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

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## ABSTRACT

*Mixed metal complexes with Cu(I) and tetrathiomolybdate have been synthesized with Schiff bases of diethylenetriamine (dien) formed from benzaldehyde, salicylaldehyde, acetophenone and acetyl acetone. The complexes are characterized by elemental and thermal analysis, IR, UV-Visible spectral studies and magnetic studies. The complexes contain tetrahedral Cu(I) and Mo(VI) as tetrathiomolybdate. The complexes have the general composition [(dien-4H) (CRR')$_2$ (Cu$_2$MoS$_4$)]. xH$_2$O, for benzaldehyde, salicylaldehyde and acetophenone complexes. where (dien-4H) stands for dien less four hydrogen atoms. However with acetyl acetone the complex, the following complex, [(dien-4H)$_2$ (CH$_3$CCH$_2$CCH$_3$)$_2$ (Cu$_2$MoS$_4$)]. 12 H$_2$O is reported.*

**Key words:** Copper tetrathiomolybdate, diethylenetriamine Schiff base, Mixed metal Copper - Molybdenum complex.

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## INTRODUCTION

Interaction of tetrathiomolybdate with copper is an important reaction having biorelevance. Copper interacts with many essential trace elements inside the organisms. These interactions either results in stimulation or antagonism of each other. Example Copper in ceruloplasmin stimulates the synthesis of hemoglobin and presence of molybdenum results in depletion of copper for metabolic purposes. Similarly high levels of molybdenum can interfere with the body's uptake of copper producing copper deficiency. Molybdenum prevents plasma proteins from binding to copper and also increases the amount of copper that is excreted in urine. This is Cu-Mo antagonism which has been widely reported earlier[1-3]. Also tetrathiomolybdate has been widely used for the treatment of Wilson's disease, a degenerative disorder of the brain caused due to excess accumulation of copper[4-7]. These have prompted the study of Co-Mo complexes.

## EXPERIMENTAL SECTION

0.02 mol of dien and 0.04 mol of aldehyde / ketone (except acetyl acetone complex where 0.02 mol is used) are added simultaneously to 0.04 mol of copper sulphate solution in water (except acetyl acetone complex where 0.02 mol $CuSO_4$ is used) and stirred well for 10 minutes. The Schiff base complex is formed. To this added tetrathiomolybdate which is prepared from 0.0014 mol of ammonium heptamolybdate by passing $H_2S$ for 3 hrs, and removing the mother liquor. The mixture is stirred continuously using a magnetic stirrer for about 30 minutes. Then the complex comes out as a brown solid 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 $BaSO_4$. TG/DTA were recorded in nitrogen atmosphere using NETZSCHSTA 409 C/CD thermal analyzer with a heating rate of $10^oC$/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. Here we report the synthesis and characterization of Cu-Mo complexes with Schiff base moiety and molybdenum as tetrathiomolybdate.

## RESULTS AND DISCUSSION

The elemental and thermal analysis data (Table I & II) indicated the composition to be [(dien-4H) $(CRR')_2$ $(Cu_2MoS_4)$]. x $H_2O$ where

| | | | |
|---|---|---|---|
| R=H | R'=$C_6H_5$ | x=12 | for the benzaldehyde complex |
| R=H | R'=$C_6H_4OH$ | x=12 | for the salicylaldehyde complex |
| R=$CH_3$ | R'=$C_6H_5$ | x=6 | for acetophenone complex and |

[$(dien\text{-}4H)_2$ $(CH_3CCH_2CCH_3)_2$ $(Cu_2MoS_4)$]. 12 $H_2O$ for acetyl acetone complex.

In all the cases Schiff base formation involves one dien molecule and two aldehydes/ketones except the acetyl acetone complex, where two dien and two acetyl acetone have been used. The complexes are insoluble in common solvents like $CHCl_3$, alcohol, and water but soluble in DMSO and DMF. 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 $Cu_2MoS_4$. However the loss of water is not a discrete step and is accompanied by an endothermic peak. Further decomposition to the sulphide is indicated by several exothermic peaks in DTA.

The magnetic susceptibilities of the complexes are negative indicating diamagnetic nature. This indicates presence of copper in +1 oxidation state and Mo in +6. The UV-Visible spectra of the complexes show peaks only in the region below 345 nm confirming absence of $d \rightarrow d$ transition and presence of $d^{10}$Cu (I).

