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Thermal and Structural Properties of Some Chelate Polymers

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New polychelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been synthesised from Schiff base derived from 4, 4'-dihydroxy-3, 3'-diacetyl biphenyl and 1, 5-diaminonaphthalene and characterized by elemental analysis, magnetic and spectral data and thermal studies. The thermal stabilities of the polychelates obtained from thermograms is in the order Fe > Cu > Ni > Mn > Co, while the activation energy follows the order Fe > Mn > Ni > Cu > Co.

INTRODUCTION

This communication describes the preparation and characterization of the chelates prepared from the ligand DDBDN derived from 4, 4'-dihydroxy,-3, 3'-diacetyl biphenyl and 1, 5-diaminonaphthalene with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

EXPERIMENTAL

All the metal acetates and chemicals used in the present work were of AR grade. All the solvents were purified by distillation.

Preparation of ligand

4, 4'-Dihydroxy-3, 3'-diacetyl biphenyl (DDABP) was prepared by a known method[1]. To a hot solution of DDABP (0.2M) in dry ethanol (50 ml) was added with stirring a solution of 1, 5-diaminonaphthalene (0.1M) in dry ethanol. The mixture was refluxed at 85–90°C for about 2 h and was allowed to cool to room temperature. The resulting dark yellow crystals of DDBDN were filtered and washed several times with dry ethanol and air dried and found isoluble in common organic solvents but soluble in DMF.

Preparation of chelates

Equimolar proportions of metal acetate and the ligand DDBDN were dissolved separately in minimum quantity (25–30 ml) of DMF. Both the solutions were filtered and then mixed in hot condition with constant stirring. The mixture was then refluxed at 135°C for 5–6 h. The resulting products were filtered, washed with DMF, and absolute ethanol and finally with dry acetone and dried in a vacuum desiccator over fused $CaCl_2$.

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RESULTS AND DISCUSSION

All the polychelates are coloured and amorphous in nature and found insoluble in common organic solvents. Elemental analysis data are of the polychelates correspond to the general formula ML or ML_n (Table 1).

TABLE 1
ANALYTICAL DATA, COLOUR AND SYNTHETIC CONDITIONS OF DDBDN AND ITS POLYCHELATES.

Polymer/Colour	Solvent used in synthesis	% Found (Calc.)			
		M	C	H	N
DDBDN	Ethanol	—	79.78	5.21	8.14
Yellow			(79.59)	(5.10)	(7.14)
$[Mn(II)(DDBDN)]_n$	DMF	11.68	67.53	4.32	6.06
Gray		(12.04)	(67.63)	(4.55)	(6.33)
$[Fe(II)DDBDN.\ 2H_2O]_n$	DMF	11.61	64.73	4.14	5.80
Leaf brown		(12.15)	(64.08)	(4.24)	(5.95)
$[Co(II)\text{-}DDBDN.2H_2O]_n$	DMF	12.16	64.33	4.12	5.77
Pale rose		(12.68)	(65.04)	(4.14)	(5.85)
$[Ni(II)\text{-}DDBDN.2H_2O]_n$	DMF	12.10	64.31	4.12	5.71
Chasis grey		(12.35)	(65.10)	(4.34)	(6.04)
$\{[Cu(II)\text{-}DDBDN]2H_2O\}_n$	DMF	14.02	68.79	3.96	6.17
Steel grey		(14.30)	(68.91)	(3.15)	(6.54)

The presence of strong band at *ca.* 1590 cm^{-1} in the ligand spectrum may be assigned to $C=N$ group. This band is shifted to higher wave numbers in the spectra of the polychelates, which suggest the strong bonding of $C=N$ group with metal ion[2]. The medium intensity broad band of the ligand in the region 3050–3140 cm^{-1} due to νOH with intramolecular hydrogen bonding[3] disappears in the complexes indicating metal-oxygen bond formation[2]. Due to the phenolic – CO band of ligand at 1200 cm^{-1} is shifted to higher wave number on complexation indicating protonation through – OH group. All the polychelates contain weak to medium intensity broad band in the region 3200–3500 cm^{-1} and weak band around 790 cm^{-1} which is due to coordinated water[4]. In all the polychelates in the neighbourhood of the 550–610 cm^{-1} and 420–480 cm^{-1} bands of the complexes may be identified as ν(M-O) and ν(M-N), respectively[4, 5].

