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Synthesis and Characterisation of Transition Metal Chelates of Polymeric Schiff Base

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Abstract. Polymeric chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been prepared from the polymeric schiff base derived from 4,4'-dihydroxy-3,3'-dipropyl biphenyl and 1,3- diaminopropane. All the chelates are coloured, insoluble in all common organic solvents and solubility in concentrated mineral acids is suggestive of their polymeric nature. They are characterized by elemental analysis, IR and reflectance spectra, magnetic and thermal studies. Electrical conductivity of these polychelates have been studied. From the TGA analyses, the kinetic and thermodynamic parameters have also been evaluated. The schiff base behaves as dibasic tetradentale ligand coordinating through the azomethine nitrogen and phenolic oxygen.

1. Introduction

The polymeric complexes of the schiff bases have been widely investigated due to their manifestation of novel structural feature, unusual magnetic properties and relevance to biological processes[1]. Coordination polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials from both polymeric and monomeric ligands. An efficient method for synthesizing such polymers consists of introduction of the inorganic component either chemically bound or as filler into the polymer. Such metal containing polymeric systems may also posses unusual electrical properties. Though coordination polymers are known since long, the study on transition metal polychelates of polyschiff base and their properties particularly electrical conductivity have been initiated only recently[2,3]. In the present paper we describe the synthesis and characterization of polyschiff base chelates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II); their thermal and electrical properties have also been studied.

2. Experimental

All the chemicals used were of AR grade and solvents DMF and ethanol were used after distillation. 4,4'-dihydroxy-3,3'- dipropyl biphenyl (DDPB) was prepared by known method[4]. The polymeric schiff base (PSB) was prepared from DDPB and 1,3-diaminopropane (DAP) as described below.

An ethanolic solution of DDPB (0.01 mol in 15 ml) was added to an ethanolic solution of 1,3-diaminopropane (0.01 mol, in 15 ml) and the mixture was refluxed on a water bath for 6 hours. On cooling PSB separated out, which was filtered, washed with ethanol and dried. It showed poor solubility in organic solvents. The observed C, H and N Contents of polyschiff base are shown in Table 1.

Key words and phrases : Metal chelates, polymeric Schiff base, electrical conductivity, dibasic tetradentale ligand.

Table 1. Analytical and Electrical conductivity data of polychelates

Compound	C	H	N	M	σ ohm^{-1}cm^{-1}	Ea (eV)
	% Found (calcd.)					
PSB	72.02 (74.31)	6.89 (7.73)	9.13 (9.75)	—	—	—
[Mn-PSB $2H_2O$]$_n$	58.41 (59.30)	6.10 (6.19)	6.48 (6.68)	11.96 (12.70)	3.10×10^{-8}	0.127
[Fe-PSB $2H_2O$]$_n$	58.65 (59.03)	5.83 (6.10)	5.69 (6.60)	12.63 (13.08)	1.67×10^{-10}	0.335
([Co-PSB] $2H_2O$)$_n$	57.34 (58.75)	5.92 (6.06)	6.12 (6.55)	12.62 (13.75)	1.62×10^{-10}	0.317
[Ni-PSB $2H_2O$]$_n$	57.92 (58.84)	5.69 (6.07)	5.82 (6.53)	13.02 (13.61)	1.23×10^{-9}	0.441
([Cu-PSB] $2H_2O$)$_n$	57.64 (58.03)	5.68 (6.01)	6.00 (6.47)	13.43 (14.69)	9.29×10^{-10}	0.624
[Zn-PSB]$_n$	61.38 (62.98)	5.03 (5.62)	6.58 (7.02)	15.96 (16.38)	1.29×10^{-8}	0.418
([Cd-PSB]$2H_2O$)$_n$	51.79 (52.03)	5.10 (5.48)	5.60 (5.80)	22.39 (23.21)	1.52×10^{-11}	0.124

The polychelates were obtained by following the known method[5]. This method offered the advantage of being rapid and of giving nearly quantitative yield. It is not possible to characterize the polychelates by known methods like osmometry, viscometry, conductometry, etc., due to their insolubility in common organic solvents.

