

## Thermal Studies on Some Metal Polychelates

H.C. RAI\*, POONAM KUMARI, ASWINI KUMAR and MRINAL CHANDRA†

*Department of Chemistry, L.S. College, Muzaffarpur-842 001, India*

Chelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been prepared with the Schiff base ligand derived from 4,4'-dihydroxy-3,3'-diacetyl biphenyl and benzildihydrazone having equimolar stoichiometry of the metal cations and ligand. All the chelates are coloured amorphous solids and highly insoluble in water and common organic solvents. Thermogravimetric analyses have been carried out. Kinetic and thermodynamic parameters have also been evaluated by using thermal decomposition pattern. D.C. electrical conductivity study has also been carried out. The ligand field and nephelauxetic parameters have also been determined from the spectra using ligand field theory of allowed transitions.

**Key Words:** Thermal studies, Metal polychelates.

### INTRODUCTION

The interaction between transition metal ions and bridging ligands may lead to the formation of coordination compounds in which the chelated metal ions are bridged by ligand molecules. The formation of macromolecular chain may be expected for a ligand with two chelating sites, which for steric reasons cannot interact with the same metal ion<sup>1, 2</sup>. The present communication describes the preparation and characterization of manganese(II), iron(II), cobalt(II), nickel(II) and copper(II) polymeric chelates of a quadridentate ligand 4,4'-dihydroxy-3,3'-diacetyl biphenyl benzildihydrazone, H<sub>2</sub>L.

### EXPERIMENTAL

All chemicals used were of analytical reagent grade. Solvents used were double distilled before use. 4,4'-Dihydroxy-3,3'-diacetyl biphenyl and benzildihydrazone were prepared by known methods.

#### Preparation of Polychelates

Equimolar amounts of metal acetates, 4,4'-dihydroxy-3,3'-diacetyl biphenyl and benzildihydrazone (dissolved and filtered separately in 25-30 mL of DMF) were mixed in hot condition while stirring. The mixture was refluxed at 140°C for 4-6 h. The resulting products were filtered, washed successively with DMF, dry ethanol and acetone and dried in a vacuum desiccator over fused CaCl<sub>2</sub>. All the polychelates gave satisfactory C, H, N and metal analyses.

†Department of Chemistry, Rajendra College, Chapra, India.

The polychelates were analysed by the standard procedures. Magnetic moments were determined by Gouy method using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as the calibrant and the values were corrected for diamagnetism using Pascal constants. Infrared spectra in KBr pellets and diffuse reflectance spectra were obtained from RSIC, CDRI, Lucknow.

TG analyses were carried out using Stanton Redcroft TG-750 thermobalance at a heating rate of  $10^\circ \text{min}^{-1}$  in air. Sample temperatures were measured by means of a platinum versus platinum-rhodium thermocouple positioned immediately below the sample crucible.

## RESULTS AND DISCUSSION

All the polymeric chelates (Table-1) are coloured amorphous solids and insoluble in water and common organic solvents. The elemental analysis suggests 1 : 1 metal-ligand stoichiometry.

TABLE-1  
THERMAL AND ELECTRICAL DATA OF Mn(II), Fe(II), Co(II), Ni(II) AND Cu(II)  
POLYMERIC CHELATES OF 4,4'-DIHYDROXY 3,3'-DIACETYL  
BIPHENYLBENZILDIHYDRAZONE  $\text{H}_2\text{L}$

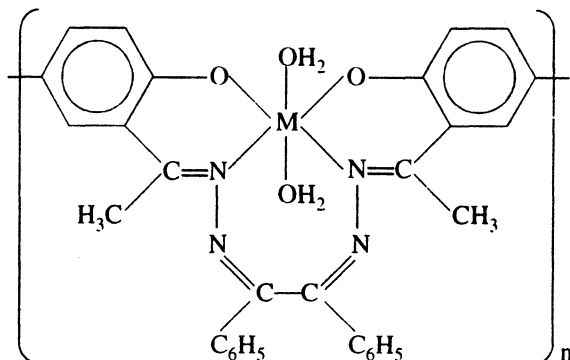
Compound (colour)	Decomposition temperature ( $^\circ\text{C}$ )	$\sigma$ ( $\Omega^{-1} \text{cm}^{-1} \text{K}$ )	$E_a$ (ev)
MnL (Pink)	270	$2.900 \times 10^{-10}$ (313)	0.639
		$1.185 \times 10^{-9}$ (373)	
		$5.942 \times 10^{-8}$ (513)	
FeL (Red)	285	$5.780 \times 10^{-11}$ (303)	0.221
		$8.510 \times 10^{-11}$ (373)	
		$7.950 \times 10^{-10}$ (513)	
CoL (Brown)	335	$8.835 \times 10^{-12}$ (303)	0.395
		$3.337 \times 10^{-11}$ (373)	
		$7.508 \times 10^{-10}$ (515)	
NiL (Green)	310	$9.875 \times 10^{-12}$ (372)	0.565
		$3.655 \times 10^{-11}$ (373)	
		$1.008 \times 10^{-9}$ (512)	
CuL (Blue)	275	$4.135 \times 10^{-9}$ (313)	0.448
		$9.098 \times 10^{-9}$ (373)	
		$1.895 \times 10^{-9}$ (513)	

