

## Synthesis and Characterization of Metal Complexes with Ligands Derived from 2,6-Diacetyl pyridine monoxime and 1,2-Diamino benzene

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A number of metal complexes with a new variety of hexadentate ligands of the type  $[ML-H_2]$ ,  $[ML]X_2$  where  $M = Co(II)$ ,  $Ni(II)$ ,  $Cu(II)$ ,  $X = Cl^-$ ,  $Br^-$ ,  $I^-$  and  $L = Bis-(2,6-diacetyl\ pyridine\ monoxime)$  and 1,2-diamino benzene have been synthesized and characterized.

**Key Words:** Synthesis, Metal complexes, 2,6-Diacetyl pyridine monoxime and 1,2-Diamino benzene.

### INTRODUCTION

Varieties of polydentate ligands, nitrogen donors and Schiff bases find their special place in binding with metal centres<sup>1-6</sup>. Recently transition metal ions have been used in template synthesis of a range of macrocyclic Schiff base ligands containing 15–30 members in the ring.<sup>7,8</sup> Sometimes this class of ligands seems to be unstable in the uncomplexed form, and so this procedure is restricted to those metal ions which are effective as templates.

In the present paper, the synthesis and structural elucidation of metal complexes with the ligand derived from the condensation of 2,6-diacetyl pyridine monoxime and 1,2-diamino benzene have been reported.

### EXPERIMENTAL

**Preparation of 2,6-diacetyl pyridine monoxime:** A concentrated aqueous solution of hydroxylamine hydrochloride (3.5 g, 0.05 mol) was added to an ethanolic solution of 2,6-diacetyl pyridine (6.5 g, 0.04 mol) and then cooled up to  $-5^\circ C$ . To this reaction mixture 20% aqueous solution of NaOH (12 g, 0.3 mol) was added dropwise with rapid stirring and the temperature of the resultant mixture was maintained below  $0^\circ C$ . The colour of the solution became pink. After 90 min it was diluted with water and acidified with glacial acetic acid. The mixture was allowed to stand for 30 min and then filtered through suction. The product was recrystallized from aqueous alcohol (60 volume % alcohol). White needle-type crystals were obtained. These were filtered, washed with water and dried. The dried product was analyzed for its constituents.

**Preparation of bis-(2,6-diacetyl pyridine monoxime)-1,2-diamino benzene:** 2,6-Diacetyl pyridine monoxime (0.02 mol) and 1,2-diamino benzene (1.08 g., 0.01 mol) were mixed with the help of agate and mortar. They went into a homogeneous viscous liquid after triturating them together for about 2 h. The mortar was kept in a refrigerator overnight. The product was dried under vacuum and recrystallized from a little ethyl alcohol and analyzed. The melting point was found to be 184°C.

**Preparation of [bis-(2,6-diacetyl pyridine monoximato)-1,2-diamino-benzene copper(II)] [CuL-H<sub>2</sub>]:** 2,6-diacetyl pyridine monoxime (0.01 mol) was dissolved in 20 mL absolute alcohol. The solution was warmed to boiling. To this solution an alcoholic solution of cupric acetate monohydrate (0.005 mol) was added dropwise with constant shaking. An alcoholic solution of 1,2-diamino benzene (0.005 mol) was added and the whole solution was refluxed on a hot water bath for 1 h. The mixture was cooled at normal temperature and filtered. The blackish cluster type product was obtained which was recrystallized from water : alcohol mixture (1 : 1). The compound was dried and analyzed for its constituents.

Similar procedures were adopted also for the preparation of other neutral complexes.

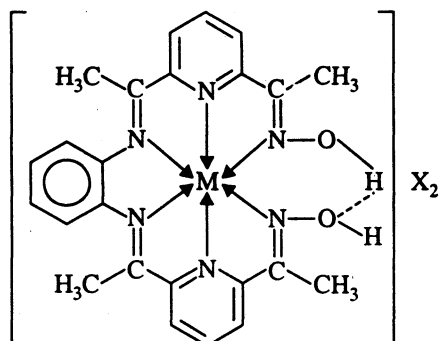
**Preparation of [bis-(2,6-diacetyl pyridine monoxime)-1,2-diamino benzene copper(II)] chloride [CuL]Cl<sub>2</sub>:** An ethanolic solution of 2,6-diacetyl pyridine monoxime (0.01 mol) was added to an ethanolic solution of cupric chloride dihydrate (0.005 mol) with constant shaking. To this solution an alcoholic solution of 1,2-diamino benzene (0.005 mol) was added and the whole solution was refluxed on a water bath for 1.5 h. A purple brown precipitate was formed after cooling. The solid product was filtered, washed with alcohol and dried. The dried product was analyzed for its constituents. Other halo complexes of Ni(II), Co(II) and Cu(II) were prepared by adopting similar procedures.

## RESULTS AND DISCUSSIONS

The analytical data of the complexes are reported in Table-1.

