPPER SYSTEMS AND THEIR GEOMETRIES

Synthesis, structure and geometries of multinuclear copper systems are very interesting and exciting [65–68]. Although they may exist as binuclear, tetranuclear, pentanuclear, hexanuclear, octa- and decanuclear species besides the infinite chain structure [1], the binuclear and tetranuclear species are relevant to our discussion of Cu–Mo–S interaction.

Binuclear species may exist as $Cu_2X_2L_4$ and $Cu_2X_2L_3$ with symmetrical and unsymmetrical structures represented in Fig. 4. An example of latter which has both three- and four-coordinate copper(I) is $[Cu_2Cl_2(PPh_3)_3]$.

Chain structures of $[CuX_3]^{2-}$ and $[CuX_3]^-$ have single and double chains respectively of linked CuX_4 tetrahedra. Another type of chain is that of $NaCu(CN)_2 \cdot 2H_2O$ where there is a spiral of almost planar bringing Cu(I) atoms linked by CN bridges.

Compounds like copper benzoate have four Cu atoms that, although part of a ring, form in themselves a parallelogram. Tetrameric Cu_4(I) complexes may have a structure in which the four Cu atoms are in a parallelogram, rectangle or square, most commonly at the vertices of a tetrahedron, (regular or slightly distorted) and halogen bridged [65].

An important example is $(CuXL)_4$ where X is halogen and L is usually a tertiary phosphine but may be pyridine. For these complexes there are two

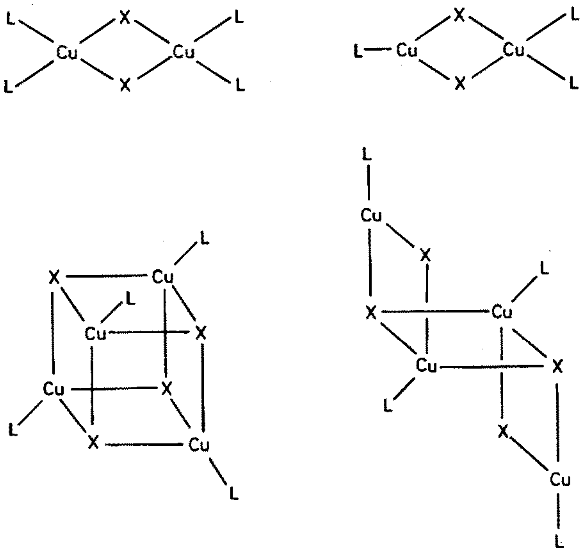


Fig. 4. Multinuclear copper systems: symmetrical, unsymmetrical, cube and chair forms.

possible structures, each of which may be distorted. The first is the cubane structure, in which there is a Cu_4 tetrahedron with a triply bridging halide and a ligand on each four coordinate Cu atom. The second has the chair form with double and triple halide bridges and two four coordinate, tetrahedral and two three coordinate trigonal copper atoms. A logical generalisation for the preference of the cube or chair form is [67]

Structure adopted by $M_4(Ph_3Y)X_4$ molecule (where M = Cu or Ag; Y = P or As; X = Cl, Br or I)

$\text{Cubane} \xrightarrow{\text{Steric repulsion}}$

Steric repulsion ↓	$P_4Ag_4Cl_4$ $As_4Cu_4Cl_4$	$P_4Ag_4Br_4$	$P_4Ag_4I_4$
	$P_4Cu_4Cl_4$	$As_4Cu_4Br_4$ $P_4Cu_4Br_4$	$As_4Cu_4I_4$ $P_4Cu_4I_4$

Chair

G. CORRELATION OF MULTINUCLEAR COPPER SPECIES WITH HETERONUCLEAR SPECIES CONTAINING Cu–Mo–S SYSTEMS

The inherent structural units of pure copper complexes are still retained when Cu(I) forms polynuclear complexes with MoS_4^{2-}. Thus, tetrathiomolybdate can replace halogen bridges from structures presented in Fig. 4 to give species like $[(PR_3)_3Cu_2MoS_4]$ [69]. However, the symmetrical structural variety (Fig. 4) could only be obtained earlier when copper was substituted by silver [19]. The stoichiometry of the tertiary phosphine used dictates the structural feature for the silver compounds. The unsymmetrical variety for this is also known [19]. As stressed by the necessity for bulkiness in the ligand it is evident that the sizes of the metal play an important role in deciding the geometry. For silver, the existence of both varieties does suggest a limiting borderline case for silver which is reflected even in some pure Ag(I) complexes. Thus, the complex $(AgIPPh_3)_4$ analogous to $(CuXL)_4$ can be isolated in both stereoisomeric forms (Fig. 4). However, the chair form is most stable [67,68] (cf. Figs. 4 and 5).