All the physicochemical measurements were made at room temperature. Carbon, hydrogen and nitrogen analyses were carried out on a Coleman C-H-N analyser. The diffuse reflectance and IR spectra were recorded on Beckman DU and Perkin Elmer spectrophotometer respectively. Magnetic susceptibility measurements were made on a Gouy balance using Hg ($Co(SCN)_4$ as calibrant and thermo- gravimetric analysis (TGA) was carried out in air on Perkin Elemer thermobalance. D.C. electrical conductivity was measured by BPL-India Million meghohmmeter MK-III in their pellet form. The metal content in each polychelate was determined by oxide method[6]

3. Results and Discussion

All the polychelates are coloured amorphous powder in nature and found insoluble in water and common organic solvents, it was impossible to characterize them by conventional techniques. Such as viscometry, osmometry, etc. The elemental analysis (Table 1) suggest 1:1 metal:ligand stoichiometry[7]. The polymeric schiff base shows a medium broad band at 3050-3120 cm^{-1} due to hydrogen bonded phenolic OH stretch, which disappeared in the spectra of the polychelates, indicating deprotonation of OH and its involvement in coordination[8]. The shift of phenolic C-O stretching frequency from

1230 to 1280cm^{-1} suggests the coordination of oxygen of the phenolic group. The ligand exhibits a strong band at 1580 cm^{-1} (C=N) which is shifted to 1610 cm^{-1} on chelation, confirming the involvement of nitrogen in the chelate formation[9]. Appearance of new bands at 440-490 and 510-610 cm^{-1} are assigned to M-N and M-O stretch respectively. All the polychelates except Zn(II), display broads band at 3350-3400 cm^{-1} (OH of water molecule). The Mn(II), Fe(II) and Ni(II) polychelates exhibit medium sharp bands at around 1560 and 800 cm^{-1} (coordinated water) suggesting six coordinated structure[10] which further confirm by TG analysis. Thus it may be concluded that polyschiff base acts as a diabasic tetradentate ligand.

The reflectance spectrum of Mn(II) polychelate exhibits band at 22230, 19230 and 12620 cm^{-1} indicating a hexacoordinated structure (11). These bands are assigned to $^6A_{1g} \rightarrow {}^4A_{1g}$, $^4E_g\,(4_G)$, $^6A_{1G} \rightarrow {}^4T_{2G}\,(4_G)$ and $^6A_{1g} \rightarrow {}^4T_{1g}\,(4_G)$ transitions respectively. The observed magnetic moment of Mn(II) polychelate is 5.69 B.M. which is in agreement with the spin only value for an octahedral environment. The electronic spectrum of Fe(II) polychelate shows absorption bands at 20830, 15870, 12820 and 10630 cm^{-1} for charge transfer and $^5T_{2g}\,(^5D) \rightarrow {}^5E_g$ transitions respectively at the expected position for an octahedral environment[12]. Fe(II) polychelate exhibits magnetic moment of 5.16 B.M. expected for high spin octahedral geometry. The Co(II) chelate absorbs at 9520, 15870 and 23190 cm^{-1} for transitions $^4A_2\,(F) \rightarrow {}^4T_1\,(F)$, $^4T_2 \rightarrow {}^4T_1\,(P)$ and charge transfer transitions respectively, considering a tetrahedral geometry[13]. The magnetic moment of 4.02 B.M. for the Co(II) polychelate is indicative of a tetrahedral geometry. The electronic spectrum of Ni(II) polychelate is characteristic of an octahedral geometry showing bands at 9735, 15145 and 23210 cm^{-1} which may be assigned to $^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F)$, $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)$ and $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)$ transitions respectively[14]. Ni(II) polychelate has magnetic moment of 2.91 B.M. expected for the spin only value for the two unpaired electrons in an octahedral of distorted octahedral geometry. The spectrum of Cu(II) polychelate shows bands at 15620 and 21700 cm^{-1} due to $^2B_{1g} \rightarrow {}^2A_{1g}$ and charge transfer transitions respectively, indicating square planar stereochemistry[15]. The magnetic moment of 1.81 B.M. is also consistent with square planar geometry. The Zn(II) and Cd(II) polychelates are found to be diamagnetic as expected and may have tetrahedral geometries around the central metal ions[7].

Thermal stability studies of the polychelates indicate that they are decomposed in a gradual manner. Aromatic backbone units are much more stable than aliphatic one and they have a significantly higher melting temperature. In the case of Cd(II), Cu(II) and Co(II) polychelates the loss of water molecules takes place around 150^{o}C and these are considered to be lattice water[10]. On the other hand, in the case of Mn(II), Fe(II) and Ni(II) polychelates, loss of water molecules is complete at around 240^{o}C which corresponds to coordinated water[10]. Orders of the thermal decomposition and the corresponding activation energies have been evaluated from the graphical Freeman-Carroll and Sharp-Wentworth methods[16,17]. It is observed from Table 2 that the degradation of

polychelates is a complex process as noted from the non-integer order of reaction. The thermodynamic parameters such as entropy change, free energy change, apparent entropy change and frequency factor have also been calculated using transition state theory and are given in Table 2. The values of the thermodynamic parameters are nearly the same for each polychelate. The similarity in values of the thermodynamic parameters indicates a common reaction mode. Low value of frequency factor (Z) suggests that the decomposition reaction of polychelates can be a classed as "slow" process. While in the -case of Cu(II) polychelate, the slight high value of frequency factor (Z) may be due to Cu(II) having d^9 (Jahn-Teller distortions) configuration stability. The negative values of S show that the activated complex has more ordered structure than the reactants and that the reactions are slower than normal[18].

