

## Mononuclear and Binuclear Complexes of Fe(II) and Cu(II) with 2,6-Diacetyl Pyridine Monoxime and Phenylene Diamine

R.N. KUMAR\*, N.K. CHAUHAN and SUDHIR KUMAR SINGH

*P.G. Department of Chemistry*

*M.L.T. Saharsa College, Saharsa-852 201, India*

Mononuclear and binuclear complexes of types  $(ML_1-H_2)$ ,  $[ML_1]X_2$ ,  $[ML_2]_2X_4$ ,  $[ML_3]_2X_4$ ,  $[M(L_2-H_2)]_2$ ,  $[ML_3-H_2]_2$  where M = Fe(II) or Cu(II), X =  $OAc^-$  or  $0.5SO_4^{2-}$ ,  $L_1$  = bis-(2,6-diacetyl pyridine monoxime) 1,2-diamino benzene,  $L_2$  = bis-(2,6-diacetylpyridine monoxime) 1,3-diamino benzene,  $L_3$  = bis-(2,6-diacetyl pyridine monoxime) 1,4-diaminobenzene have been synthesised and characterised by elemental analysis, IR electronic and magnetic susceptibility studies.

### INTRODUCTION

In an extension of our studies<sup>1</sup> on metal complexes of macrocyclic complexes derived from 2,6-diacetyl pyridine and different isomers of phenylene diamine, we have investigated the synthesis and structure of Fe(II) and Cu(II) complexes of bis-(2,6-diacetylpyridine monoxime) 1,2-diamino benzene as well as 1,3- and 1,4-diamino benzene. The results of these investigations are reported in the present paper.

### EXPERIMENTAL

The 2,6-diacetyl pyridine, phenylene diamine (Aldrich, USA), Metal salt, solvents and hydroxylamine were of reagent grade. The ligand as well as macrocyclic complexes were prepared according to the report<sup>2</sup> and its authenticity was determined by chemical and physical methods.

**2,6-Diacetyl pyridine monoxime:** This compound was prepared by adding the concentrated aqueous solution of 0.05 mole of hydroxylamine hydrochloride to an alcoholic solution of 2,6-diacetyl pyridine (0.04 mole) and then cooled to 5°C. To this solution further added 20% aqueous solution of NaOH (0.3 mole) dropwise with constant stirring and the temperature of the resultant mixture was maintained below 0°C. After allowing it to stand for about 2 h, it was diluted with water and just acidic with glacial acetic acid. Then it was allowed to stand for 45 min followed by filtration through a suction pump. The residue was recrystallised from aqueous alcohol (60%) leaving behind a white macrocyclic solid having melting point 218°C.

**Metal complexes:** Complexes of type  $[ML_1]X_2$  where M = Fe(II), Cu(II) and X =  $0.5SO_4^{2-}$  were isolated by the following general procedure or template reaction method<sup>2</sup>. To a solution of metal (II) salt in the minimum ethanol, a hot alcoholic solution of bis(2,6-diacetyl pyridine monoxime) 1,2-diamino benzene (1 : 2 mole) was added slowly with constant stirring. The whole mixture refluxed on water-bath for 0.5 h. A coloured precipitate was appeared on cooling which was washed with absolute alcohol, ether and dried over  $P_2O_5$  *in vacuo*.

*Template reaction:* Binuclear complexes of type  $[ML_2]_2X_2$  and  $[ML_3]_2X_2$  where  $M = \text{Fe(II)}$ ,  $\text{Cu(II)}$  and  $X = 0.5\text{SO}_4^{2-}$  were prepared by mixing an alcoholic solution of the metal salt (0.005 mole) with a hot alcoholic solution of (2,6-diacetyl pyridine monoxime) 1,3-diamino benzene or 1,4-diamino benzene. The whole mixture was refluxed on hot water bath for 1 h. A coloured precipitate were appeared on cooling which was washed with absolute alcohol. ether and dried over  $\text{P}_2\text{O}_5$  *in vacuo*.

In case of inner complex salt in place of metal sulphate, we have taken metal acetate and the resultant complexes are  $[M(L_2-H_2)]_2$  and  $[ML_3-H_2]_2$  where  $M = \text{Fe(II)}$  or  $\text{Cu(II)}$ ,  $L_2 = \text{bis-(2,6-diacetylpyridine monoxime) 1,3-diamino benzene}$ ,  $L_3 = \text{bis-(2,6-diacetylpyridine monoxime) 1,4-diamino benzene}$ .