The exploration of Cu–Mo–S systems reveals the structural features of the pure copper compounds. Thus the cubane structural variety (Fig. 4) could be obtained in the heteropolynuclear complex, $[Cu_3MoS_3Cl(PPh_3)_3S]$ [70]. This structural unit may be thought to be formed by substitution of a $[X_3CuL]^{2-}$ fragment in the cube by a $[S_3MoS]^{2-}$ unit (cf. Figs. 4 and 5). Generation of this heterocube is almost identical to the parent homocubane variety where all the constituent atoms used for cubane structure retain their coordination number. However, this distorted cube can adopt another chair-

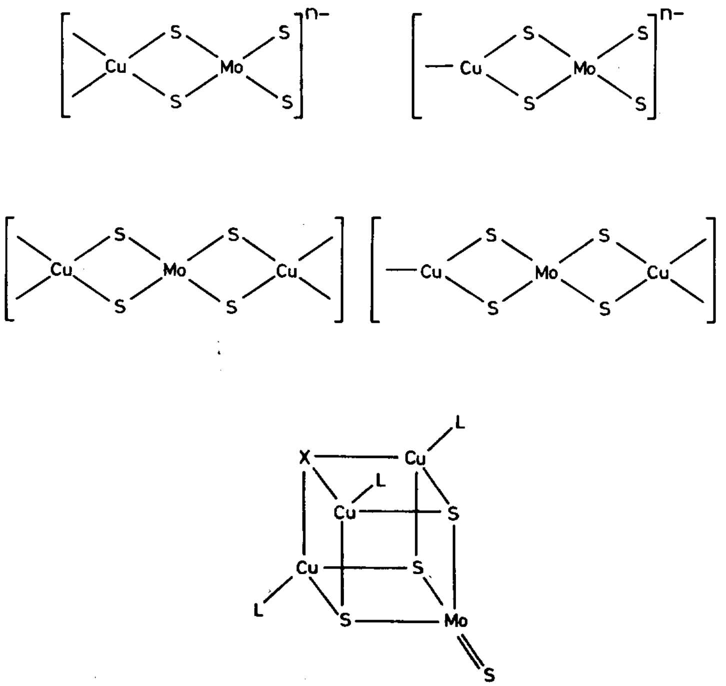


Fig. 5. Heteronuclear copper systems having Cu–S–Mo core.

like structure and for the corresponding silver complex it is the most stable form. The chair form comprising a M_4X_4 core contains three- and four-coordinate metal and two- and three-coordinate X in pairs respectively. Recently, a complex of the composition $[(PPh_4)_2[(CuCl)_3MoS_4]$ [71] has been isolated; its structure resembles that of the chair form where it may be thought that a unit of $\{LCuX_3\}$ from the base of the chair form and one $[X]^-$ from the bottom edge have been replaced by a MoS_4 unit. The resultant hetero-complex resembles the parent core where the only difference lies in the reduction of a pair of two coordinate halogen bridges by one two-coordinate sulphur bridge in the heterosystem and an increase of one more three-coordinate S bridge atom. This apparent change in coordination number for halogen and sulphur bridges in the two structures lies in the use of MoS_4^{2-} units as replacements for CuX_3 and X from the parent compound. The missing link in CuX_3 and X already exists in the substituent MoS_4^{2-} where all four bridging sulphurs are primarily attached to molybdenum. The structure of this heterospecies is shown in Fig. 6. The generation of $[L_4Cu_4(SCN)_2MoS_4]$ species may be envisaged by removing the four bridging Cl^- by one MoS_4^{2-} unit (cf. Figs. 4 and 5).

