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Synthetic, Structural, Thermal and Electrical Studies of Some Chelate Polymers†

N. S. BHAVE* and A. S. ASWAR

Department of Chemistry
Nagpur University, Nagpur–440 010, India

Chelate polymers of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with 4,4′-dihydroxy-3-3′-diacetyl biphenyl-2,6-diaminopyridine (DDBDP) have been prepared. These polychelates were characterised with the help of magnetic, spectral (IR and electronic), thermal and electrical studies. Analytical data suggest 1 : 1 (M : L) stoichiometry. The thermal activation energies and order of reaction of all polychelates were calculated by Freeman-Carroll and Sharp-Wentworth methods.

INTRODUCTION

The rapidly expanding field of coordination polymers and polychelates of polymeric ligands are interestingly attracting attention by scientists and undergone a spectacular growth during the last few years. This inspired us to prepare a polymeric chelating ligand which would be able to form complexes with a variety of transition metals. In the present communication we describe the synthesis and characterization of new Schiff base ligand derived by condensation of 4,4′-dihydroxy-3,3′-diacetyl biphenyl with 2,6-diaminopyridine and their coordination polymers with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ions.

EXPERIMENTAL

The ligand was prepared from hydroxy ketone 4,4′-dihydroxy-3,3′-diacetyl biphenyl (DDABP) and 2,6-diaminopyridine as follows. DDABP and 2,6-diaminopyridine were dissolved separately in ethanol in stoichiometric proportion and were mixed and refluxed for 10 hrs. It was cooled and yellowish grey coloured product was separated out. It was filtered, washed with ethanol and dried. It was insoluble in common organic solvents and found soluble in DMF.

Preparation of Chelates

Equimolar quantities of metal acetate and ligand DDBDP were dissolved separately DMF and mixed in hot condition. The reaction mixture was refluxed for 4–6 hrs. The coloured products obtained with different metals were filtered, washed thoroughly first with DMF then with absolute

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alcohol and dried in vacuum desiccator over $CaCl_2$. All the coordination polymers are dark coloured solids insoluble in common organic solvents. Therefore, it was not possible to characterize them by conventional methods, like osmometry, viscometry etc.

RESULTS AND DISCUSSION

Elemental analysis showed that polychelates exhibit 1 : 1 metal to ligand stoichiometry (Table 1). From the data, it is revealed that all the polychelates have general formula $[ML]_n$.

The IR spectrum of DDBDP and its polychelates are similar, but are found to be comparable with each other, which suggests a definite difference from that of coordinating ligand. Strong bands of C=N in the ligand at 1650 cm^{-1} show shift toward lower wavenumber. The observable shift obtained in C=N stretch after complexation confirms the formation of a coordinated bond from imine nitrogen to the metal ion[1]. The medium band observed at 1220 cm^{-1} in the ligand is ascribed to —C—O stretching vibration on chelation. This shows marked shift indicating metal-oxygen bonding. The spectrum of the ligand shows a medium broad band in the region 3000–3040 cm^{-1} which is assigned to the intramolecular hydrogen bonded OH group[2]. On complexation, this band disappears indicating metal oxygen bond formation in the polychelates. All the polychelates contain weak to medium intensity broad band in the region 3300–3400 cm^{-1}. These bands are assigned to ν_{OH} of water[3]. Nature of water molecules (coordinated/lattice) is confirmed by TG analysis. The absorption band due to pyridine ring appears more or less at same position after complexation, indicating pyridine nitrogen is free from bonding. In all the polychelates the observed band around 500 cm^{-1} and 520–600 cm^{-1} may be identified as M—N and M—O stretching frequencies[3].

Thermal stabilities of the coordination polymers were suggested on the basis of thermogravimetric analysis. From the TG curves it was observed that the weight losses of Fe(II), Co(II) and Ni(II) polychelates at 160–200°C are 7.9, 9.5 and 9.4% respectively. These weight losses correspond to two coordinated water molecules per repeating unit of polychelate[4]. The Cu(II) polychelates show weight loss at 140°C–150°C equal to 9.2% corresponding to two lattice water molecules[4]. The perusal of thermogram of Mn(II) polychelate shows absence of water molecules in polychelates. The procedural decomposition temperatures of the polychelates decrease in the order Co $>$ Ni $>$ Mn $>$ Cu $>$ Fe. The analysis of thermogram indicates that the polychelates decomposed in two stages and the decomposition of first stage is fast as compared to the second stage. The thermal activation energies have been calculated using Freeman-Carroll[5] and Sharp-Wentworth methods[6] and various thermodynamic parameters have been calculated and values are summarised in Table 2.