**Table – I Elemental analysis data on Cu-Mo complexes**

| COMPLEXES | %Cu Expt (Theo) | %Mo Expt (Theo) | %N Expt (Theo) | %S Expt (Theo) | Λmax nm |
|---|---|---|---|---|---|
| [(dien-4H) $(CCH_3C_6H_5)_2$ $(Cu_2MoS_4)$].6$H_2O$ | 17.23<br>(16.59) | 12.03<br>(12.53) | 4.62<br>(5.48) | 16.20<br>(16.71) | 266 |
| [(dien-4H) $(CHC_6H_5)_2$ $(Cu_2MoS_4)$].12$H_2O$ | 15.92<br>(15.02) | 11.98<br>(11.34) | 4.90<br>(4.96) | 14.89<br>(15.13) | 314.5 |
| [(dien-4H)$_2$$(CH_3CCH_2CCH_3)_2$$(Cu_2MoS_4)$].12$H_2O$ | 14.85<br>(14.10) | 10.72<br>(10.65) | 8.38<br>(9.30) | 13.96<br>(14.21) | 328.5 |
| [(dien-4H) $(CHC_6H_4OH)_2$ $(Cu_2MoS_4)$].12$H_2O$ | 15.67<br>(14.47) | 11.31<br>(10.93) | 5.12<br>(4.78) | 13.72<br>(14.58) | 312,<br>344.6 |

**Table-II TGA and DTA data on Cu-Mo complexes**

| COMPLEXES | %RESIDUE | Point of inflection °C | DTA PEAKS °C |
|---|---|---|---|
| [(dien-4H) $(CCH_3C_6H_5)_2$ $(Cu_2MoS_4)$].6$H_2O$ | 45.0<br>(45.8) | 67.1, 253.8 | -100, +173.9, +262.5, +529.3 |
| [(dien-4H) $(CHC_6H_5)_2$ $(Cu_2MoS_4)$].12$H_2O$ | 40.5<br>(41.4) | 181.5, 270.8 | -60, +125.3, +277, +639.1 |
| [(dien4H)$_2$$(CH_3CCH_2CCH_3)_2$$(Cu_2MoS_4)$].12$H_2O$ | 36.0<br>(38.9) | 33.4, 71.1, 210 | -62.5, -125, +129.9, +156.3, +260, |
| [(dien-4H) $(CHC_6H_4OH)_2$$(Cu_2MoS_4)$].12$H_2O$ | 39.0<br>(39.9) | 64.2, 185.2, 274.4, 544.3, 1075 | -100, +148.4 |

IR spectra of the complexes (Table-III) show $\upsilon_{OH}$ in the region 3430-3450 $cm^{-1}$ while $\upsilon_{NH}$ appears around 3220 $cm^{-1}$. $\upsilon_{C=C}$ and $\upsilon_{C=N}$ appear merged in the region 1585-1625 $cm^{-1}$. The bands characteristic of tetrathiomolybdate namely $\upsilon_{Mo=S}$ and $\upsilon_{Mo-S}$ appears in the regions 915-947 $cm^{-1}$ and 466-532 $cm^{-1}$ respectively.

**Table – III IR spectral data on complexes (wave numbers $cm^{-1}$)**

| COMPLEXES | $\upsilon_{OH}$ | $\upsilon_{NH}$ | $\upsilon_{CH}$ (ali) | $\upsilon_{C=N}$ $\upsilon_{C=C}$ | $\upsilon_{Mo=S}$ | $\upsilon_{Mo-S}$ |
|---|---|---|---|---|---|---|
| [(dien-4H) $(CCH_3C_6H_5)_2$ $(Cu_2MoS_4)$].6$H_2O$ | 3430 | 3200 | 2837 | 1589 | 916 | 471 |
| [(dien-4H) $(CHC_6H_5)_2$ $(Cu_2MoS_4)$].12$H_2O$ | 3450 | 3233 | 2933 | 1623, 1600 | 932 | 471 |
| [(dien-4H)$_2$$(CH_3CCH_2CCH_3)_2$$(Cu_2MoS_4)$].12$H_2O$ | 3431 | 3236 | 2949 | 1608, 1598 | 923 | 483 |
| [(dien-4H) $(CHC_6H_4OH)_2$ $(Cu_2MoS_4)$].12$H_2O$ | 3450 | 3220 | 2942 | 1625 | 922 | 466 |

Based on the above discussions the complexes are assigned the structure with Cu(I) tetrahedrally linked to two nitrogens of the Schiff base and two sulphur atoms of tetrathiomolybdate. The tetrathiomolybdate is linked to the second Cu(I) through the other two sulphur. The third and the fourth coordinating sites of the second copper may be satisfied by aquo ligands. In the acetyl acetone complex a macrocycle may have been formed with two acetyl acetone and two dien molecules with all four carbonyl groups of the acetyl acetone being involved in the Schiff base formation. One of the Cu(I) may be linked to three of these nitrogen atoms and the other Cu(I) linked to tetrathiomolybdate through two sulphur atoms may have a linkage with the NH hydrogen of dien. The fourth coordinating site of both copper may be satisfied by aquo ligand.

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