H. RELEVANCE OF HETEROMETAL Cu–Mo–S SPECIES TO Cu–Mo ANTAGONISM

"Cu–Mo antagonism" may be reviewed as an interaction between Cu, Mo and S. Interestingly, there is a difference in the mode of interaction between these elements in monogastrics and ruminants attributed to the difference in

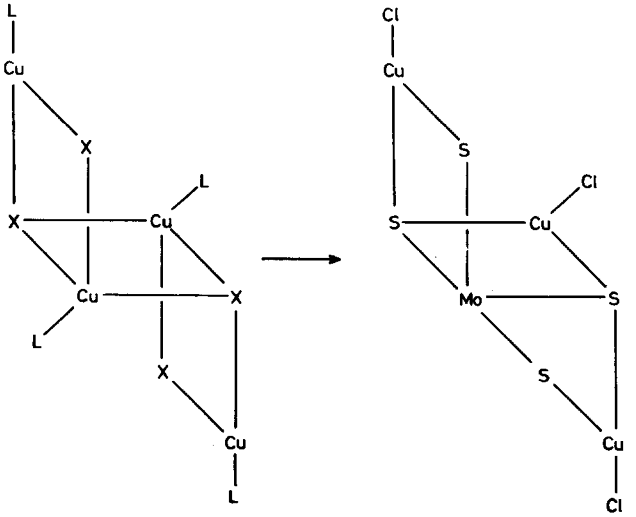


Fig. 6. Correlation of chair forms of $(CuXL)_4$ and $[(CuCl)_3MoS_4]^{2-}$.

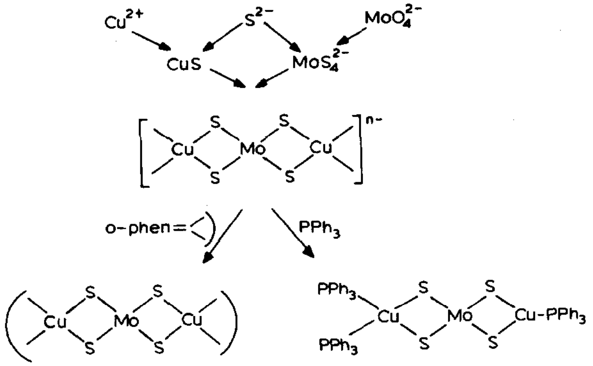
their digestive systems. In ruminants, the microbial activity in the forestomachs (rumen) is responsible for production of S^{2-} by the reduction of sulphate as well as from the degradation of sulphur-containing amino acids. Moreover, since molybdenum inhibits sulphite oxidase, the accumulation of S^{2-} may also take place in the liver of the ruminants. In monogastrics, sulphate inhibits the absorption of molybdate hence the accumulation of molybdenum in the liver is less. Hence ruminants are more affected than monogastrics by such an interaction. It is notable that in ruminants, the antagonism of copper metabolism by molybdenum is potentiated by dietary sulphur, occurs at low molybdenum concentration and results in depletion of tissue copper whereas in monogastrics it is alleviated by sulphur, occurs at high molybdenum concentration and results in tissue copper accretion.

Now it is established, at least in vitro, that thiomolybdate is formed by interaction between MoO_4^{2-} and S^2 [72]. Mills in 1979 in a comprehensive account of these interactions concluded that molybdenum interferes with copper metabolism both before and after resorption [73]. A Cu–thiomolybdate–protein complex of poor physiological availability is suggested to be responsible for the depletion of copper. Hence, the synthesis of copper–thiomolybdate–protein complex may shed some light on the chemical implication of this phenomenon and may contribute towards rationalising the difference in its modus operandi in ruminants and monogastrics.

Although the polymeric compound, $NH_4[CuMoS_4]$, may be an example of a complex obtained by interaction of copper ions with $(NH_4)_2MoS_4$ (see above), this does not take into account the protein interaction. Synthesis of some copper–thiomolybdate complexes flanked by P-donor ligands reported earlier (see above) may not be taken as models because the presence of P-donor ligands is questionable either in monogastrics or ruminants. Thus, complexes of copper–thiomolybdate flanked by N-donor ligands may be close to a realistic situation because N is a potential donor site in most proteins. Hence complexes with N-donor Cu–Mo–S systems (see above) are considered to be the closest models for the Cu–Mo interaction [45].

Furthermore, in earlier attempts to rationalise the Cu–Mo interaction, the interaction between Cu^{n+} ion and S^{2-} before the interaction of Cu^{n+} with MoS_4^{2-} has been ignored [74–77]. There is no reason why Cu^{n+} would not react in situ with S^{2-} in preference to MoO_4^{2-}. In fact, even in a competitive reaction between Cu^{n+} and MoO_4^{2-} interacting with S^{2-}, it is CuS which would be formed first in preference to MoS_4^{2-} according to the solubility product concept. Hence, the possibility of the formation of CuS and MoS_4^{2-} separately in the rumen in an earlier phase of interaction cannot be ignored. If this is the situation then one might be tempted to think that the heterometal aggregate responsible for this antagonism is formed by the reaction between CuS and MoS_4^{2-}.

