Magnetic, Spectral, Thermal and Electrical Properties of Manganese, Cobalt, Nickel, Copper and Zinc Polychelates of 4,4'-Dihydroxy-3,3'-dipropionyl biphenyl-(3,4-diaminoanisole)

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Metal polychelates of the type $[ML(H_2O)_2]$ where M = Mn(II) Ni(II), Cu(II), Zn(II) an·' H_2L = 4,4'-dihydroxy-3,3'-dipropionyl bi-phenyl-(3,4-diaminoanisole) have been sythesized. Their structures have been elucidated on the basis of analytical, magnetic, electric and spectral study as well as elemental analysis. D.C. electrical conductivity has been measured over a temperature range 400–425 K. The ligand and its polychelates have also been screened for their antimicrobial activity using various microorganisms.

Key Words: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} Polychelates, Thermogravimetric analysis, Electrical conductivity.

INTRODUCTION

Much attention has been focussed on the synthesis, characterization, structural elucidation and thermal studies of polychelates during the recent past[1–4]. In continuation of our interest[5], the present communication describes the preparation and characterization of some divalent metal polychelates of Mn, Co, Ni, Cu and Zn with the ligand H_2L.

EXPERIMENTAL

All the chemicals and metal acetates used were of AnalaR grade. All the solvents were used after double distillation. Hydroxy ketone was prepared by Friedel-Craft's reaction.

Preparation of the ligand

The ligand H_2L was prepared from dihydroxy ketone, 4,4'-dihydroxy-3,3'-dipropionyl biphenyl and 3,4-diaminoanisole as described below:

To a hot solution of 4,4'-dihydroxy-3,3'-dipropionyl biphenyl (0.02 mol) in dry ethanol (25 mol), a solution of 3,4-diaminoanisole (0.02 mol) in dry ethanol (25 mol) was added with stirring. The mixture was refluxed for about 3 h and allowed to cool to room temperature. The resulting pale yellow solid was filtered and washed several times with hot water followed by ethanol and dried. The product was insoluble in water and common organic solvents but soluble in hot DMF. The resulting product was crystallized from DMF. Yield 86%; m.p. 325 ± 1°C.

The polychelates were analyzed by the standard procedures[6]. Magnetic moments were determined by Gouy method using $[Hg(Co(NCS)_4]$ as the calibrant. Infrared spectra in KBr pellets and diffuse reflectance spectra were obtained

from RSIC, CDRI, Lucknow. TG analysis were carried out using Stanton Redcraft TG-750 thermo balance at a heating rate of $10°C$ min^{-1} in air.

RESULTS AND DISCUSSION

All the polychelates are coloured, amorphous powders and insoluble in water and common organic solvents. Elemental analysis suggests 1 : 1 metal : ligand stoichiometry (Table-1).

TABLE-1
ANALYTICAL AND ELECTRICAL CONDUCTIVITY DATA OF
POLYCHELATES OF TYPE $[ML(H_2O)_2]_n$

| Compound	% Analysis: Found (Calcd.)				m.w. of repeating unit	Electrical conductivity (σ), ohm^{-1} cm^{-1}	Activation energy (E_a) (eV)
	C	H	N	M			
$C_{25}H_{25}O_3N_2$ (H_2L)	74.78 (74.81)	6.37 (6.23)	6.95 (6.98)	—	401	—	—
$[MnL(H_2O)_2]_n$	61.15 (61.22)	5.40 (5.51)	5.60 (5.71)	11.00 (11.22)	490	5.24×10^{-8}	1.07
$[CoL(H_2O)_2]_n$	60.65 (60.77)	5.65 (5.67)	5.55 (5.66)	11.80 (11.94)	494	0.02×10^{-5}	0.56
$[NiL(H_2O)_2]_n$	60.80 (60.72)	5.60 (5.67)	5.75 (5.66)	11.85 (11.94)	494	0.01×10^{-5}	0.35
$[CuL(H_2O)_2]_n$	62.30 (62.43)	5.22 (5.20)	5.85 (5.82)	13.24 (13.22)	480.5	3.62×10^{-8}	0.09
$[ZnL(H_2O)_2]_n$	60.15 (60.00)	5.75 (5.60)	5.70 (5.60)	13.25 (13.12)	500	7.82×10^{-9}	0.78

The infrared spectrum of the ligand exhibits a broad band having medium intensity at 3230 cm^{-1}. The band can be assigned to $v(O—H)$. The width of the band indicates the presence of hydrogen bonding intramolecular in nature[7]. The band is absent in the spectra of all the polychelates indicating the breakdown of O—H band and subsequent coordination of oxygen with the metal ions.

