



## Synthesis and Characterization of Manganese, Copper and Zinc Complexes Derived from Schiff - Base Ligand

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<http://dx.doi.org/10.13005/ojc/330563>

(Received: August 03, 2017; Accepted: September 02, 2017)

### ABSTRACT

A Schiff base has been prepared by the condensation of 4- amino -3,5-dimercapto, 1,2,4-triazole with 2,4-diaminobenzaldehyde. The ligand has been used for complexation with Mn(II), Cu(II) and Zn(II) metal ions. The complexes have been characterized by their elemental analysis, molar conductivity, magnetic susceptibility, IR spectra and electronic spectra. The very low value of molar conductivity of complexes shows their non-electrolytic nature. The comparison of IR spectra of complexes with that of free ligand reveals that the ligand is coordinated through azomethine nitrogen and deprotonated thiol sulphur forming five membered heterochelates. The magnetic moment values and electronic spectral bands clearly indicate the octahedral geometry around metal ions in complexes

**Keywords:** Heterochelates, Non- electrolytic, Schiff Base.

### INTRODUCTION

The schiff base transition metal complexes have invited the attention of Inorganic Chemists because of vast applications in pharmaceutical and industrial fields.<sup>1-5</sup> Due to their simple synthesis and versatility, Schiff complexes continue to remain an important and a popular area of research as such complexes persistently play a very significant role in understanding the various aspect of coordination chemistry of transition metals<sup>6-10</sup>. The schiff base of triazole derivatives have been found pharmaceutically active.<sup>11-13</sup> The pharmaceutical activity of these Schiffbase have

been found to get enhanced on complexation with metal ions<sup>14</sup>. The literature reveals that schiff base complexes of 4-(2',4'-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole has not been taken care of. Therefore, in continuation of our previous work,<sup>15</sup> in the present paper we report the synthesis and characterization of Mn(II), Cu(II) and Zn(II) complexes with Schiff base, 4-(2',4'-diamino-benzaldimino)-3,5-dimercapto-1,2,4-triazole.

### MATERIAL AND METHOD

All the reagents used in the present work were of AnalR grade and were used as received.

Thiocarbohydrazide, carbon disulphide,  $\alpha$ -picoline, pyridine, ethanol, 2,4-diaminobenzaldehyde were procured from Merck (India) and metal salts of Mn(II), Cu(II) and Zn(II) procured from Lova Chemic (India). For the preparation of the ligand at first the pyridinium salt of 4-amino-3,5-dimercapto-1,2,4-triazole was prepared by refluxing the mixture of thiocarbohydrazide and carbon disulphide in pyridine on oil bath for one hour. There after, the pyridinium salt was treated with hydrochloric acid to get 4-amino-3,5-dimercapto-1,2,4-triazole. This amine was refluxed with 2,4-diaminobenzaldehyde in ethanol in the presence of 2 drops conc<sup>n</sup> sulphuric acid for one hour to get yellow crystals of Schiff base, i.e., 4-(2',4'-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazole. This ligand was used for complexation with metal chloride in ethanolic medium by usual method of reflux by adding 2 ml of  $\alpha$ -picoline. On cooling the reaction mixture the solid complex was separated out which was filtered and washed with alcohol. It was dried in desiccator over anhydrous calcium chloride. The C, H and N elemental analysis were carried out using Perkin Elmer 2400 II elemental analyzer. IR spectra of ligand as well as complexes were recorded on Perkin-Elmer FTIR spectrophotometer (spectrum II) using KBr pellet. The magnetic moment of complexes were determined by Gouy balance method at room temperature. Determination of molar conductivity of complexes with  $10^{-3}$  M solution in DMSO was done

using Elico direct reading conductivity meter. The electronic spectra of complexes were recorded on Perkin-Elmer Lambda 950 spectrophotometer. Results are given in Table .1

## RESULT AND DISCUSSION

The molar conductivity values of complexes are indicative of their non electrolytic nature<sup>16-17</sup>. On the basis of elemental analysis and molar conductivity values, the complexes are formulated as  $[ML_2(\alpha\text{-pico})_2]$ , where L is the Schiff base ligand. IR spectra of complexes are very cumbersome and hence only important bands have been assigned and explained. The IR spectra of free ligand display two bands at 3013 and 2859  $\text{cm}^{-1}$  which are assigned to  $\nu_{\text{asym NH}_2}$  and  $\nu_{\text{sym NH}_2}$  stretching vibration<sup>18</sup>. These two bands do not undergo any appreciable change in their frequencies in the spectra of complexes. It shows no coordination of  $\text{NH}_2$  group to the metal ions. The band at 3010  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{CH}}$  aromatic group while the band at 2950  $\text{cm}^{-1}$  is fairly assigned to  $\nu_{\text{CH}}$  of azomethine group<sup>19-21</sup>. The strong band at 2560  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{SH}}$  stretching vibration of the ligand. In the spectra of complexes this band appears at lower frequency with highly decreased intensity. It shows that out of two SH group one has undergone deprotonation and coordination occur though deprotonated mercapto sulphur.<sup>22</sup> The other