TABLE 1. ANALYTICAL AND ELECTRICAL DATA OF POLYCHELATES OF DDBDP

Proposed composition	Colour	Elemental analysis Found (Calc.)				Electrical data	
		C%	H%	N%	M%	σ (ohm^{-1} cm^{-1}) (309, 519 K)	E$_a$ (eV)
$[Mn(DDBDP)]_n$	Off white	63.79 (63.89)	3.78 (3.95)	10.60 (11.09)	13.87 (14.04)	2.71×10^{-11} 2.03×10^{-9}	0.334
$[Fe(DDBDP)2H_2O]_n$	Golden brown	63.37 (64.03)	3.79 (3.05)	10.55 (10.69)	14.24 (14.38)	2.32×10^{-11} 1.25×10^{-9}	0.238
$[Co(DDBDP)2H_2O)_n$	Special grey	57.80 (58.03)	3.44 (3.68)	9.63 (10.10)	13.51 (13.66)	1.78×10^{-12} 1.78×10^{-10}	0.425
$[Ni(DDBDP)2H_2O]_n$	Tata grey	57.83 (58.61)	3.44 (3.65)	9.63 (10.01)	13.51 (14.12)	2.15×10^{-10} 4.73×10^{-9}	0.409
$\{[Cu(DDBDP)]2H_2O\}_n$	Dirty grey	57.20 (57.93)	3.40 (3.68)	9.53 (10.03)	14.42 (14.05)	2.47×10^{-11} 1.27×10^{-9}	0.463

TABLE 2. RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF POLYCHELATES OF DDBDP

Polymer	Decomposition temp. (°C)	Activation energy (Kcal/mole)		ΔS (cal)	ΔF (k cal)	Z (sec^{-1})	S* (cal)	n
		FC	SW					
$[Mn(DDBDP)]_n$	260	4.25	4.24	−77.64	28.55	89.07	−51.38	0.72
$[Fe(DDBDP)2H_2O]_n$	240	3.55	3.88	−76.17	27.39	42.47	−52.96	0.78
$[Co(DDBDP)2H_2O]_n$	290	4.51	4.59	−77.11	28.65	122.00	−50.54	0.61
$[Ni(DDBDP)2H_2O]_n$	280	4.97	4.26	−79.07	29.72	41.51	−52.90	0.88
$\{[Cu(DDBDP)]2H_2O\}_n$	250	5.59	5.98	−75.07	29.08	68.59	−51.84	0.60

FC = Freeman-Carroll SW = Sharp-Wentworth

The electronic spectra provide the most detailed information about the electronic structure. The diffuse electronic spectrum of the Mn(II) polychelate shows two bands at 20,000 cm^{-1} and 22,720 cm^{-1}, which may arise due to $^6A_1 \rightarrow {}^4T_{1(G)}$ and $^6A_1 \rightarrow {}^4A_{1(G)}$, $^4E_{(G)}$ for Mn(II) ion in tetrahedral environment[7]. The magnetic moment 5.13 B.M., lower than generally observed for spin free d^5 system. The Fe(II) polychelate shows a double band in 10,860–12,820 cm^{-1} region. The band in 10,000–10,980 cm^{-1} region is characteristic of Fe(II) high spin octahedral complex and could be assigned to $^5T_{2g}(D) \rightarrow {}^5E_g$ transition. Crystal field parameters Dq, B, C and β have been determined[8]. The values of crystal field parameters and nephelauxetic ratio are $Dq = 1086\ cm^{-1}$, $B = 584\ cm^{-1}$, $\beta = 0.55$ and $C = 2337\ cm^{-1}$. These values are in favour of octahedral geometry. The reduction of B value upon chelation indicates the partial covalent nature of M—L bond[9, 10]. The magnetic moment 5.61 B.M. is in the expected range for Fe(II) derivatives in high spin octahedral geometry.