The IR spectrum of the ligand shows a sharp and intense band at  $1600 \text{cm}^{-1}$  which can be assigned to  $\nu(\text{C}=\text{N})$ .<sup>3</sup> In the IR spectra of polymeric metal chelates, this band is seen to be shifted to a lower frequency by  $8.25 \text{cm}^{-1}$  indicating the coordination to the central metal atom through nitrogen of the azomethine group<sup>4</sup>. The ligand benzildihydrazone shows a medium broad band at  $2925 \text{cm}^{-1}$  assignable to  $\nu(\text{N}-\text{H})$ .<sup>5</sup> The polymeric chelates do not show  $\nu(\text{N}-\text{H})$  group frequency suggesting thereby condensation of  $\text{NH}_2$  group with CO group of substituted biphenyl. This is further evidenced by the disappearance of C—O

stretching frequency in the IR spectra of polymeric chelates<sup>6</sup>. The ligand band at  $920\text{ cm}^{-1}$  (N—N) shifts to higher frequency by 15 to  $45\text{ cm}^{-1}$  upon chelation. The magnitude of the shift indicates the monodentate coordination<sup>7</sup> of the N—N residue as a shift of  $> 75\text{ cm}^{-1}$  is usually observed in bidentate coordination.

A shift to a higher frequency in  $\nu(\text{N—N})$  is expected due to the reduction of the lone-pair repulsive forces of the adjacent nitrogen atom<sup>8</sup>. A band appeared in the region  $595\text{--}540\text{ cm}^{-1}$  in the far IR spectrum of polymeric chelates may be attributed to  $\nu(\text{M—O})$  vibrations and a band at  $500\text{--}450\text{ cm}^{-1}$  may be ascribed to  $\nu(\text{M—N})$ .<sup>8</sup> The weak broad bands observed in the IR spectrum of polymeric chelates at  $3450\text{--}3300\text{ cm}^{-1}$  may be attributed to  $\nu\text{OH}$  of water molecules<sup>9</sup>. The Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) polymeric chelates also exhibit sharp peak at around  $1560$  and  $830\text{ cm}^{-1}$  assignable to the presence of coordinated water molecules<sup>9</sup>.

On the basis of discussions *vide supra* the polychelates may be proposed to have the structures as shown in Fig. 1.



where  $M = \text{Mn(II), Fe(II), Co(II), Ni(II) or Cu(II)}$ .

Fig. 1

The electronic spectrum of the Mn(II) polymeric chelate shows three weak bands at  $13900$ ,  $17800$  and  $22700\text{ cm}^{-1}$  which have been assigned to transitions  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ ,  ${}^4E_g(G)$  respectively in an octahedral field of Mn(II).<sup>10, 11</sup>

The observed magnetic moment of the Mn(II) chelate (6.06 B.M.) is slightly greater than the spin only value (5.92 B.M.) but within the limits of spin free values for five unpaired electrons indicating that the polymer is high spin octahedral<sup>12</sup>.

The Fe(II) polychelate shows doublet band at  $10,000\text{--}12,000$  shoulder at  $14,700$  and  $20,830\text{ cm}^{-1}$  assigned to  ${}^5T_{2g}(D) \rightarrow {}^5E_g$  and  $t_{2g} \rightarrow \pi^*$  as charge transfer transitions respectively.

Cotton and Meyers<sup>13</sup> suggested that such a doublet bands in six coordinated Fe(II) complexes could be due to either Jahn-Teller distortion or  $D_{4h}$ . Crystals field parameters and nephelauxetic ratio have been calculated<sup>14</sup> for the iron(II) polychelates:  $D_q = 1050\text{ cm}^{-1}$ ,  $B = 560\text{ cm}^{-1}$ ,  $\beta = 0.536$  and  $C = 2274\text{ cm}^{-1}$ . These values are in favour of tetragonally distorted octahedral geometry of Fe(II)

polymeric chelates which is consistent with the results reported by Shah and Shah<sup>15</sup>.

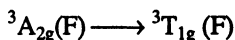
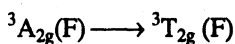
The reduction of  $\beta$  values upon chelation indicates that a small amount of the  $\sigma$  and  $\pi$  electron density on the metal may be transferred on to the ligand. Such delocalisation will increase the mean distance between d-electrons and thereby reduce B. In other words, a decrease in B value suggests the presence of covalent character in the M-L bond<sup>16</sup>.

