



ISSN No: 0975-7384  
CODEN(USA): JCPRCS

*J. Chem. Pharm. Res.*, 2011, 3(3):635-638

## Mixed metal Cu-Mo complexes with schiff bases of triethylenetetramine

R. Vijayanthimala\*, A. Nirmala and C. H. Swathy

*Department of Chemistry, Ethiraj College for Women, Chennai, Tamilnadu, India*

### ABSTRACT

Mixed metal complexes of Cu(I) and tetrathiomolybdate and Cu(II) and Oxomolybdate have been synthesized with Schiff bases of triethylenetetramine (trien) formed from salicylaldehyde and acetophenone. The complexes are characterized by elemental and thermal analysis, IR, UV - Visible spectral studies, magnetic and EPR studies. The tetrathiomolybdate complexes probably have a structure with  $Cu_2Mo_2S_4$  cluster linked to two more Cu (I) through sulphide bridges and have a composition  $[(trien-4H)(C_6H_4(OH)CH)_2Cu^I_2MoS_4].6H_2O$  &  $[(trien4H)(C_6H_5CCH_3)_2Cu^I_2MoS_4] ..6H_2O$  where (trien-4H) stands for trien less four hydrogens. The Oxo molybdate complexes have the compositions  $[(trien-4H) (C_6H_4(OH)CH)_2 2Cu^{II}MoO_4].4H_2O$  and  $[(trien-4H)(C_6H_5CCH_3)_22Cu^{II}MoO_4].4H_2O$  with copper in +2 oxidation state.

**Key Words:** Copper tetrathio and oxo molybdate, triethylenetetramine Schiff base, Mixed metal Copper - Molybdenum complex.

### INTRODUCTION

Interaction of tetrathiomolybdate with copper is an important reaction having biorelevance, with respect to Copper-molybdenum antagonism[1-3] and Wilson's disease[4-7.] Vijayanthimala et al [8] have earlier reported copper complexes with tetrathiomolybdate and dien based Schiff base ligands. Here we report trien based Schiff base complexes with copper and both tetrathio and oxo molybdate.

## EXPERIMENTAL SECTION

All reagents used were of analytical grade and used without purification. Triethylenetetramine and salicylaldehyde/ acetophenone (1:2 mole ratio) were mixed simultaneously and stirred well. To the yellow coloured gel added 2 mole equivalent of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dissolved in water. To the Schiff base complex formed added 2/7 mole equivalent of ammonium hepta molybdate dissolved in water, stirred well for 30 minutes and the blue complex isolated, filtered and dried. In the case of tetrathiomolybdate complex as reduction to Cu(I) was observed, in the same above preparation, 4 mole equivalent of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were used and to the Schiff base complex formed, added tetrathiomolybdate prepared from 2/7 mole equivalent of ammonium hepta molybdate by passing  $\text{H}_2\text{S}$  for 3 hrs, and removing the mother liquor. After constant stirring for 30 minutes brown solid separates out which is filtered and dried. Copper and Molybdenum in the complex were determined by optical emission spectroscopy using ICP-OES Perkin Elmer optima 5300 DV Spectrometer and Nitrogen is estimated by Kjeldhal's method. Sulphur in the complexes was analyzed gravimetrically as  $\text{BaSO}_4$ . TG/DTA were recorded in nitrogen atmosphere using NETZSCHSTA 409 C/CD thermal analyzer with a heating rate of  $10^\circ\text{C}/\text{min}$ . Magnetic susceptibility studies were carried out using vibrating magnetometer EG and GPARC model 155. UV-Visible absorption spectra were recorded in DMSO using Varian Cary Spectrophotometer 5E-UV-Vis-NIR. IR spectra were recorded in KBr using Bruker IFS 66V FT IR spectrometer. Conductivity of the complexes in DMSO was measured using simple conductivity bridge. EPR spectra of the Cu(II) complexes were recorded using Varian E-112 EPR spectrometer in the region from 1000-8000 gauss. Operating frequency was 9.3 GHz.

## RESULTS AND DISCUSSION

The elemental and thermal analysis data (Table I & II) indicated the composition to be  $[(\text{trien}4\text{H})(\text{C}_6\text{H}_4(\text{OH})\text{CH})_2\text{Cu}^{\text{I}}_2\text{MoS}_4]6\text{H}_2\text{O}$ ,  $(\text{trien}4\text{H})(\text{C}_6\text{H}_5\text{CCH}_3)_2\text{Cu}^{\text{I}}_2\text{MoS}_4 \cdot 6\text{H}_2\text{O}$ ,  $[(\text{trien}4\text{H})(\text{C}_6\text{H}_4(\text{OH})\text{CH})_2\text{Cu}^{\text{II}}\text{MoO}_4] \cdot 4\text{H}_2\text{O}$  and  $[(\text{trien}4\text{H})(\text{C}_6\text{H}_5\text{CCH}_3)_2\text{Cu}^{\text{II}}\text{MoO}_4] \cdot 4\text{H}_2\text{O}$ . The complexes are highly soluble in DMSO, sparingly soluble in alcohol and insoluble in  $\text{CHCl}_3$  and water. TG and DTA data (Table II) indicates two stages. The first stage corresponds to loss of water and the second stage leads to formation of  $\text{Cu}_2\text{MoO}_4$  and  $\text{Cu}_2\text{MoS}_4$  respectively in the oxomolybdate and tetrathiomolybdate complexes. The loss of water is accompanied by an endothermic peak below  $1000^\circ\text{C}$ . Further decomposition to the sulphide is indicated by several endothermic and exothermic peaks in DTA.

