Coordination Polymers. II. Physicochemical Studies on Chelate Polymers of Cu(lI), Ni(ll), Co(lI), Zn(II), and Mn(lI)

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ABSTRACT

Chelate polymers of Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) with 4,4'-bis(m-formyl-p-hydroxy phenyl) biphenyl sulfone have been prepared. All the chelates are dark, amorphous, and insoluble in common organic solvents. The probable octahedral structures of the complexes were determined on the basis of their IR and electronic spectral data in conjunction with their magnetic susceptibility data. The ligand field parameters have been determined for Ni(II) and Co(II) polychelates using ligand-field theory of spin-allowed transitions.

INTRODUCTION

In continuation of our studies on polychelates obtained from monomeric ligand [1-5], here we report the synthesis of polychelates of Cu(II), Ni(II), Co(II), Zn(II), and Mn(II) with 4,4'-bis(m-formyl-p-hydroxy phenyl azo) biphenyl sulfone. We have also investigated their IR, diffuse reflectance, and magnetic properties. Important ligand field parameters have been calculated using ligand field theory of spin-allowed transitions for Ni(II) and Co(II) polychelates.

EXPERIMENTAL

Materials

Salicylaldehyde (B.D.H.) was used after distillation. 4,4'-diamino diphenyl sulfone (B.D.H.) was used after recrystallization. Metal chlorides (B.D.H.) have been used for the preparation of chelate polymers. N,N-dimethylformamide (DMF, SM) was used without further purification. All other chemicals used were of AnalaR grade.

Preparation of the Ligand

A cold tetrazotized solution of 4,4'-diamino diphenyl sulfone (12.5 g) was added to a cold solution of salicylaldehyde (6.5 g) in 100 mL water containing 23 g Na_2CO_3. The resulting mixture was stirred for 3 h. After that a cold solution of salicylaldehyde (6.5 g) in NaOH was added and stirred for 2 h. The precipitated compound was filtered, washed, and dried.

Preparation of Polychelates

The ligand (0.01 mol) was dissolved by refluxing it in about 100 mL DMF. To the refluxing ligand solution the metal salt solution (0.01 mol in about 20 mL water) was added slowly and with constant shaking. To the resulting mixture about 0.5 g of sodium acetate was added and then the mixture was refluxed for 4 h. The precipitated solid was filtered and washed several times with hot water and then with hot DMF and finally with ethanol. The products were dried at 80°C. All the polychelates are dark colored, amorphous solids. They are found to be insoluble in all common organic solvents, and therefore their characterization by conventional methods like osmometry and viscometry was not possible.

Measurements

All physicochemical measurements were made at room temperature (30°C). Magnetic measurements were made on a Sartorious semi-micro Gouy balance. The diffuse reflectance spectral measurements were made on a Beckman-DU spectrophotometer. The IR spectra were recorded in KBr on a Spectromon-2000 IR spectrophotometer.

For establishing the composition, the metal content in each chelate polymer was determined by independent gravimetric and volumetric methods. Carbon-hydrogen analyses were made on a "University," India, C–H analyzer.

TABLE 1. Analytical Data

Compound	Elemental analysis found (calc) (%)		
	C	H	M
[$C_{26}H_{18}N_4O_6S$]	62.6 (60.67)	3.577 (3.5)	-
[$Cu_2(C_{26}H_{17}N_4O_6S)_3$].$4H_2O$	53.87 (50.93)	3.39 (3.501)	7.5 (7.30)
[$(NiC_{26}H_{17}N_4O_6S)(H_2O)_2$]	52.89 (51.36)	3.496 (3.456)	9.25 (9.661)
[$(CoC_{26}H_{17}N_4O_6S)(H_2O)_2$]	53.71 (51.34)	3.563 (3.454)	9.54 (9.696)
[$Mn_2(C_{26}H_{17}N_4O_6S)_3$.$4H_2O$]	57.32 (54.36)	3.546 (3.431)	6.63 (6.383)
[$Zn_2(C_{26}H_{17}N_4O_6S)_3$.$4H_2O$	58.35 (53.78)	3.742 (3.39)	7.17 (7.504)

RESULTS AND DISCUSSION

Elemental analysis (Table 1) suggests a 1:1 (metal:ligand) stoichiometry for the Ni(II) and Co(II) polychelates and 2:3 for the Cu(II), Zn(II), and Mn(II) polychelates.