Conductance measurements were made on a Toshniwal conductivity bridge type CL01/01. The magnetic susceptibility measurements at various temperature down to liquid nitrogen temperature were made on polycrystalline samples on a standard Gouy balance. The susceptibility standard was  $\text{Hg}[\text{CO}(\text{NCS})_4]^{3-}$ . Diamagnetic corrections were made using Pascal's constant<sup>4</sup>. Diffuse reflectance spectra at room temperature were recorded on a Cary 14 spectrophotometer. Electronic absorption spectra in aqueous solution were recorded on a cary 14 spectrophotometer; infrared spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) were measured on a Perkin-Elmer 337 spectrometer in CsI.

## RESULTS AND DISCUSSION

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

The important vibrational bands and the metal complexes are given in Table-2. The IR spectrum of ligand ( $L_1$ ) shows a broad band in the region  $3500\text{--}3200\text{ cm}^{-1}$  which is centred at  $3350\text{ cm}^{-1}$ , is due to stretching vibrations of oxime groups<sup>5-7</sup>. In complexes of types  $[ML_1]X_2$ ,  $[ML_2]_2X_4$ ,  $[ML_3]_3X_4$  and inner complexes of type  $[ML_1-H_2]$ ,  $[M(L_2-H_2)]_2$  and  $[ML_3-H_2]_2$   $M = \text{Fe(II)}$  or  $\text{Cu(II)}$ ;  $X = \text{AcO}^-$ ,  $0.5\text{SO}_4^{2-}$  and the bands observed at  $3350$ ,  $3250\text{--}3150$ ,  $3100\text{--}3000$  and  $2930\text{--}2780\text{ cm}^{-1}$  are assigned<sup>5</sup> to free  $\nu(\text{OH})$ , H bonded  $\nu(\text{OH})$ ,  $\nu(\text{C—H})$  and coupled  $\nu(\text{OH})$  respectively. The bands at  $1595\text{ cm}^{-1}$  and at  $970\text{ cm}^{-1}$  in case of free ligand are due to  $\nu(\text{C=N})$  and  $\nu(\text{N—O})$  stretching vibrations respectively. These bands are shifted to lower frequencies in case of  $\nu(\text{C=N})$  and higher frequencies in case of  $\nu(\text{N—O})$  in the spectra of all complexes indicating that azomethine nitrogen is involved in bonding<sup>8</sup>. An additional band located at  $1695\text{ cm}^{-1}$  may be due to  $\text{N—}\hat{\text{O}}\text{—H}$  scissoring in case of ligand was observed but no such band was identified in the spectra of the inner salts, mononuclear  $[ML_1-H_2]$ , binuclear  $[ML_2-H_2]_2$  and  $M[L_3-H_2]_2$  respectively.

There is no band in IR spectra at *ca.*  $1700\text{ cm}^{-1}$  showing the absence of the keto-groups of 2,6-diacetylpyridine. There is no doubt that the pyridine nitrogen atom is involved in coordination too. Bands below<sup>9,10</sup>  $650\text{ cm}^{-1}$  are sensitive to coordination of pyridine. Thus the strong band in plane ring deformation near  $610\text{ cm}^{-1}$  and the weak out-of-plane ring deformation near  $420\text{ cm}^{-1}$  are shifted towards higher energies by  $60\text{--}40\text{ cm}^{-1}$  respectively upon coordination<sup>11-14</sup>