The Co(II) polychelates exhibit two main absorption maxima at 9430 and 21,730 cm^{-1} which may be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and third transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ is not clear. Using Ballhauson equation[10], $Dq = 1069\ cm^{-1}$, $B = 904\ cm^{-1}$, $\beta = 0.80$, $\beta^\circ = 19.28\%$, $\nu_2/\nu_1 = 2.13$ and $\nu_2 = 20120\ cm^{-1}$ have been calculated. The magnetic moment of the Co(II) polychelate is 5.19 B.M. which is in good agreement with high spin octahedral geometry.

The Ni(II) polychelate has a magnetic moment 3.11 B.M. which is in the range required for six coordinated spin-free octahedral complex. Its diffuse reflectance shows bands at 9610, 15.620 and 23,250 cm^{-1} which are in the range required for octahedral structure[11]. These bands can be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively. Values of $10\ Dq = 9610\ cm^{-1}$, $B = 669\ cm^{-1}$, $\beta = 0.62$, $\beta^\circ = 15.09\%$ and $\nu_2/\nu_1 = 1.56$ have been obtained by using diagonal sum rule[11]. The low values of B and β suggest the appreciable amount of the covalent character in M—L bond[9].

The Cu(II)-polychelate shows two bands at 13,330 and 17,850 cm^{-1} and third band around 22,720 cm^{-1}. The first two bands may be due to the d-d transition which suggests the tetragonally distorted octahedral geometry[12]. Intense band at 22720 cm^{-1} may be assigned to charge transfer or intra-ligand transition[13]. The room temperature magnetic moment 1.87 B.M. also supports the distorted octahedral geometry.

The coordination polymers are well known for their behaviour as semiconductor. In fact, their conductivity and other properties such as thermoconduction, photoconduction, luminescence, etc. are in close connection with their physical and chemical structures. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relationship[14]

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

where E_a is the activation energy of the semiconduction and σ_0 is a constant. At higher temperature the above equation seems to hold good, and a linear relationship has been observed when the logarithm of the conductivity is plotted against reciprocal of absolute temperature. The linear relationship has not been observed at lower temperatures. The values of σ and E_a are given in Table 1. The electrical conductivity at 100°C is in the order Ni > Fe > Cu > Mn > Co and the activation energy increases the order Cu > Co > Ni > Mn > Fe. The results indicate that electrical conductivity and activation energy of conduction of these polychelates varies with the metal ions, which may be explained on the basis of the influence of the incorporation of different metal ions in the polymer which increases the ionization tendency[15].

TABLE 3

MAGNETIC AND ELECTRONIC SPECTRAL DATA OF POLYCHELATES OF DDBDP

Compound	μ_{eff} B.M.	Energies (cm^{-1})	Assignment	Crystal field parameter
Mn(II)-DDBD	5.13	22720	$^6A_1 \rightarrow {}^4A_1(G), {}^4E(G)$	
		20000	$^6A_1 \rightarrow {}^4T_1(G)$	
		15380	C.T.	
Fe(II)-DDBDP	5.61	21050	C.T.	Dq = 1086 cm^{-1}
		15620 12820	C.T.	B = 584 cm^{-1} β = 0.55
		10860	$^5T_{2g} \rightarrow {}^5E_g$	C = 2337 cm^{-1}
Co(II)-DDBDP	5.19	21730	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Dq = 1069.47 cm^{-1}
		17850	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	B = 904 cm^{-1}
		9430	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	v_2/v_1 = 2.13
				v_2 = 20120 cm^{-1}
				β = 0.80
				β° = 19.20%
Ni(II)-DDBDP	3.11	23250	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Dq = 9610 cm^{-1}
		15620	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	B_{35} = 669 cm^{-1}
		9610	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	β = 0.62
				β° = 15.03%
				ν_2 = 15030 cm^{-1}
				ν_3 = 23820 cm^{-1}
				ν_2/ν_1 = 1.62
Cu(II)-DDBDP	1.87	22720	C.T.	
		17850	$^2B_{1g} \rightarrow {}^2E_g$	
		13330	$^2B_{1g} \rightarrow {}^2B_{2g}$	

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