Synthesis and characterization of copper(I) tetrathiomolybdates

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A few copper(I) complexes with tetrathiomolybdates of the type A[CuMoS₄]₃ [where A is ethylenediammonium (0.5enH₂), hydrazinium (0.5-N₂H₆)”, dimethylammonium, piperidinium, pyrrolidinium, morpholinium, tetraethylammonium, tetrabutylammonium, and tetraphenylphosphonium] have been prepared and characterized. The magnetic and EPR results indicate that copper and molybdenum are in +1 and +6 oxidation states respectively. The infrared spectral results suggest the tetradentate nature of MoS₃²⁻. The cathodic peak potential observed at −0.90 VSCE for ([NEt₄][CuMoS₄]) in cyclic voltammogram is assigned to the reduction of copper(I) to copper(0). The reaction of replacement of the ligand from Cu(Et₂dtc)₂ by MoS₃⁻ followed by the reduction of Cu(II) to Cu(I), giving [CuMoS₄]⁻ reveals that MoS₃⁻ can act as a potential antagonist to copper.

The mechanism of antagonistic behaviour of molybdenum towards copper is not well understood and more studies on the coordination aspects of copper-molybdenum-sulphur complexes are needed which may throw light on the mode of copper-molybdenum interaction in ruminants. Mallo et al. have isolated (NH₄)₂CuMoS₄ and studied its crystal structure. We report in this study, the preparation of tetrathiomolybdate complexes of copper(I) derived from various amines.

Experimental
Preparation of piperidinium tetrathiomolybdate(VII)cuprate(I), (PipH)[CuMoS₄]—To CuCl₂·2H₂O (0.17g) in ethanol(25 cm³), piperidinium tetrathiomolybdate (40 cm³) in 1:1 ethanol-water mixture was added and the solution stirred for half an hour. The pH of the solution was maintained between 7-9 by adding piperidine base as otherwise MoS₃ precipitates at a lower pH. A dark red complex precipitated out, which was filtered, washed with ethanol followed by acetone and dried over anhydrous CaCl₂, yield: 45%.

In a similar way, copper(I) tetrathiomolybdates of ethylenediammonium, hydrazinium, dimethylammonium, pyrrolidinium, piperidinium, morpholinium, tetraethylammonium, tetrabutylammonium, and tetraphenylphosphonium were prepared by taking the corresponding tetrathiomolybdate in place of (pipH)₂[MoS₄]. The quarternary ammonium or tetraphenylphosphonium salts of copper(I) tetrathiomolybdate were prepared by adding a solution of (NH₄)₂MoS₄(0.001 mol) to an ethanolic solution containing the quarternary ammonium salt (0.001 mol) and CuCl₂·2H₂O (0.001 mol). The less soluble salt of [CuMoS₄]⁻ containing the bulky cation separated out which was filtered, washed with ethanol, acetone and dried over anhydrous CaCl₂, yield: 50-55%.

Reaction of bis(diethyldithiocarbamato)copper(II) with MoS₃²⁻—[Cu(Et₂dtc)₂] (0.36 g) was dissolved in methanol (40 cm³) and to this was added (NH₄)₂MoS₄ (0.26 g) in water (40 cm³) while stirring for 2h. There was no colour change and no solid mass separated out. However, when the amine-onium or quarternary ammonium salt was added in excess (0.001 mol) to this solution and stirred, a red precipitate appeared. The separated complex was found to have identical composition of A[CuMoS₄], similar to the complex obtained by the interaction of copper(II) chloride with amine-onium tetrathiomolybdates.

The IR and far IR spectra were recorded on Perkin-Elmer 983 and Polytech IR 12 respectively. The electronic spectra were recorded on Carl Zeiss DMR recording spectrophotometer. The EPR spectra were obtained on a Varian E-4, X-band spectrometer. The magnetic measurements were made at room temperature using Gouy balance. The voltamograms of the complex were recorded in CH₃CN using NaClO₄ as the supporting electrolyte. The voltammetric measurements were carried out by a three electrode McKee Pedersen potentiostatic circuit constructed from operational amplifiers. The working electrode was a Pt foil and a Pt wire, served as an auxiliary electrode along with a saturated calomel electrode as a reference electrode. The non-aqueous solution under investigation and the reference electrode were separated by a...
non-aqueous salt bridge. The sweep rates varied between 0.01 and 5Vs⁻¹. The deaeration of the solution was carried out by passing purified nitrogen gas. The X-ray powder patterns were taken on Philips X-ray generator using nickel filtered CuKα radiation.

**Results and discussion**

The analytical data are given in Table I. The dhkl values of the same complex prepared by either synthetic routes are identical and the compounds are crystalline. The magnetic susceptibility measurements of the complexes indicate that they are diamagnetic and are found to be EPR silent. When thiomolybdate is added to Cu(II) solution, the latter is reduced to Cu(I) and coordinates to the thiomolybdate to give copper(I) tetrathiomolybdate anion. The observation is similar to that of Fe(Et₂dtch and Mosl⁻ as the interaction of the latter resulted in the formation of [Fe[MoS₄]P⁻, wherein Fe(II) is reduced to Fe(I).