TABLE-1  
ANALYTICAL DATA OF METAL(II) COMPLEXES

Compound	Yield (%)	% Found (Calcd.)				
		M	C	N	H	Anion
[CuL <sub>1</sub> -H <sub>2</sub> ]	80	12.71 (12.96)	58.53 (58.82)	16.90 (17.15)	4.46 (4.56)	—
[CuL <sub>1</sub> ](SO <sub>4</sub> )	85	10.42 (10.81)	48.84 (49.01)	13.87 (14.29)	3.98 (4.08)	16.10 (16.33)
[CuL <sub>2</sub> -H <sub>2</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	75	10.51 (10.81)	48.76 (49.01)	14.10 (14.29)	3.87 (4.08)	16.15 (16.33)
[CuL <sub>3</sub> -H <sub>2</sub> ] <sub>2</sub>	70	12.68 (12.97)	58.54 (58.82)	16.95 (17.15)	4.32 (4.56)	—
[FeL <sub>1</sub> -H <sub>2</sub> ]	80	11.34 (11.59)	59.45 (59.76)	17.25 (17.43)	4.32 (4.56)	—
[FeL <sub>1</sub> ](SO <sub>4</sub> )	85	9.24 (9.62)	59.15 (59.76)	14.25 (14.48)	3.95 (4.13)	16.35 (16.55)
[FeL <sub>2</sub> -H <sub>2</sub> ]	75	11.32 (11.59)	59.23 (59.76)	17.15 (17.43)	4.13 (4.56)	—
[FeL <sub>2</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	70	9.25 (9.62)	49.35 (49.66)	14.15 (14.48)	3.95 (4.16)	5.25 (5.52)
[FeL <sub>3</sub> -H <sub>2</sub> ] <sub>2</sub>	70	11.41 (11.59)	59.56 (59.76)	17.13 (17.43)	4.24 (4.56)	—
[FeL <sub>3</sub> ](SO <sub>4</sub> ) <sub>2</sub>	75	9.46 (9.62)	49.15 (49.66)	14.16 (14.48)	3.75 (4.16)	5.15 (5.52)

L<sub>1</sub> = bis-(2,6-diacetyl pyridine) 1,2-diamino benzene.

L<sub>2</sub> = bis-(2,6-diacetyl pyridine) 1,3-diamino benzene.

L<sub>3</sub> = bis-(2,6-diacetyl pyridine) 1,4-diamino benzene.

TABLE-2  
SELECTED INFRARED VIBRATIONS (cm<sup>-1</sup>) OF LIGAND AND ITS METAL(II) COMPLEXES

Complexes	v(O—H)	v(C—H)	v(C—N) azomethine	v(C=N)	v(N—O)	v (Pyridine)	
L <sub>1</sub>	3350b	3000s	1595s	1430m	970s	610m	420m
[CuL <sub>1</sub> ](SO <sub>4</sub> )	3180b	3050s	1580s	1440m	1020s	620m	440m
[CuL-H <sub>2</sub> ]	—	3100s	1585s	1435s	1150s	640m	445m
[CuL <sub>2</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3250b	3100b	1570m	1440m	1070m	650m	435m
[CuL <sub>3</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3250b	3000b	1580m	1445m	1090s	640m	430m
[CuL <sub>2</sub> -H <sub>2</sub> ] <sub>2</sub>	—	3050s	1580s	1435s	1150s	645s	420m
[CuL <sub>3</sub> -H <sub>2</sub> ] <sub>2</sub>	—	3100s	1585m	1440m	1155s	645s	420m
[FeL <sub>1</sub> ](SO <sub>4</sub> )	3250b	3080b	1580m	1445m	1090s	645s	430m
[FeL-H <sub>2</sub> ]	—	3095s	1580m	1440m	1190m	635m	420m
[FeL <sub>2</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	3210b	3080s	1565s	1460s	1090s	640m	420m
[FeL <sub>2</sub> -H <sub>2</sub> ]	—	3090b	1570m	1465m	1190m	635m	420m
[FeL <sub>3</sub> -H <sub>2</sub> ]	—	3100b	1575m	1470s	1195s	630s	420m
[FeL <sub>3</sub> ](SO <sub>4</sub> ) <sub>2</sub>	3215b	3100b	1580m	1474s	1090w	650s	440m