In the diffuse reflectance spectra of the Mn(II) complex shows some novel features of interest and exhibits the transition sextet-quartes for the $^6A_1$ ground term. Mn(II) exhibits three intense absorption maxima 23.80, 20.83 and 19.23 kK for a tetrahedral environment[6] due to $^6A_1 \rightarrow {}^4A_1(G), {}^4E(G) \rightarrow {}^4T_2(G)$ and $\rightarrow {}^4T_1(G)$, respectively. The observed magnetic moment of Mn(II) chalate is 5.31 B.M. towards tetrahedral geometry. The Fe(II) polychelate exhibits absorption bands in the 10.32–12.19 kK region. The bands in this region is characteristic of Fe(II) high spin octahedral complex[7] and could be assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition. Crystal field parameters Dq = 1032 cm^{-1}, B = 557 cm^{-1}, $\beta = 0.52$ and C = 2231 cm^{-1} have been calculated by using known method[8]. The magnetic moment of Fe(II) chelate is 6.10 B.M. suggest the 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 Dq sufficiently enough to alter the ground state[9] to the high spin $^5T_{2g}$. The diffuse reflectance spectrum of Co(II)-DDBDN exhibits two bands at 21.73 and 10.86 kK which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $\rightarrow {}^4T_{2g}(F)$ transition for distorted octahedral geometry[7]. The third transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ is observed in the range 15–18 kK which is weak. Different crystal field parameters like $Dq = 1215.24\ cm^{-1}$, $B = 810\ cm^{-1}$, $\beta = 0.72$, $\beta° = 27.66$, $\nu_2/\nu_1 =$ 2.11, 1.56 (obs) and $\nu_2 = 23.02$ kK have been calculated using known relation[10]. The magnetic moment of Co(II) chelate is 4.91 B.M., which is in good agreement with high spin octahedral geometry, since spin only value for three unpaired electron is only 3.99 B.M. The high value in the present case may be attributed to high orbital contribution. The diffuse reflectance spectra of the Ni(II)-DDBDN shows absorption bands at 10.10, 13.52 and 23.80 kK due to $^3B_{1g} \rightarrow {}^3E_g$, $\rightarrow {}^3A_{2g}$ and $\rightarrow {}^3T_{1g}(P)$ transition, respectively for an octahedral or distorted octahedral spin free Ni(II) complex[11]. The structure is also supported by the ratio of $\nu_2/\nu_1 = 1.33$, close to the value expected for the distorted octahedral structure. To compute the important ligand field parameters, we have used the ligand field theory of spin allowed transitions[12]. The values are $Dq = 1010\ cm^{-1}$, $B = 467\ cm^{-1}$, $\beta = 0.43$, $\beta° = 56$, $\nu_2 = 14.58$, $\nu_3 = 22.71$ kK $\nu_2/\nu_1 = 1.33$, $Dq^{xy} = 1098\ cm^{-1}$, $Dq^z = 923\ cm^{-1}$ and $Dt = 100\ cm^{-1}$. The Ni(II) chelate has a magnetic moment of 3.37 B.M. which is higher than the spin only value for octahedral geometry. Higher value of magnetic moment in the present case may be due to the departure from octahedral geometry towards tetragonal geometry[13]. The electronic spectrum of Cu(II) polychelate shows three bands at 17.24, 13.88 and 10.52 kK in their normally expected region for square planar Cu(II) complex[2] assigned as $^2B_1g \rightarrow {}^2E_g$, $\rightarrow {}^2B_{2g}$ and $\rightarrow {}^2A_{1g}$ transition respectively. The broadness of these bands may be an indication towards lower symmetry. The magnetic moment of Cu(II) chelate is 2.05 B.M., which offers the possibility of octahedral symmetry[11]

The possibility of water molecules suggested by elemental and IR spectra is confirmed by TG analysis. In the present study weight losses of Fe(II), Co(II) and Ni(II) polychelates at around 140–230°C are 7.90, 9.70 and 9.30% respectively. These weight losses correspond to two coordinated water molecules per repeating unit of polychelate[14]. The Cu(II) complex lost water at 130°C this is probably crystal water[13]. The observed weight loss is a little higher than required in these regions and this may be due to some other chain degradation reaction involved in pyrolysis of chelates. In the case of Mn(II) polychelate, there is no thermal decomposition up to 280°C. It means no water of hydradion or water of coordination is present in the Mn(II) chelate polymer. The procedural decomposition temperatures for the polychelates decrease in the order Fe > Cu > Ni > Mn > Co. In some cases decomposition occurred at a lower temperature which may be due to oxidation of the polymer by the catalytic action of these metal ion[15]. The analysis of the thermograms indicates that the polychelates decompose in two stages after the loss of water molecules. The first step in the decomposition is rapid as compared to the second step. Decomposition is complete at about 700°C. The thermal activation energy has been calculated using both Freeman-Carroll[16] and Sharp-Wentworth[17] method and follows the order Fe > Mn > Ni > Cu > Co. By using the data of Freeman-Carroll method it was also possible to calculate thermodynamic parameters ΔS, ΔF, S* and Z for the polychelates. The values of these thermodynamic parameters for all the chelates were near (Table 2) about same, which indicated a common reaction mode[15]. From the abnormaly low values of Z, it may be concluded that the decomposition reaction of DDBDN polychelates can be classed as a 'slow' reaction.

TABLE 2

THERMOGRAVIMETRIC ANALYSIS OF DDBDN POLYCHELATES.

Polymer	Decom-position Temp. (°C)	Activation energy		Entropy change	Free energy	Apparent entropy	Frequency factor	Order of reaction
		FC	SW	ΔS	ΔF	S*	Z	n
		(Kcal/mole)		cal	Kcal	cal	Sec^{-1}	
Mn-DDBDN	260	6.57	5.33	–74.08	29.76	–25.88	61.68	0.55
Fe-DDBDN	330	7.02	6.40	–76.65	31.01	–25.32	135.45	0.72
Co-DDBDN	240	5.08	5.33	–73.67	28.14	–25.36	110.17	0.73
Ni-DDBDN	220	5.72	5.56	–77.10	29.85	–25.19	86.00	0.68
Cu-DDBDN	320	5.49	4.16	–76.81	29.53	–26.42	45.88	0.77

FC = Freeman-Carroll SW = Sharp-Wentworth

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