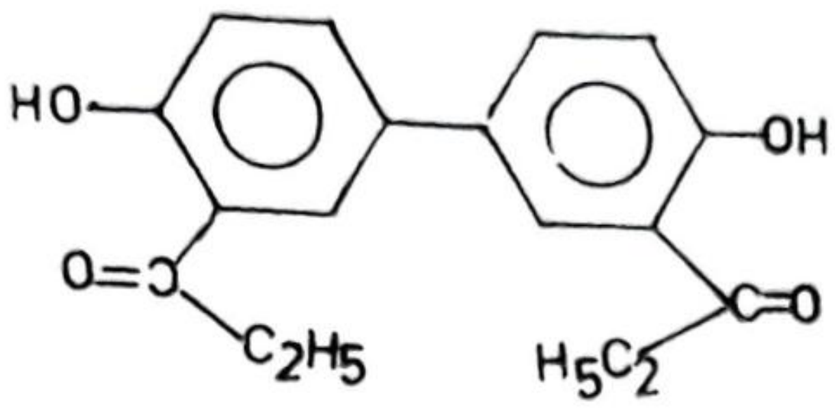
Table 2. Thermal data of polychelates

Compound	Decomposition Temp (^{0}C)	Activation Energy kJ mol^{-1}		ΔS Jk^{-1} mol^{-1}	ΔF kJmol^{-1}	S* kJK^{-1} mol^{-1}	Z (S^{-1})	Order of reaction (n)
		FC	SW					
Mn-PSB	255	40.54	33.94	–307.06	134.01	96.72	501.60	0.59
Fe-PSB	270	22.94	24.95	–322.02	127.94	108.51	290.34	0.63
Co-PSB	270	24.41	22.94	–313.12	122.47	107.96	333.06	0.67
Ni-PSB	335	35.69	35.02	–317.72	135.18	100.23	222.79	0.71
Cu-PSB	220	29.88	25.91	–314.87	128.40	104.91	731.50	0.55
Zn-PSB	285	27.43	26.12	–342.19	141.31	115.32	342.30	0.63
Cd-PSB	310	24.62	27.31	–310.49	138.30	120.60	360.51	0.71

FC = Freeman-Carroll; SW = Sharp-Wentworth

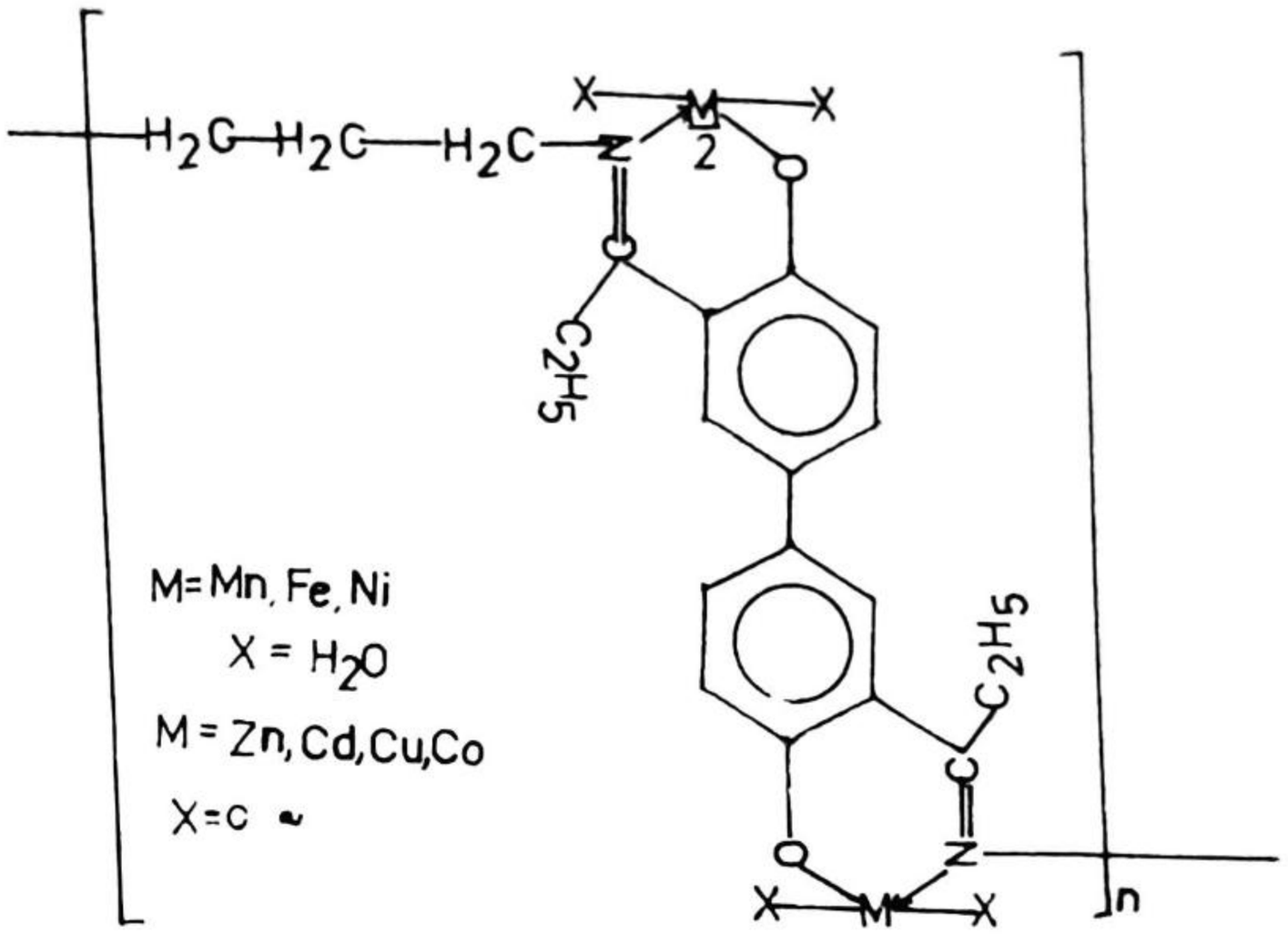
The electrical conductivity of the polychelates were studied in the temperature range 310-520°K. In all cases, the conductivity with increasing temperature indicating that these polychelates lie in the range of typical semiconductors. A plot of lnσ Vs 1/T of the compounds under investigation obeyed the equation[6] $\sigma = \sigma_0 \exp(Ea/kT)$ where σ_0 is a constant, Ea is the activation energy of semicon- ductor and k is Blotzmann constant. The activation energy decreases in the order: Cu>Ni>Zn>Fe>Co>Mn>Cd. The low value of the electrical conductivity may be attributed to low molecular weight due to which the extent of conjugation becomes low and undesirable morphology due to the pressing of the sample into hard, brittle pellet form.