The medium intensity band at 1245 cm^{-1} in the spectnrm of the ligand is attributed to phenolic C—O stretching vibration. In the spectra of polychelates, this band shows a blue shift (1265 cm^{-1}) which supports the bands of the ligand through the phenolic oxygen.

An intense band at 1640 cm^{-1} in IR spectrum of. the ligand is attributed to $v(C{=}N)$ and undergoes a red shift, appearing in the region 1615–1600 cm^{-1}, indicating the coordination of azomethine nitrogen to the metal ions[8].

The additional bands, appearing in the spectra of polychelates as compared to the spectra of the ligand, in the regions 570–450 and 440–400 cm^{-1} are assigned to $v(M—O)$ and $v(M—N)$ moles of vibrations respectively. The broad band in the region 3430-3425 cm^{-1} in the spectra of polychelates may be assigned to $v(O—H)$ of coordinated water molecules. This gains further support by the appearance of moderately strong bands at 820 and 1575 cm^{-1} in the spectra of polychelates assignable to $\delta(H_2O)$ and $\rho(H_2O)$[10].
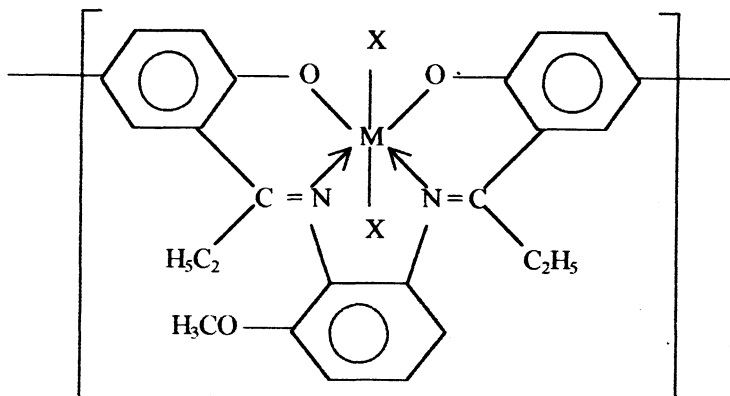
where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II); X = H_2O.

Fig. 1

Electronic spectra and magnetic properties

The diffuse reflectance spectrum of the Mn(II) polychelate consists of two weak bands at 24000 and 20000 cm^{-1}. These bands may be assigned to $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$, $^4E_g(G)$ and $^6A_{2g}(G)$ transition respectively and one sharp band is observed at 17000 cm^{-1} assigned to $^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$, transition for octahedral chelates[11, 12]. The magnetic moment (6.2 B.M) of the polychelate indicates high spin octahedral environment[13]. The electronic spectrum of Co(II) polychelate shows three d-d absorption bands at 10000, 18000 and 21000 cm^{-1} assignable to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, in conformity with octahedral stereochemistry around Co(II). The observed magnetic moment of Co(II) chelate is 5.4 B.M. attributed to high spin octahedral geometry[14].

The Ni(II) polychelate has a magnetic moment of 3.20 B.M., which is in the range required for six coordinate spin-free octahedral complex[15]. Ni(II) polychelate exhibits three bands at 10800, 16700 and 24000 cm^{-1} which may be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively. The position and assignments of the bands indicate octahedral environment around the Ni(II) ion.

In the electronic spectrum of Cu(II) polychelate exhibits two bands at 17700 and 16600 cm^{-1} which can be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. The broad band at 23000 cm^{-1} is assigned to charge transfer transition. These transitions are observed in normally expected region for square planar geometry[16]. The magnetic moment of Cu(II) polychelate is 1.70 B.M. which also supports the square-planar geometry. The Zn(II) polychelate is found to be diamagnetic as expected and may have tetrahedral geometry.