The infrared spectra of the complexes show marked similarity in the band position indicating the support of similar structure. The ligand showed a broad band at 1,450 cm<sup>-1</sup> due to  $\nu(\text{C}=\text{N})$  of oxime group which shifted to high frequency side (5–15 cm<sup>-1</sup>) on complexation. A band at 1,690 cm<sup>-1</sup> in the free ligand exhibits the presence of  $>\text{N}-\text{OH}$  group which remained intact in case of  $[\text{ML}]\text{X}_2$ . No such band appeared in this range in the spectra of inner complexes such as  $[\text{ML}-\text{H}_2]$ . A pair of bands located in the vicinity of 1030 and 985 cm<sup>-1</sup> have been assigned to  $\nu(\text{N}-\text{O})$  stretching vibrational modes of the oxime group. A band near 3,300 cm<sup>-1</sup> was completely missing that exhibits the absence of hydrogen bonding in case of inner complexes. The appearance of three more bands in the vicinity of 1,575–1585, 600–615 and 400–415 cm<sup>-1</sup> is an evidence in support of the attachment of pyridine nitrogen with the metal ions<sup>7</sup>.

The infrared studies and analytical data clearly manifest the mode of bonding of ligand with metal ions and they have been assigned the following structure (Fig. 1).



M = Co(II), Ni(II); X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>

M = Co(II); X = Cl<sup>-</sup>, Br<sup>-</sup>

Fig. 1

TABLE-1  
COLOUR AND ANALYTICAL DATA OF THE COMPLEXES OF  
Co(II), Ni(II) AND Cu(II) WITH THE LIGAND BIS-(2,6-DIACETYL  
PYRIDINE MONOXIME)-1,2-DIAMINO BENZENE.

Complex (Colour)	Metal %		Carbon %		Nitrogen %		Hydrogen %		Anion %	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
[CuL-H <sub>2</sub> ] (Blackish)	12.65	12.96	58.34	58.82	16.85	17.15	4.23	4.52	—	—
[CuL]Cl <sub>2</sub> (Purple brown)	10.95	11.28	50.86	51.20	14.45	14.93	4.02	4.26	12.15	12.62
[CuL]Br <sub>2</sub> (Brown)	9.21	9.74	43.95	44.20	12.37	12.89	3.26	3.68	24.05	24.55
[NiL-H <sub>2</sub> ] (Blackish)	11.83	12.07	59.03	59.44	17.01	17.33	4.13	4.54	—	—
[NiL]Cl <sub>2</sub> (Brownish green)	10.20	10.49	51.02	51.65	14.79	15.05	4.13	4.30	12.06	12.73
[NiL]-Br <sub>2</sub> (Light brown)	8.76	9.04	44.01	44.54	12.22	12.99	3.26	3.71	24.03	34.74
[NiL]I <sub>2</sub> (Dark red)	7.23	7.90	38.31	38.89	10.86	11.34	3.01	3.24	33.92	34.30
[CoL-H <sub>2</sub> ] (Dark brown)	11.85	12.16	59.12	59.39	16.97	17.31	4.23	4.53	—	—
[CoL]Cl <sub>2</sub> (Light red)	10.02	10.57	51.21	51.61	14.76	15.03	4.02	4.30	12.03	12.72
[CoL]Br <sub>2</sub> (Red)	8.89	9.11	44.02	44.51	12.33	12.98	3.21	3.70	24.06	24.72
[CoL]I <sub>2</sub> Reddish brown	7.21	7.96	38.04	38.56	10.86	11.33	2.98	3.23	33.92	34.27

A further support to the structure has been provided by the electronic and magnetic moment studies. The nickel(II) complexes are of spin-free type with the values of magnetic moments lying in the range 3.60–3.66 B.M. The data indicate the characteristic features of octahedral arrangement of ligands around the metal ion with slight distortion. The electronic spectra of the nickel(II) complexes of the types  $(\text{NiL-H}_2)$  and  $[\text{NiL}]X_2$  show three distinct bands. The low energy band observed at  $12,600 \text{ cm}^{-1}$  which can be assigned to  ${}^3B_{1g} \rightarrow {}^3B_{2g}$  transition. The next higher band occurs at  $13,500 \text{ cm}^{-1}$  assignable to  ${}^3B_{1g} \rightarrow {}^3E_g$  transition. The third band at  $35,600 \text{ cm}^{-1}$  can be assigned to the transition  ${}^3B_{1g} \rightarrow {}^3T_{1g}(P)$ .<sup>8</sup>

The cobalt(II) complexes possess magnetic moment values within the range 2.19–2.30 B.M. which show that the complexes are of low spin type. The electronic spectra of Co(II) complexes exhibit three bands at  $14,500$ ,  $37,200$  and  $47,300 \text{ cm}^{-1}$  which have been assigned to  ${}^4T_{1g} \rightarrow {}^4T_{2g}$ ,  ${}^4T_{1g} \rightarrow {}^4A_{2g}$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$  transitions respectively characterizing tetragonally distorted octahedral ligand field about metal ions<sup>9, 10</sup>.

The complexes  $[\text{CuL-H}_2]$  and  $[\text{CuL}]X_2$  (where  $X = \text{Cl}^-$ ) with  $\mu_{\text{eff}}$  ranges between 1.85–1.90 B.M. give three bands at  $13,700$ ,  $17,100$  and  $23,700 \text{ cm}^{-1}$  which have been assigned as follows:

$$\Delta E({}^2B_{1g} \rightarrow {}^2A_{1g}) = 13,700 \text{ cm}^{-1}$$

$$\Delta E({}^2B_{1g} \rightarrow {}^2B_{2g}) = 17,100 \text{ cm}^{-1}$$

$$\Delta E({}^2B_{1g} \rightarrow {}^2E_{1g}) = 23,700 \text{ cm}^{-1}$$

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