The diffuse reflectance electronic spectral and magnetic data of the chelate polymers are given in Table 2. The spectrum of Ni(II) polychelate shows three bands in their normally expected regions for Ni(II) octahedral [6]. These bands may be assigned as follows:

ν_1: $^3T_{2g} \longleftarrow {}^3A_{2g}$ 9,524 cm^{-1}

ν_2: $^3T_{1g} \longleftarrow {}^3A_{2g}$ 14,400 cm^{-1}

ν_3: $^3T_{1g}(P) \longleftarrow {}^3A_{2g}$ 21,510 cm^{-1}

These data are utilized to compute the important parameters using ligand field theory of spin-allowed transitions in the d^8 configuration [7]. The results are given in Table 3. The low energy ν_1 band is observed as a weak and broad band with some sign of splitting. This might be because of a lower symmetry field. The ν_2 band also shows splitting which may be attributed to the spin-forbidden transition

TABLE 2. Magnetic and Electronic Spectral Data

Compound	Magnetic moment (B.M.)	Transition energies (cm^{-1})
[$Cu_2(C_{26}H_{17}N_4O_6S)_3$].$4H_2O$	1.50	14,290, 22,220, 25,000
[$Ni(C_{26}H_{17}N_4O_6S).2H_2O$]	2.92	9,524, 10,810, 13,330, 14,400, 21,510
[$Co(C_{26}H_{17}N_4O_6S).2H_2O$]	4.49	9,346, 12,350, 14,390, 20,620, 22,730, 25,000
[$Mn_2(C_{26}H_{17}N_4O_6S)_3.4H_2O$]	3.79	20,830, 23,260
[$Zn_2(C_{26}H_{17}N_4O_6S)_3.4H_2O$]	Diamagnetic	–

occurring due to spin-orbit coupling to $^1E(D)$, lying close to $^3T_{1g}(F)$ [8]. The ν_2/ν_1 ratio lies in the range required for octahedral structure [6]. An attempt has been made to calculate the approximate value of λ by using [9]

$$\lambda_{cal} = \frac{2.7 \times B_{35}^2}{10Dq}$$

The average value of B_{35} (Table 3) has been used in the calculation. Its value was found to be 81.7. This is lower than the free ion value. The magnetic moment is in the range required for octahedral stereochemistry. We have also calculated μ_{eff} from λ_{cal} by using [10]

$$\mu_{eff}^{cal} = \mu_{eff}^{s.o.} \ (1 - 4\lambda_{cal}/10Dq)$$

The calculated value (2.94) is found to be in good agreement with the observed magnetic moment. The spectrum of Co(II) polychelate shows a broad asymmetric band centered around 22,730 cm^{-1}, which may be assigned to the $^4T_{1g}(P)$ —— $^4T_{1g}$ (ν_3) transition. The shoulder on the high energy side at 25,000 cm^{-1} can be assigned to a spin-forbidden transition [11]. The band at 20,620 cm^{-1} may be assigned to the $^4A_{2g}$ —— $^4T_{1g}$ transition. The weak shoulders at 14,390 and 12,350 cm^{-1} might be because of spin-forbidden transitions. The $^4T_{2g}$ —— $^4T_{1g}$ (ν_1) transition is observed as a very weak and broad band centered at 9346 cm^{-1}. The spin allowed transition energies have been used to calculate 10Dq and B_{35} [7]. The results are given in Table 2. The ν_2/ν_1 ratio comes very close to the ratio required

TABLE 3. Electronic Spectral Data and Calculated Transition Energies in cm^{-1} of Ni(II) and Co(II) Poly-chelates