From the elemental, magnetic, reflectance and infrared studies, it is concluded that the metal ion is coordinated to positions on two (or more) neighbouring ligand chains indicating the polymeric structure[7]. Fig. I.



+ $H_2N(CH_2)_3NH_2$

$\xrightarrow[\Delta]{M(CH_3COO)_2}$



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References

1. M.R. Maurya and A. Syamal, *Trans. met. chem.*, **11** (1986) 172.
2. M.M. Patel and R.S. Manavalan, *J. Macromol Sci. Chem.*, **A20** (1983) 487.
3. K.L. Madhok, *Polyhedron*, **1** (1984) 39.
4. A.L. Wild, C.H. Shunkh and C.H. Hoffman, *J. Am. Chem. Soc.*, **76** (1954) 1333.
5. H.A. Goodwin and J.C. Bailar Jr., *J. Am. Chem. Soc.*, **83** (1961) 2467.
6. A.S. Aswar, P.J. Bahad and N.S. Bhave, *Rev. Romania de, Chiem.*, **40(1)** (1995) 53.
7. M.N. Patel, D.H. Sutaria and J.R. Patel, *Synth. React. Inorg. Met-org. Chem.*, **24(3)** (1994) 401.
8. S. Thamiznarasi and A.V. Rami Reddy, *Eur. Polym. J.*, **28(2)** (1992) 119.
9. V. Mishra and D.S. Parmar, J. Ind. Chem. Soc. 72 (1995) 811.

10. B.S. Patel and S.R. Patel, *Makromol Chem.*, **180** (1979) 1159.
11. L.J. Paliwal and R.B. Kharat, *Die. Angew Makromol Chem.*, **160** (1988) 67.
12. A.S. Aswar and N.S. Bhave, *J. Ind. Chem. Soc.*, **68** (1991) 191.
13. M.N. Patel and S.H. Patil, *J. Macromol. Sci. Chem.*, **A17** (1981) 675.
14. M.M. Patel and H.R. Patel, *J. Ind. Chem. Soc.*, **73** (1996) 313.
15. B.K. Mahapatra and D.V. Rama Rao, *J. Inorg. Nu. Chem.*, **49** (1972) 1065.
16. E.S. Freeman and B. Carroll, *J. Phy. Chem.*, **62** (1958) 394.
17. J.B. Sharp and S.A. Wentworth, *Anal. Chem.*, **41** (1969) 2060.
18. V. Indira and G. Parameshwaran, *J. Thermal Anal.*, **32** (1987) 115.