



## Studies on Some Hetero Binuclear Copper(II) Schiff base Complexes

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### ABSTRACT

A series of new hetero binuclear complexes of copper(II) and lead(II) using Schiff base have been synthesized. The Schiff base has been derived from the condensation reaction between Salicylaldehyde and 1,2-Ethylenediamine. The hetero binuclear complexes have been characterized by using elemental analysis, molar conductance measurement, magnetic susceptibility studies, UV-Vis and IR spectra. The studies revealed square planar geometry for the complexes with coordination number four.

**Keywords:** Schiff base, Hetero binuclear complexes, Electronic spectra, IR spectra, etc.

### INTRODUCTION

Schiff bases are studied extensively as they form large number of complexes with transition metals<sup>1</sup>. The structural design of the metal complexes of Schiff base, their applications as antibacterial and antifungal agents and use in catalytic activity supplement their importance<sup>2-5</sup>. Studies on metalloenzymes help in the study of drug remedy and in designing new compounds with improved potency<sup>6</sup>. Schiff bases having nitrogen, oxygen or sulphur donor atoms can bind to one or more metal ions to form metal complexes with interesting medicinal properties<sup>7,8</sup>. Binuclear Schiff base complexes finds wide applications in various industrial processes<sup>9</sup>. Numerous Schiff base metal complexes have been reported in the past several years<sup>10,11</sup> but little work on binuclear Schiff base

metal complexes have been published. In the present paper, we have discussed the synthesis and spectral characteristics of hetero binuclear complexes involving copper(II) ion and lead(II) metal salts of organic acids viz. *o*-nitrophenol, 2,4-Dinitrophenol, 8-Hydroxyquinoline and 1-Nitroso-2-naphthol.

### MATERIALS AND METHODS

For the synthesis of the hetero binuclear complexes, the ligands used were of A.R. grade. IR spectra were recorded using FTIR spectrophotometer, Shimadzu model 8201 PC in KBr phase. The UV-Vis absorption spectra were studied on Systronics Double Beam Spectrophotometer 2202. Electrical conductance was measured on Systronics digital direct conductivity meter-306. Faraday method was adopted for magnetic measurements of the



complexes. Elemental analyses were done on Heraeus B6450 CHN elemental analyzer. Electrical tempo T-1150 melting point apparatus was used for melting point measurements.

### Synthesis of the Schiff base

Salicylaldehyde and 1,2-Ethylenediamine were mixed in 2:1 molar ratio in ethanolic medium. The solution was refluxed for 15 minutes. The solution was then cooled in ice bath to obtain yellow coloured solid *N,N'*-Ethylenebis(salicylalimine). The solid yield was separated and recrystallized with ethanol.

### Synthesis of copper(II) complex of Schiff base

Ethanolic solution of copper acetate was

added slowly to a hot solution of Schiff base in 1:1 stoichiometric proportion. The mixture was refluxed for 2 h at 80°C to yield dark green solid. The solid obtained was isolated by filtration and dried in an electric oven.

### Synthesis of the hetero binuclear Schiff base complexes

A solution of *N,N'*-Ethylenebis(salicylalimine)copper(II) in alcohol was taken in a conical flask and lead chelate of *o*-Nitrophenol, 2,4-Dinitrophenol, 1-Nitroso-2-naphthol or 8-Hydroxyquinoline were added to it in 1:1 stoichiometric ratio. The mixture was refluxed for 60-90 min at 80°C. The mixture was concentrated, the coloured precipitate separated out which was filtered, washed with absolute ethanol and dried in an electric oven.