Compound	Methods of calculation	Transitions			B_{35}	β_{35}	δv	10Dq	ν_2/ν_1
		ν_1	ν_2	ν_3					
[Ni(C$_{26}$H$_{17}$N$_4$O$_6$S)·(H$_2$O)$_2$]	Expt	9,524	14,400	21,510	-	-	-	-	1.51
	(1)	10Dq	Fitted	22,449	552.4	0.51	+939	-	
	(2)	10Dq	14,062	21,848	489.3	0.45	±338	-	
	(3)	10Dq	14,462	Fitted	562.3	0.52	+62	-	
[Co(C$_{26}$H$_{17}$N$_4$O$_6$S)(H$_2$O)$_2$]	Expt	9,346	20,620	22,730	-	-	-	-	2.2
	(1)	Fitted	15,012	Fitted	803.7	0.712	-5,608	8,018	
	(2)	8,714	Fitted	Fitted	959.4	0.756	-632	9,967	
	(3)	Fitted	Fitted	23,810	1,021	0.91	+1,120	11,274	

TABLE 4. Infrared Spectral Data[a]

Ligand	Cu	Ni	Co	Mn	Zn
3300 Sbr	3300 Sbr	3300 Sbr	3300 Sbr	3250 Sbr	3250 Sbr
1660 Svs	1600 SVS	1620 Sbr	1620 Sbr	1600 SVS	1600 SVS
1380 SM	-	-	-	-	-
1280 SVS	1280 Sm	1300 SS	1300 SS	1300 Sm	1300 Sm

[a]SVS = sharp very strong. Sm = sharp medium. Sbr = sharp broad.

for an octahedral structure. The magnetic moment is found to be lower than required for a high-spin octahedral structure.

Cu(II), Mn(II), and Zn(II) chelates do not show higher polymerization. The absorption spectrum of Cu(II) is found to be consistent with the square planar structure. It shows a band at 14,290 cm^{-1}, which may be assigned to the $^2A_{2g}$ ———— $^2B_{2g}$ transition. The band at 25,000 cm^{-1} might be charge transfer in origin, while the shoulder at 22,220 cm^{-1} might be because of ^2E_g ———— $^2B_{2g}$ transition. The low magnetic moment suggests the presence of metal-metal interaction [12]. The spectrum of Mn(II) suggests an octahedral structure. It shows two bands at 20,830 and 23,260 cm^{-1} which may be assigned to $^4T_{1g}$ ———— $^6A_{2g}$ and $^4T_{2g}$ ———— $^6A_{2g}$ transitions. The observed lower magnetic moment indicates the presence of metal-metal interaction [13]. The Zn(II) derivative is diamagnetic and may have an octahedral structure.

Important IR spectral data are given in Table 4. The IR spectra of all the chelates are found to be comparable. All the compounds studied here contain four aromatic rings and hence the region characteristics of double bonds will comprise several bands which overlap. This renders the $\nu_{C=C}$ region complicated. The out-of-plane bending region is also rendered complicated. However, some important observations are indicated below.

1. The ligand and the polychelates show a strong and broad band in the range 2950-3500 cm^{-1} which may be due to coupling of the ν_{OH} of water as well as that of the phenolic group. This suggests that the ligand as well as the polychelates contain water. Except for Cu(II), the octahedral stereochemistry of the polychelates requires the association of two water molecules per metal ion. In the case of Cu(II), they may be outside the coordination sphere.

2. The strong band at 1660 cm^{-1} in the ligand may be assigned

to $\nu_{C=O}$. This band is found to be shifted to a lower energy, indicating coordination through the oxygen atom of the C=O group.

3. The band at 1380 cm^{-1} in the ligand might be due to phenolic OH deformation. This band is absent in all the polychelates. This suggests the dissociation of the phenolic proton on coordination.

4. The ligand and the polychelates show medium strong band around 1300 cm^{-1}, which may be assigned to phenolic ν_{C-O}.

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