In view of this the reactivity of CuS in the presence of MoS_4^{2-} in aqueous medium with S^{2-} is of immense importance [45,78]. The proposition of Mills [73] which provides resorption of MoS_4^{2-} in the form of MoS_4^{2-}-protein complex followed by its interaction with copper in the tissue may not be the only pathway for the resorption process. The solubilisation of CuS by MoS_4^{2-} and the subsequent isolation of *o*-phenanthroline and triphenylphosphine complex from the aqueous solution (containing CuS and MoS_4^{2-}) is suggestive enough to hypothesise that copper–thiomolybdate complexes can be formed by a direct resorption process. These reactions may be schematically represented as



In a varied stoichiometry between CuS and MoS_4^{2-} (1 : 1, 2 : 1, 3 : 1 and 4 : 1) such reaction shows a high tendency for formation of the core unit $\{CuS_2MoS_2Cu\}$. This core reflects the stoichiometry between Cu : Mo as 2 : 1 which is the ratio obtained from the plasma Cu and Mo by in vivo experiments using MoS_4^{2-} [80]. The isolated complexes are very stable even in acidic medium up to pH 2 which justifies that within the slightly acidic milieu of the stomach these types of derivatives are stable and remain unabsorbable.

A very interesting observation that such a type of reaction namely, resorption of CuS and hence isolation of multimetal complexes does not take place with WS_4^{2-} in aqueous solution reflects the nature's choice for molybdenum over tungsten for biological incorporation [45]. These observations are consistent with a recent in vivo experiment by Mills and co-workers where the behaviour of molybdenum and tungsten was different when MoO_4^{2-}/WO_4^{2-} were allowed to interact with S^{2-} (generated intraruminally from SO_4^{2-}) [79,80].

Based on the above observations the scheme represented in Fig. 7 has been proposed for the Cu–Mo interaction responsible for clinical deficiency of copper in physiological conditions [45].

Had the protein–Cu–MoS_4 complex been synthesised incorporating im-

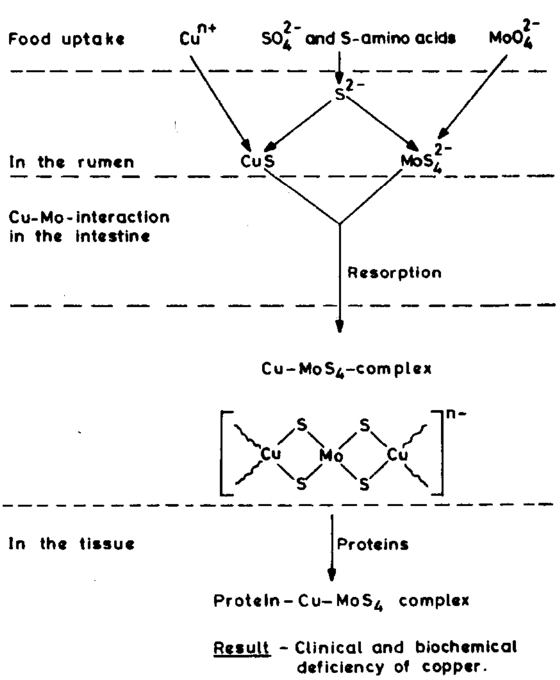


Fig. 7. Modified scheme for Cu–Mo–S interaction in ruminants.

idazole, histidine, cysteine and other N, S, O donor amino acids, one can envisage that the model would have been more realistic and comprehensive. Attempts to synthesise complexes using these ligands resulted in species with varied stoichiometry [45]. However, tailor-made metal clusters using desirable units are difficult to synthesise. The difficulty is augmented by the presence of different heterometal species in the solution and hence a proper choice of counter ions, solvent system and an inherent methodology is necessary. An encouraging approach may be to explore the use of resonance Raman and ^{95}Mo NMR studies on the in vivo culture contents of the heterometal units which can give the relevant information in modeling the systems in vitro.

I. CONCLUSIONS

In the present review an up-to-date account of the synthetic structural and biochemical aspects of the Cu–Mo–S system has been presented with a view to stimulating further research into the area whereby novel synthetic and structural methodology could be used. Moreover, the exploration of such an area would have a considerable effect not only on our understanding of the role these vital metal atoms play in this system but also on other biological aspects of these metals where their toxicity plays a vital role in causing various diseases even in humans.

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