The magnetic moment of the Fe(II) polychelates (6.14 B.M.) suggests a high spin octahedral geometry. The higher value of magnetic moment can be attributed to the steric volume of the bulky ligand causing an increase in M-L bond distance thereby decreasing  $D_q$  sufficiently enough to alter the ground state to the high spin  ${}^5T_{2g}$ .<sup>14, 16</sup>

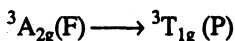
The electronic spectrum of cobalt(II) polymeric chelate exhibits two bands at 9,500 and 21,000  $\text{cm}^{-1}$  which can be assigned to the transitions  ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)(\nu_1)$  and  ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$  respectively. However, the transition  ${}^4T_{1g}(F) \rightarrow {}^3A_{2g}(F)(\nu_2)$  is not clear since it is a two electron transfer process and has a much lower oscillation strength than the other two transitions and is therefore much weaker<sup>17, 18</sup>.

The value of  $D_q = 1048 \text{ cm}^{-1}$ ,  $B = 852 \text{ cm}^{-1}$ ,  $\beta = 0.760$ ,  $\beta^\circ = 23.92\%$ ,  $\nu_2/\nu_1 = 1.63$  and  $\nu_2 = 19733 \text{ cm}^{-1}$  calculated using Balhausen equation<sup>19</sup> is within the limit reported for octahedral cobalt(II) complexes. The observed magnetic moment of cobalt(II) polymeric chelate (5.33 B.M.) is in good agreement with high spin octahedral geometry, since spin only value for three unpaired electrons is only 3.99 B.M.; the high value in the present case may be attributed to high spin orbital contribution<sup>20</sup>.

The electronic spectrum of the Ni(II) polychelate shows three d-d transition bands at 10,000, 14,000 and 24,000  $\text{cm}^{-1}$  corresponding to the transitions:



and



respectively which are in the range required for the spin free octahedral Ni(II) chelates<sup>19, 21</sup>. The structure is further supported by the ratio of  $\nu_2/\nu_1$  (1.4) which is close to the value expected for a distorted octahedral structure<sup>22</sup>.

The Racah parameters  $D_q = 985 \text{ cm}^{-1}$ ,  $B = 551 \text{ cm}^{-1}$ ,  $\beta = 0.51$ ,  $\beta^\circ = 48\%$ ,  $\nu_2 = 14700 \text{ cm}^{-1}$ ,  $\nu_3 = 22930 \text{ cm}^{-1}$  and  $\nu_2/\nu_1$  (1.4) have been obtained using diagonal sum value<sup>23</sup>.

Low values of B and  $\beta$  suggest appreciable amount of the covalent character in the metal ligand bonds. It is possible to calculate  $D_t = 69 \text{ cm}^{-1}$ ,  $D_q^{xy} = 1041$  and  $D_q^z = 919 \text{ cm}^{-1}$ .

The magnetic moment of Ni(II) polychelate (3.63 BM) is higher than the spin only value for octahedral stereochemistry. Higher value of magnetic moment in the present case may be due to the departure from octahedral geometry towards tetragonal  $D_{4h}$  geometry<sup>24</sup>.

The diffuse reflectance spectrum of the Cu(II) polychelate contains two bands, one in the range 14280–13510 and another at 10410  $\text{cm}^{-1}$  in their normally expected region for square-planar geometry<sup>25</sup>.

The first band which is broad suggests a distorted octahedral geometry which may be assigned to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transitions respectively<sup>26</sup>.

The magnetic moment of the copper(II) polychelate (1.92 BM) is very close to the spin only value (1.73 BM) expected for one unpaired electron which offers the possibility of octahedral geometry<sup>27</sup>.

### Thermal properties of polymeric chelates

In the thermograms weight losses of the Mn(II), Fe(II), Co(II) and Ni(II) polymeric chelates in the range 180–230°C are 9.02, 8.90, 9.40 and 8.80% respectively corresponding to two coordinated water molecules per repeating unit of polychelate<sup>28</sup>.

The copper(II) polychelate shows a weight loss of 9.10% around 130°C corresponding to two crystal water molecules<sup>29</sup>.

The observed higher weight loss than that required may be due to some other chain degradation reaction involved in pyrolysis of the polychelate<sup>30</sup>.

From the procedural decomposition temperature (Table-1) it can be concluded that the thermal stability order of the polychelates is  $\text{Co} > \text{Ni} > \text{Fe} > \text{Cu} > \text{Mn}$ .

The analysis of thermogram indicates that the polychelates decompose in two stages after loss of water molecules. In all chelates the rate of decomposition in the first stage is slow as compared to the second stage and decomposition completes at about 600°C.