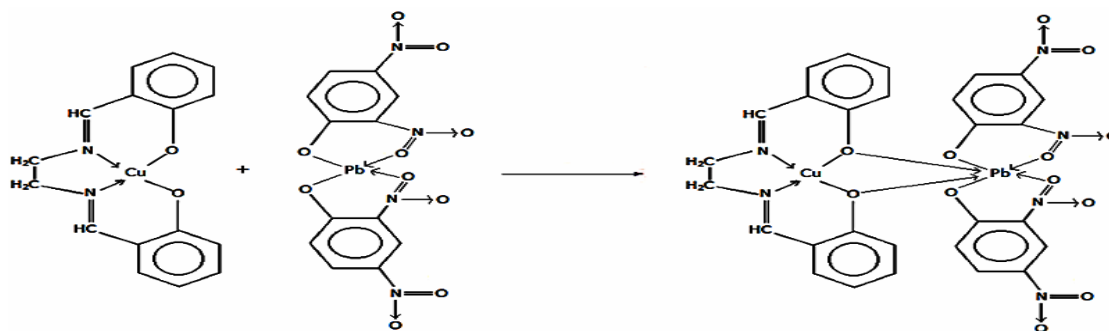


Fig. 1. Schematic representation of the synthesis of hetero binuclear Schiff base complex,  $C_{26}H_{20}N_6O_{12}CuPb$

## RESULTS AND DISCUSSION

The hetero binuclear complexes obtained are crystalline, coloured and non-hygroscopic in nature. They are soluble in methanol, acetone,

DMF and DMSO but insoluble in water. All the hetero binuclear complexes decomposed in the temperature range 232-258°C. The elemental data of the complexes are in good agreement with their calculated value Table 1.

Table 1: Physical characterization, molar conductance and analytical data of the complexes

Compound	Colour	Melt.(m)/Dec.(d)/ Trans.(t) temp.(°C)	Molar Conductance (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	C	Analysis (%) Found (Calculated)				Yield (%)
					H	N	Cu	Pb	
$C_{16}H_{14}N_2O_2Cu$	Dark Green	249 (d)	0.4	39.52 (41.05)	2.50 (2.48)	10.75 (10.88)	9.75 (9.88)	12.85 (13.29)	80.46
$C_{26}H_{20}N_6O_{12}CuPb$	Light Brown	258 (md)	1.6	38.21 (37.22)	2.21 (2.22)	10.31 (9.30)	7.05 (7.03)	20.26 (22.93)	65.24
$C_{26}H_{22}N_4O_8CuPb$	Brown	232 (d)	2.8	42.33 (41.34)	2.61 (2.72)	7.89 (6.88)	7.88 (7.81)	25.48 (25.47)	68.06
$C_{34}H_{26}N_4O_4CuPb$	Yellowish Green	253 (d)	3.7	49.36 (49.47)	3.21 (3.17)	6.84 (6.78)	7.70 (7.69)	25.25 (25.10)	72.73
$C_{36}H_{26}N_4O_6CuPb$	Deep Brown	240 (d)	3.6	48.12 (49.0)	2.95 (2.97)	6.25 (6.35)	7.4 (7.2)	23.7 (23.5)	70.42

where d – decomposition temperature, md – melting with decomposition

### Molar Conductance

The molar conductivity studies of the complexes in methanol were measured at 30(±5)°C and at a concentration of 10<sup>-3</sup> M. The molar

conductance of the hetero binuclear complexes lies in the range of 1.6-3.7 Ω<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup> Table 1. This indicates the non-electrolytic nature of the hetero binuclear complexes<sup>12</sup>.

### Magnetic moment

The copper(II) complex of *N,N'*-Ethylenebis(salicylaldehyde) and the hetero binuclear complexes  $C_{28}H_{20}N_6O_{12}CuPb$ ,  $C_{34}H_{26}N_4O_4CuPb$  and  $C_{36}H_{26}N_4O_6CuPb$  are paramagnetic. The magnetic moment values which lies in the range 1.87-2.10 B.M. Table 3 correspond to square planar geometry of  $C_{16}H_{14}N_2O_2Cu$  in the hetero binuclear complex<sup>13</sup>. The hetero binuclear complex  $C_{28}H_{22}N_4O_8CuPb$  shows diamagnetic behavior which suggest that it assumes a dimeric structure<sup>14</sup>.

### IR Spectra

For the copper(II) complex of *N,N'*-Ethylenebis(salicylaldehyde), a band at  $1546\text{ cm}^{-1}$  is observed. This band is due to C–O str. of the phenolic group<sup>15</sup>. When the hetero binuclear complex is formed, there is a slight shifting in the position of the C–O str. band and is observed in  $1530\text{-}1561\text{ cm}^{-1}$  range. For the hetero binuclear complexes  $C_{34}H_{26}N_4O_4CuPb$  and  $C_{28}H_{20}N_6O_{12}CuPb$ , splitting of band is also observed. The shifting and splitting of the band in the hetero binuclear complexes indicates the coordination of the phenolic oxygen to the lead metal Table 2.