Thermal Studies

Thermal decomposition results indicate that all the polychelates decomposed in a two-stage process. It is obvious to compare TGA data of H_2L and its polychelates only up to certain stages of decomposition as in the latter purely

inorganic residue, much less susceptible to decomposition, begins to accumulate in proportionately large amount. The elimination of lattice and coordinated water molecules takes place in the first stage. In the present study, the Mn(II), Co(II) and Ni(II) polychelates exhibit weight loss, in the temperature range 170–190°C, equal to 7.00, 7.17 and 8.00% (calcd. 7.84, 7.77 and 7.78%) respectively which corresponds to two coordinated water molecules per repeating unit of polychelates[17]. Then continuous mass loss is observed up to 590°C indicating the decomposition of the organic part of the chelate. Above 590°C, TG curves attain a constant level corresponding to their metal oxides Mn_3O_4 (20.22% found, 23.14% calcd.), Co_3O_4 (17.00% found, 19.24% calcd.) and NiO (21.00% found, 22.22% calcd.). In case of Cu(II) polychelate weight loss at about 120°C equal to 3.35% (4.00% calcd.) corresponds to one lattice water molecule[18]. The decomposition is completed at 450°C forming CuO (20.00% found, 17.69% calcd.). In case of Zn(II) polychelate, the weight loss 7.85% (7.66% calcd.) at 100°C corresponds to two lattice water molecules.

Both Sharp-Wentworth[19] and Freeman-Caroll[20] equations analyze the thermal data of polychelates and the comparative values are summarized in Table-2. It is observed that the degradation of polychelates at elevated temperatures is a complex process as noted from the non-integer order of reaction and follows the first order kinetics. The values of thermodynamic parameters such as entropy change (ΔS), free energy change (ΔG), apparent entropy (S^*) and frequency factor (Z) are nearly same for each polychelate which indicates similar type of reaction in all polychelates (Table-2). The low values of frequency factor suggest that the decomposition reaction of the polychelates can be classified as a slow reaction[21]. The negative values of ΔS indicate that the activated complex has more ordered structure than reactants and that the reactions are slower than normal.

TABLE-2
ANALYTICAL AND ELECTRICAL CONDUCTIVITY DATA OF
POLYCHELATES OF THE TYPE $[ML(H_2O)_2]_n$

Compound	Decomp. temp. (°C)	Activation energy (kJ mol^{-1})		$-\Delta S$ (J K^{-1} mol^{-1})	$-\Delta G$ (kJ mol^{-1})	$-S^*$ (kJ K^{-1} mol^{-1})	Z (S^{-1})	Order of reaction
		FC	SW					
$C_{25}H_{25}O_3N_2$ (H$_2$L)	325	30.65	31.48	—	—	—	—	—
$[MnL(H_2O)_2]_n$	368	26.80	27.37	306.15	123.15	219.22	70.10	0.88
$[CoL(H_2O)_2]_n$	270	27.63	27.39	295.04	121.28	216.71	85.68	0.89
$[NiL(H_2O)_2]_n$	278	25.42	25.53	300.61	121.15	218.21	70.08	0.65
$[CuL(H_2O)_2]_n$	315	20.86	21.18	292.78	112.02	222.62	34.32	0.82
$[ZnL(H_2O)_2]_n$	338	33.61	34.12	307.15	130.15	210.15	186.60	0.62

In the electrical domain, the temperature dependence of electrical conductivity obeys the well known equation[22]

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

where σ_0 is a constant, E_a is activation energy and k is the Boltzmann constant. The values are given in Table-1. The temperature dependence of electrical conductivity in case of Ni(II) and Cu(II) polychelates exhibits two distinct regions. 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 regions, a linear dependence with high value of slope was observed. In this temperature domain these polychelates may behave as intrinsic semiconductors[23]. The plots of log σ vs. 1/T for all the other polychelates are found to be linear over a temperature range 403–523 K indicating the semi-conducting nature of polychelates. The electrical conductivity of polychelates at room temperature declines in the order Co > Ni > Mn > Cu > Zn respectively while the activation energies of electrical conduction decrease in the oder Mn > Zn > Co > Ni > Cu. The observed low values of activation energy may be attributed to the interaction between the electrons of the metal d-orbitals and π-orbitals of the ligand.