TABLE-3  
ELECTRONIC SPECTRAL DATA AND MAGNETIC MOMENT VALUES

Complexes	Absorption max in (cm <sup>-1</sup> )			$\mu_{\text{eff}}$ (B.M.)
	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>	CT	
[FeL <sub>1</sub> ](SO <sub>4</sub> )	9090	14290	21250	5.20
[FeL <sub>1</sub> -H <sub>2</sub> ]	9050	14550	21100	5.26
[FeL <sub>2</sub> -H <sub>2</sub> ]	9065	14750	21270	5.30
[FeL <sub>2</sub> ](SO <sub>4</sub> ) <sub>2</sub>	9055	14350	21000	5.25
[FeL <sub>3</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	9050	14450	21350	5.45
[FeL <sub>3</sub> -H <sub>2</sub> ] <sub>2</sub>	9055	14280	21320	5.58
	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub>		
[CuL <sub>1</sub> ]SO <sub>4</sub>	8750	12800	—	1.85
[CuL <sub>1</sub> -H <sub>2</sub> ]	9545	13500	—	1.80
[CuL <sub>2</sub> -H <sub>2</sub> ]	8850	12900	—	1.95
[CuL <sub>2</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	8870	12770	—	1.90
[CuL <sub>3</sub> -H <sub>2</sub> ] <sub>2</sub>	9350	13450	—	1.85
[CuL <sub>3</sub> ] <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub>	9550	13600	—	1.95

### Electronic Spectra

The reflectance spectra of the copper(II) complexes display two symmetrical bands at 9550–8750 cm<sup>-1</sup> which are assigned to the ligand field transitions commonly observed for Cu(II) complexes. The  $\mu_{\text{eff}}$  value ranges from 1.8–1.95 B.M.

The electronic spectra of some distorted octahedral copper(II) complexes display two bands split by *ca.* 5000 cm<sup>-1</sup>.<sup>15-18</sup> Consequently, a distorted octahedral configuration is assigned to the copper(II) complexes as shown in Figs. 1–4.