**Table. 1 : Analytical data and Conductivity of the Synthesis of Compound**

Compound	%Metal Calc (Found)	% C Calc (Found)	% H Calc (Found)	% N Calc (Found)	% S Calc (Found)	$\mu_{\text{eff}}$ (B.M.)	Conductivity mhos $\text{cm}^{-1}$ mole <sup>-1</sup>
LH	— (—)	42.857 (42.902)	3.968 (4.051)	27.778 (27.805)	25.397 (25.401)		
$[\text{MnL}_2(\alpha\text{-pico})_2]$	7.375 (7.405)	48.326 (48.352)	4.564 (4.581)	22.552 (22.538)	17.183 (17.201)	5.96	16.20
$[\text{CuL}_2(\alpha\text{-pico})_2]$	8.432 (8.425)	47.775 (47.485)	4.512 (4.506)	22.295 (22.307)	16.986 (16.978)	2.12	15.48
$[\text{ZnL}_2(\alpha\text{-pico})_2]$	8.654 (8.634)	47.659 (47.672)	4.501 (4.488)	22.241 (22.245)	16.945 (17.013)	—	14.00

LH = 4-(2',4'-diaminobenzaldimino)-3,5-dimercapto-1,2,4-triazol.  $\alpha$ -pico =  $\alpha$ -Picoline,  
Calc=Calculated

major change is found in the absorption frequency of azomethine group of the free ligand which absorbs at  $1630\text{ cm}^{-1}$  in the spectrum of free ligand and shifts to lower frequencies by  $30\text{-}40\text{ cm}^{-1}$  in the spectra of the complexes. It is indicative of coordination through azomethine nitrogen of ligand. The coordination through deprotonated mercapto sulphur and azomethine nitrogen is further confirmed by appearance of new bands at  $510$  and  $370\text{ cm}^{-1}$  due to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-S}}$  stretching vibration respectively in complexes. The new band appearing at  $755\text{ cm}^{-1}$  in the spectra of complexes shows the presence of coordinated  $\alpha$ -picoline in complexes<sup>24-28</sup>.

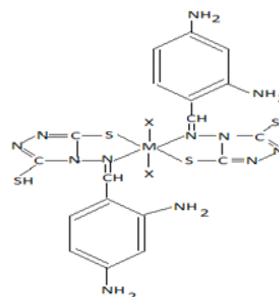
The magnetic moment of Mn (II) complex is determined to be  $5.96\text{ B.M.}$  which corresponds to 5 unpaired electrons. It shows that Mn (II) complex is paramagnetic and it is high spin complex<sup>29-32</sup>. Mn(II) complex displays three bands in its electronic spectra which may be assigned to spin forbidden transition as below:-

$19500\text{ cm}^{-1}(\nu_1)=^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g} (^4\text{G})$ ,  $23480\text{ cm}^{-1}(\nu_2)=^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g} (^4\text{G})$  and  $19500\text{ cm}^{-1}(\nu_3)=^6\text{A}_{1g} \rightarrow ^4\text{E}_g (^4\text{D})$ . As the transitions are spin forbidden and also Laporte forbidden the intensity is very very poor. Using Tanabe – Sugano diagram the various crystal field parameters have been calculated with values  $=\frac{\nu_2}{\nu_1} 1.204$ ,  $B=844.15\text{ cm}^{-1}$ ,  $D_q=1063.63\text{ cm}^{-1}$ . So  $\beta=0.879$ ,  $0.137$ , as according to Orgel the energy of  $^4\text{G}$  lies above  $^6\text{A}_{1g}$  by  $17B + 5C$ . So  $17B + 5C = \nu_3$ . From this the value of C is calculated to be  $3029.89\text{ cm}^{-1}$ . Hence,  $\frac{C}{B} = 3.589$  which is very close to theoretical value  $\frac{C}{B}$  (3.8) for Mn (II) complexes. The values of various crystal field parameters are in good agreement with the reported value for octahedral complexes of Mn (II).<sup>28,33-34</sup>

The magnetic moment of Cu (II) complex is found to be  $2.12\text{ B.M.}$  at room temperature which shows it is magnetically dilute octahedral complex.<sup>35-38</sup> The electronic spectra of Cu (II) complex exhibit a broad band at  $20350\text{ cm}^{-1}$  due to  $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$  spin allowed transition. The broadness of band clearly indicates the further splitting of both  $^2\text{E}_g$  and  $^2\text{T}_{2g}$  due to departure of symmetry from  $\text{O}_h$  to  $\text{D}_{4h}$  symmetry. However, the value is in good agreement with the reported value of distorted  $\text{O}_h$  complexes of Cu (II).<sup>5,39-43</sup>

Zn (II) complex is diamagnetic which is in accordance with its  $d^{10}$  configuration. Hence it doesn't display any band in electronic spectra. However, on the basis of elemental analysis and molar conductivity  $\text{O}_h$  structure is assigned to Zn (II) complex.

The tentative structure of complexes may be given below:-



M=Mn, Cu and Zn X= $\alpha$ -picoline

## ACKNOWLEDGEMENT

One of the authors Mr. Bishwanath Kumar is thankful to the Principal, M.G. College, Gaya for carrying out research work in its P.G. Department laboratory.

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