The thermal decomposition studies showed that the complexes decomposed in air giving a mixture of CuMoO₄, CuSO₄ and MoO₃, in nitrogen atmosphere metal sulphides and in hydrogen atmosphere the metals. The wet chemical analysis of the residues obtained on heating the complexes to about 300°C in air suggests the presence of sulphide in addition to Cu and Mo. The final products in air around 420°C exhibit IR spectral frequencies at 1110, 980, 660 and 320, 990, 970, 910, 780 and 760; and 720 cm⁻¹ corresponding to ν(SO) of SO₃⁻, ν(MoO) of MoO₃ and ν(MoO) of MoO₂⁻ vibrations respectively. Further, the X-ray powder diffraction patterns of the residues obtained around this temperature heating the thiometallates in air exhibited dhkl values (in A) at 5.45s, 4.65s, 4.01s, 3.65s and 2.72s due⁶ to CuSO₄·5H₂O, 3.81m, 3.26s and 2.65s due⁸ to MoO₃ and 3.72s, 3.46s, 3.00s, 2.91s and 2.51s attributed⁹ to CuMoO₄. The corresponding DTA curves show several exothermic effects suggesting the complexity of the oxidation process. The X-ray powder patterns of the residues obtained on heating the sample in nitrogen atmosphere to 320°C exhibited dhkl values (in A) at 2.40s, 1.97m, 1.88s, and 1.51m due[to Cu₂S and 2.71m, 2.61m, 2.11m and 1.81m corresponding¹¹ to MoS₂.

The absorption bands observed in the regions 500-520, 350-400 and 300-330 nm with molar absorptivities of 10³ to 10⁴ l mol⁻¹cm⁻¹ in the electronic spectra of the complexes are assigned¹² to π₁(S) → d(Mo) charge transfer transitions. The IR spectral frequencies of amine-onium cations appear¹³ in 4000-600 cm⁻¹ region. The [MoS₄]²⁻ ion with Td point group symmetry has two IR active bands 458(A₁) and 472(T₂) cm⁻¹. On complexation, the tetrahedral point group symmetry is lowered. In contrast to the splitting of the Mo-S band appearing ~ 450-460 cm⁻¹ which is usually accompanied by the coordination of Mosl⁻ to a metal ion, in a few cases of the present study, a single broad band ~ 460 cm⁻¹ with inflexion due to unresolved spectral frequencies is observed. This feature is indicative¹⁴ of the polymeric nature of Mosl⁻ bonded copper. Thus it is inferred that Mosl⁻ acts as a tetraderate ligand to copper. A band appearing ~ 245 cm⁻¹ is assigned to (Cu-S) vibration. The mass spectrum of (n-Bu₄N)[CuMoS₄] consists of molecular ions due to fragmentation of tetrabutyl cation and isotopic patterns due to elemental molybdenum, copper and sulphur.

A single cathodic irreversible wave (Fig. 1) is observed at -0.90 Vs SCE in the cyclic voltamogram of (Et₄N)[CuMoS₄] when recorded at a sweep rate of 100 mVs⁻¹. The coulometry performed at the controlled potential of -0.9V indicates that the process involves one electron
transfer. The studies made on simple MoS$_4^{2-}$ species and MoS$_4^{2-}$ bonded to Fe$^{2+}$ or Ru$^{2+}$ indicate that MoS$_4^{2-}$ gets reduced at a potential above -2.1V. The organic cation was also expected to undergo reduction at a higher potential (> -2.0V) only. In the reported Cu(I) compounds, the peak potential values for the reduction of Cu(I) to Cu(O) is found to be in the range -6.0 to -1.1V depending on the environment of copper, solvent and supporting electrolyte used. The reduction wave observed $\sim$ -0.9V for (Et$_4$N)[CuMoS$_4$] is thus assigned to Cu(I) to Cu(O) reduction.

A chain like structure is proposed for [CuMoS$_4$]$^-\text{Cu}$ with Cu(I) and Mo(VI) in tetrahedral geometry bonded through disulphide bridges as detailed for NH$_4$CuMoS$_4$. Further, it is observed that dithiocarbamate ligand bonded to copper can be replaced by MoS$_4^{2-}$. Thus, MoS$_4^{2-}$ reduces copper(II) to Cu(I) in Cu(Et$_2$dtch) and coordinates to copper(I) giving rise to [CuMoS$_4$]$^-\text{Cu}$ species. The present systems take up molybdenum as MoO$_4^{2-}$ which can undergo sulphide substitution by H$_2$S generated by hydrolysis of Fe-S proteins. Probably MoS$_4^{2-}$ can interact with bound copper even when it is strongly bonded by methionine or cysteine residue of the protein. Thus, our studies give an insight into the powerful antoganistic behaviour of MoS$_4$ to copper.

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**References**