### Electrical properties of polychelates

The coordination polymers are known for their behaviour as semiconductors. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the equation<sup>31</sup>

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where  $k$  is the Boltzmann constant,  $\sigma$  the electrical conductivity at temperature  $T$ ,  $\sigma_0$  the electrical conductivity at temperature  $T = \alpha$  obtained by extrapolation,  $E_a$  the activation energy of electrical conduction and  $T$  the absolute temperature. This relation has been modified<sup>32</sup> as  $\log \sigma = \log \sigma_0 + (-E_a/2.303) \text{KT}$

According to this relation a plot of  $\log \sigma$  vs  $1/T$  would be linear with a negative slope.

In the present study, temperature dependence of the electrical conductivity exhibits two distinct patterns. In low temperature region the slopes of the plots have small values. This may be due to extrinsic conduction present in them, whereas in high temperature region a linear relation is obtained between  $\log \sigma$  and  $f(10^3/T)$ . In this temperature domain, these polychelates may behave as intrinsic semiconductors<sup>33</sup>.

The electrical conductivity of these polychelates increases in the order

$$\text{Mn} > \text{Cu} > \text{Fe} > \text{Ni} > \text{Co}$$

at 100°C and the activation energy of electrical conduction increases in the order  
 $Mn > Ni > Cu > Co > Fe$

The values of electrical conductivity and activation energy vary with the ionization tendency<sup>34</sup> of the metal ion in the polychelates.

### REFERENCES

1. B.P. Block, *Inorg. Macromol. Rev.*, **1**, 115 (1970).
2. J.J. Grodzinski, *Makromol. Chem.*, **181**, 2441 (1980).
3. L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Edn., Methuen, London (1958).
4. R.C. Stouffer and D.H. Busch, *J. Am. Chem. Soc.*, **82**, 3491 (1960).
5. ———, *J. Am. Chem. Soc.*, **78**, 6016 (1956).
6. H.C. Rai and B. Sahoo, *J. Indian Chem. Soc.*, **53**, 646 (1976).
7. K.C. Satpathy, *J. Indian Chem. Soc.*, **69**, 119 (1992).
8. D. Sen, *J. Chem. Soc.*, 2900 (1969).
9. N.K. Singh and R. Tripathi, *Trans. Met. Chem.*, **13**, 346 (1988).
10. S. Satpathy, H.C. Rai and B. Sahoo, *J. Indian Chem. Soc.*, **52**, 701 (1975).
11. A.B.P. Lever, *J. Chem. Soc.*, 1821 (1965).
12. M.N. Patel and P.B. Jathi, *J. Indian Chem. Soc.*, **63**, 278 (1986).
13. F.A. Cotton and A.D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).
14. D. Sutton, *Electronic Spectra of Transition Metal Complexes*, McGraw-Hill, London (1968).
15. N.R. Shah and J.R. Shah, *J. Indian Chem. Soc.*, **60**, 1092 (1983).
16. A.A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).
17. A.C. Rande and V.V. Subba Rao, *Indian J. Chem.*, **4**, 42 (1966).
18. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York (1968).
19. C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York (1962).
20. A.K. Rana and J.R. Shah, *J. Indian Chem. Soc.*, **63**, 281 (1986).
21. B. Singh, Lakshmi and V. Agarwal, *Inorg. Chem.*, **8**, 2341 (1969).
22. K. Kobi, *Inorg. Chem.*, **31**, 676 (1992).
23. G.L. Chaudhary, S.R. Prasad and A. Rahman, *J. Indian Chem. Soc.*, **74**, 683 (1997).
24. L.D. Dave, H.K. Kothari and P. Sudhamshumouli, *Indian J. Chem.*, **12**, 771 (1974).
25. C.L. Sharma and T.K. Dey, *J. Indian Chem. Soc.*, **59**, 101 (1982).
26. B.T. Thakur, A. Patel, J. Lekhadia and P. Thakur, *Indian J. Chem.*, **35A**, 483 (1996).
27. D.K. Rastogi and K.K. Sharma, *J. Inorg. Nucl. Chem.*, **36**, 2219 (1974).
28. A. Syamal and M.R. Maurya, *Synth. React. Inorg. Metal-Org. Chem.*, **16**, 39 (1986).
29. Y.Z. Ahmed, *Indian J. Chem.* **33A**, 20 (1994).
30. A.V. Nekolave, *Thermal Analysis*, Academic Press, New York, **22**, p. 779 (1969).
31. W.H. Brattain and C.G.B. Garratt, *Bell. Synth. Tech.*, **34**, 129 (1955).
32. M.N. Patel and S.H. Patel, *J. Macromol. Sci. Chem.*, **17**, 675 (1982).
33. J.S. Dewar and A.M. Talati, *J. Am. Chem. Soc.*, **86**, 1592 (1964).
34. D.H. Busch and J.C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956).