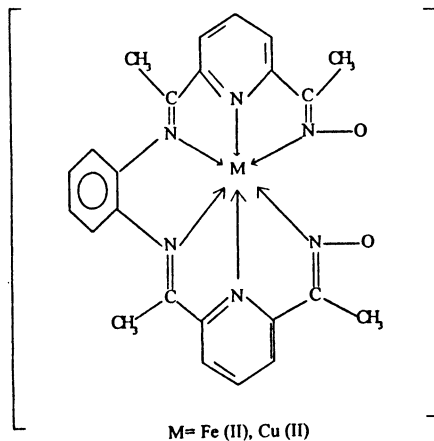


Fig. 1

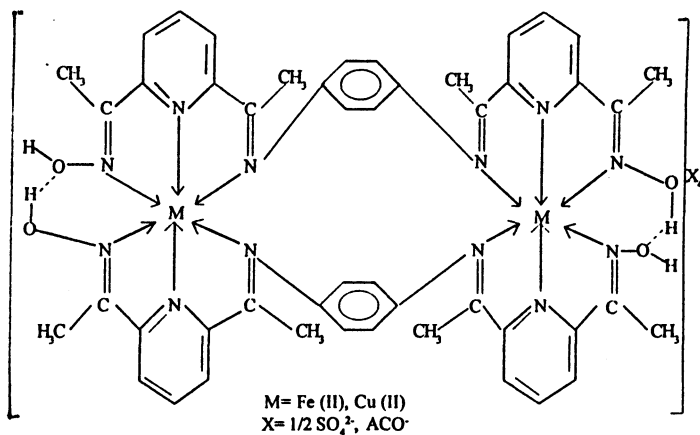


Fig. 2

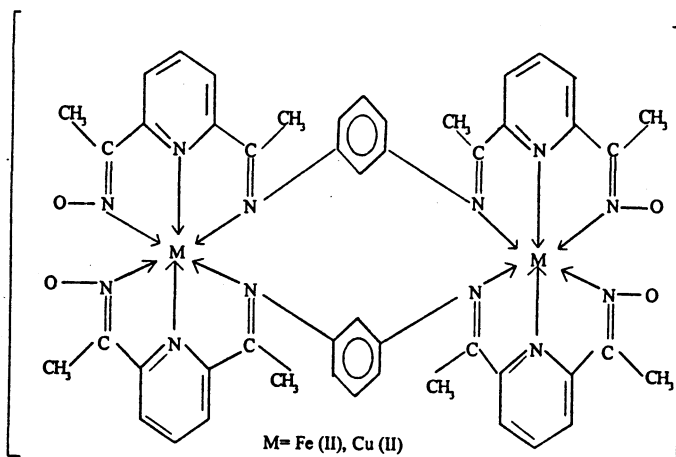


Fig. 3

The  $\mu_{\text{eff}}$  values of ferrous(II) complexes range from 5.20–5.58 BM. Thus spectrum of Fe(II) complexes exhibits two broad bands near 9090 and 14290  $\text{cm}^{-1}$  which are assigned to compounds of  ${}^5T_{2g} \rightarrow {}^5E_g$ . The centroid of these bands near 11510  $\text{cm}^{-1}$  corresponds to Dq.<sup>19</sup> This spectrum also contains sharp bands near 16700 and 21250  $\text{cm}^{-1}$  which are assigned as charge transfer absorption bands. Thus visible spectra along with infrared and magnetic moment data has supported octahedral structure with considerable distortion in mononuclear and binuclear complexes as shown in Figs. 1–4.

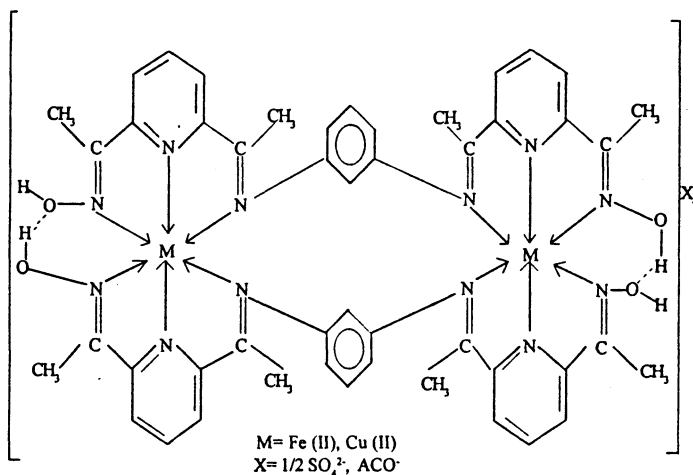


Fig. 4

### ACKNOWLEDGEMENTS

Authors are thankful to the authorities of RSIC, Calcutta for recording electronic spectra. Thanks are due to the authorities of RSIC, IIT Madras for recording magnetic moments. We are also thankful to UGC for financial support under TRF scheme.

### REFERENCES

1. R.N.Kumar, R.S. Thakur and A.K. Das, *J. Indian Coun. Chem.*, **11**, 46 (1996).
2. David St.C. Black and N.E. Rothnic, *Aust. J. Chem.*, **36**, 2387 (1983).
3. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
4. F.E. Mabbs and D.J. Machin, *Mechanism of Transition Metal Complexes*, Chapman and Hall, London (1961).
5. M. Mohan and B.D. Paramhans, *Indian J. Chem.*, **19A**, 759 (1980).
6. A. Palm and H. Werbin, *J. Chem. Soc.*, **31**, 1004 (1953).
7. R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).
8. A. Braibanti and F. Dallavalle, *Inorg. Chem.*, **7**, 1430 (1968).
9. B.F. Little and G.J. Long, *Inorg. Chem.*, **17**, 3401 (1978).
10. S. Krishnan and C.S. Balasubramanian, *J. Madras Univ., Sec. B*, **52**, 50 (1989).
11. C. Lorenzini, C. Pelizzi and G. Pelizzi, *J. Chem. Soc. Dalton. Trans.*, 2155 (1983).
12. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York (1986).
13. S.K. Sengupta, S.K. Sahxi and R.N. Kapoor, *J. Coord. Chem.*, **12**, 113 (1982).
14. H.S. Yadava, S.K. Sengupta and S.C. Tripathi, *Acta Chem. Hung.*, **119**, 333 (1985).
15. J.M. Procter, B.J. Hathaway and D.E. Billing, *J. Chem. Soc. A*, 1192 (1969).
16. B.J. Hathaway, M.J. Bew, D.E. Billing, R.D. Dudley and P. Nicholls, *J. Chem. Soc. A*, 2312 (1969).
17. B.J. Hathaway and A.A.G. Tomlinson, *Coordination Chem. Rev.*, **5**, 1 (1970).
18. R.L. Farmer and F.L. Urbach, *Inorg. Chem.*, **13**, 587 (1974).
19. B.N. Figgis, *Introduction to Ligand Field Theory*, Interscience, New York.