**Table 2: infrared spectral data of the complexes**

Complexes	$\nu_{C-O}$ str (in $\text{cm}^{-1}$ )	$\nu_{M-O/M-N}$ str (in $\text{cm}^{-1}$ )
$C_{16}H_{14}N_2O_2Cu$	1546	465, 520
$C_{28}H_{20}N_6O_{12}CuPb$	1530, 1561	491, 536, 559, 607
$C_{28}H_{22}N_4O_8CuPb$	1531	464, 498, 569
$C_{34}H_{26}N_4O_4CuPb$	1535, 1561	486, 559, 600
$C_{36}H_{26}N_4O_6CuPb$	1533	466, 503, 570, 629

Further, bands at  $465\text{ cm}^{-1}$  and  $520\text{ cm}^{-1}$  are observed for copper(II) complex of *N,N'*-Ethylenebis(salicylaldehyde) which are respectively assigned to M–N str and M–O str modes<sup>16-19</sup>. In the hetero binuclear complexes, a shifting in the position of these bands is observed<sup>20</sup> which further confirms the coordination of the phenolic oxygen to the lead metal Figure 2.

### UV-Vis Spectra

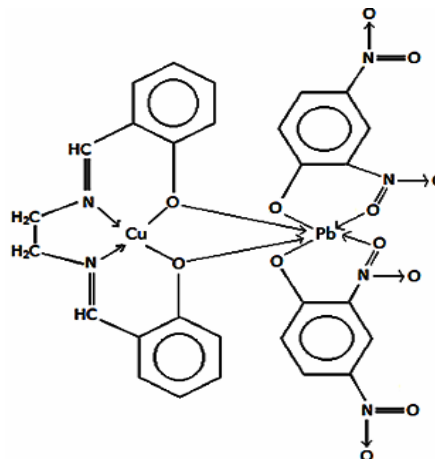
The UV-Vis spectra for the copper(II) complex of *N,N'*-Ethylenebis(salicylaldehyde) are observed in the range  $245\text{-}562\text{ nm}$  Table 3. The bands at 245, 314 and 387 nm are due to  $\pi \rightarrow \pi^*$  transitions in the complexes<sup>21,22</sup>. The band at 562 nm suggests d-d transition and charge transfer in the

complex<sup>23,24</sup>. The bands at 387 nm and 562 nm also suggest for square planar geometry<sup>24,25</sup> of copper(II) with coordination number four.

For the hetero binuclear complexes, electronic absorption spectral bands obtained are in the range  $217\text{-}562\text{ nm}$  similar to those of copper(II) complex of *N,N'*-Ethylenebis(salicylaldehyde). Hence, there is no change in the stereochemistry around copper(II) after the formation of the hetero binuclear complex.

**Table 3: Magnetic moment and UV-Vis spectral data of the complexes**

Complexes	Magnetic moment (in B.M.)	Electronic transitions (in nm)
$C_{16}H_{14}N_2O_2Cu$	1.90	245, 312, 387, 562
$C_{28}H_{20}N_6O_{12}CuPb$	1.85	284, 358, 559
$C_{28}H_{22}N_4O_8CuPb$	diamagnetic	273, 355, 558
$C_{34}H_{26}N_4O_4CuPb$	1.87	267, 366, 559
$C_{36}H_{26}N_4O_6CuPb$	2.10	217, 355, 562



**Fig. 2. Hetero binuclear Schiff base complex,  $C_{28}H_{20}N_6O_{12}CuPb$**

From the above results and discussion, it may be summarized that copper complex of the Schiff base and further hetero binuclear complexes with lead(II) salts of various organic acids were synthesized. They were characterized by molar conductance, magnetic susceptibility measurements, IR spectra and UV-Vis spectral studies. Spectral characterization of these hetero binuclear complexes revealed square planar geometry of copper(II) with coordination number four.

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#### Conflict of interest

The authors declare that there is no conflict of interest.

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