The magnetic susceptibilities of the tetrathiomolybdate complexes are negative indicating diamagnetic nature. This indicates presence of copper in +1 oxidation state and Mo in +6. The plot of magnetic moment Vs magnetic field runs linear for the oxo complexes corresponding to the presence of two unpaired electrons per molecule. This indicates the two copper atoms in the molecule are in +2 oxidation state ( $d^9$  system). The UV-Visible spectra of the tetrathiomolybdate complexes show peaks in the region below 400 nm only confirming absence of  $d \rightarrow d$  transition and presence of  $d^{10}\text{Cu}$  (I) while the oxo complexes show peaks above 400 nm corresponding to  $d \rightarrow d$  transition of Cu(II).

Table – I elemental analysis data on Cu-Mo complexes

COMPLEXES	%Cu Expt (Theo)	%Mo Expt (Theo)	%N Expt (Theo)	%S Expt (Theo)	$\lambda_{max}$ nm
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ]. 6H <sub>2</sub> O	22.13 (21.83)	16.51 (16.48)	4.01 (4.81)	20.43 (21.99)	295
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ].6H <sub>2</sub> O	20.97 (21.91)	16.2 (16.54)	4.21 (4.83)	21.08 (22.07)	261,331
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ].4H <sub>2</sub> O	14.25 (14.55)	21.3 (21.9)	6.18 (6.41)	--	291,342 430
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ].4H <sub>2</sub> O	13.94 (14.62)	21.95 (22.08)	6.00 (6.44)	--	507, 624

Table-II TGA and DTA data ON Cu-Mo complexes

COMPLEXES	% Water	%Residue	DTA PEAKS °C
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ]. 6H <sub>2</sub> O	8.51 (9.27)	60.00 (60.31)	-68.5, -188.4, -279.8, +300.9,+950
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ]. 6H <sub>2</sub> O	8.71 (9.31)	59.45 (60.52)	-95.2,-187, -420.6,+900
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ]. 4H <sub>2</sub> O	7.51 (8.24)	52.01 (51.2)	-55.5, +172, +360 +579, +891
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ].4H <sub>2</sub> O	8.24 (8.28)	52.72 (51.44)	-68.6,+108.7, +260,+582.9,+668.7

IR spectra of the complexes (Table-III) indicate a broad band around 3420 cm<sup>-1</sup> corresponding  $\nu_{OH}$  and  $\nu_{NH}$  appears in the region 3265-3210 cm<sup>-1</sup> and  $\nu_{C=N}$  of the Schiff base and  $\nu_{C=C}$  of the phenyl ring could not be distinctly assigned and appear in the region 1630-1530 cm<sup>-1</sup>. In oxomolybdate complexes Mo=O stretching appears in the region 845-912 cm<sup>-1</sup> while tetrathiomolybdate complexes show bands in the region 890-900 cm<sup>-1</sup> and 475-493 cm<sup>-1</sup> corresponding to  $\nu_{Mo=S}$  and  $\nu_{Mo-S}$  stretching respectively. The EPR spectra of the oxo molybdate complexes give two signals corresponding to the g values 2.76-2.78 and 3.38-3.4 indicating an anisotropic environment around Cu(II).

TABLE – III IR spectral data on complexes (wave numbers cm<sup>-1</sup>)

COMPLEXES	$\nu_{OH}$	$\nu_{NH}$	$\nu_{C=N}$ $\nu_{C=C}$	$\nu_{Mo=O/}$ $\nu_{Mo=S}$	$\nu_{Mo-S}$
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ]. 6H <sub>2</sub> O	3413	3222	1630 1540	901	465 488
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>I</sup> <sub>2</sub> MoS <sub>4</sub> ]. 6H <sub>2</sub> O	3413	3244	1590	891	490 475
[(trien-4H)(C <sub>6</sub> H <sub>4</sub> (OH)CH) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ]. 4H <sub>2</sub> O	3434	3234	1540 1601	845 912	--
[(trien-4H)(C <sub>6</sub> H <sub>5</sub> CCH <sub>3</sub> ) <sub>2</sub> 2Cu <sup>II</sup> MoO <sub>4</sub> ].4H <sub>2</sub> O	3434	3289, 3244	1607, 1530	850, 890	--

Based on the above discussions the oxo complexes are assigned the structure with one Cu(II) coordinated to two -NH nitrogens of trien while the other Cu(II) atom coordinated to the two C=N nitrogens of Schiff base. Two molybdate units are each linked to the two Cu(II) through the

O. The tetrathiomolybdate complexes are assigned a structure with  $\text{Cu}_2\text{Mo}_2\text{S}_4$  cubane cluster with alternating metal and sulphide ions and the two molybdenum are linked to two more sulphide ions as part of the tetrathiomolybdate which are attached to Cu linked to the NH nitrogen of the Schiff base.

#### **Acknowledgement**

Thanks are due to Ethiraj College for Women, Chennai for providing the research grant and SAIF, IIT Chennai for recording the various spectra.

#### **REFERENCES**

- [1] Dowdy, R. P. & Matrone, G.. *J. Nut*, **1968**, 95, 191.
- [2] Dowdy, R. P. & Matrone, G. *J. Nutr*, **1968**. 95, 197
- [3] N.F.Suttle, *Proc.Nutr.Soc*, **1974**, 33, 299
- [4] Brewer GJ, Dick RD, Yuzbasiyan-Gurkan V, et al. *Arch Neurol* **1991**, 48, 42.
- [5] Brewer GJ, Dick RD, Johnson V, et al. *Arch Neurol* **1994**, 51, 545.
- [6] Brewer GJ, Johnson V, Dick RD, et al. *Arch Neurol* **1996**; 53: 1017.
- [7] Brewer GJ, Hedera P, Kluin KJ, et al. *Arch Neurol* **2003**, 60, 379.
- [8] R.Vijayanthimala, C.H.Swathy, *J. Chem. Pharm. Res.*, **2011**, 3(1):349-352.