All the polychelates along with ligand were screened for their antibacterial activities by disc diffusion method against the bacterial species *E. coli, S. aureus, K. pneumoniae* and *Bacillus 19*. Antibacterial activity is usually tested by making aqueous solution of samples. However, polychelates used in the present study were insoluble in water and common organic solvents but make suspension in dimethyl formamide. Therefore, to study the antibacterial activity of polychelates, their dilutions were prepared in dimethyl formamide. Dimethyl formamide may have some antibacterial activity; therefore, blank of dimethylformamide was tested. *E. coli* is moderately inhibited by all the polychelates and the ligand, while no effect on Co(II) polychelate. *S. aureus* is highly inhibited by all the polychelates and the ligand, whereas Co(II) and Ni(II) polychelates show moderate effect. *K. pneumoniae* is moderately inhibited by all the polychelates and the ligand except Ni(II) polychelates. Polychelates and the ligand show moderate action on B[19].

REFERENCES

1. S. Sandi-Urena and E. Parson , *Inorg. Chem.*, **33**, 303 (1994).
2. V. Casellato and P. A. Vigato, *Coord. Chem. Rev.*, **23**, 31 (1977).
3. F. Cassandra and B. Boshich, *Inorg. Chem.*, **33**, 338 (1994).
4. V. Mishra, *J. Polym. Mater.*, **12**, 63 (1995).
5. V.G. Kher and C.S. Adgaonkar, *Indian J. Pure Appl. Phys.*, **10**, 902 (1972).
6. R. Ananthanarayan and C.K. Jayaram Panikar, Text Book of Microbiology, 5th Edn. (1996).
7. B.T. Thaker, J. Lakhedia, A. Patel and P. Thaker, *Transition Met. Chem.*, **19**, 623 (1994).
8. P. Teygi and J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963).
9. B. Singh, R.L. Maurya, B.V. Agrawala and A.K. Dey, *J. Indian Chem. Soc.*, **59**, 1130 (1982).
10. B.B. Mahapatra, N.P. Ajitkumar and P.K. Bhoi, *J. Indian Chem. Soc.*, **67**, 800 (1990).

11. L.J. Heidt, G.F. Koster and A.M. Johnson, *J. Am. Chem Soc.*, **80**, 6471 (1959).

12. N.R. Shah, *J. Indian Chem. Soc.*, **58**, 831 (1981).

13. B.K. Shah and B.K. Mahapatra, *J. Indian Chem. Soc.*, **56**, 825 (1979).

14. F.A. Cotton and M. Goodgame, *J. Phys. Chem.*, **65**, 191 (1961).

15. N.S. Bhave and R.B. Kharat, *J. Inorg. Nucl. Chem.*, **43**, 414 (1981).

16. H. Singh, U.K. Srivastava, S.N. Shukla and M.K. Upadhyay, *Indian J. Chem.*, **33A,** 350 (1994).

17. P.S. Patel, R.M. Ray and M.M. Patel, *J. Indian Chem. Soc.*, **70**, 99 (1993).

18. B.K. Kumar, V. Ravinder, G.B. Swamy and S.J. Swamy, *Indian J. Chem.*, **33A**, 136 (1994).

19. J.B. Sharp and S.A. Wentworth, *Anal. Chem.*, **41**, 2060 (1969).

20. E.S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).

21. K.K. Arvindakshan and K. Muraleedharan, *Thermochim. Acta*, **140,** 325 (1989).

22. J.E. Katon, Organic Semiconducting Polymers, Marcell-Dekker Inc., N.Y. (1986).

23. M. Spriatos, G.I. Rusu, A. Airinei and A. Ciobanu, *Die Angew Makromol. Chemie*, **107**, 33 (1982).

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