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Synthesis and Physicochemical Studies of Chelate Polymers Obtained from the Schiff Base of 5,5′-Methylene-bis-salicylaldehyde with Aniline

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ABSTRACT

Cu(II), Ni(II), and Co(II) chelate polymers were prepared from Schiff base of 5,5'-methylene-bis-salicylaldehyde with aniline. All the polymers are amorphous and insoluble in common organic solvents. They are characterized on the basis of conductivity, infrared, and electronic spectral properties in conjunction with magnetic susceptibility measurements. Various ligand field and nephelauxetic parameters have been evaluated for Ni(II) and Co(II) polychelates. They are consistent with octahedral structure for the former and tetrahedral structure for the latter. Their thermogravimetric analysis show the Co(II) > Ni(II) > Cu(II) order of thermal stability. Kinetic parameters were also obtained.

INTRODUCTION

Transition metal complexes derived from Schiff bases have occupied a central role in the development of coordination chemistry. Polychelates derived from poly-Schiff bases have been extensively studied [1]. However, very little work seems to have been done on Schiff bases of bis-aldehyde forming polychelates [2]. In such symmetric tetrafunctioning Schiff bases the donor atoms on the rings are widely separated, so that the ligand can coordinate with two metal ions from either end, giving chelate polymers. Here we report the preparation of chelate polymers of Cu(II), Ni(II), and Co(II) with the Schiff base of 5,5'-methylene-bis-salicylaldehyde with aniline. We have also investigated their IR, diffuse reflectance, magnetic, electrical conductance, and thermal 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

Aniline and salicylaldehyde, both from B.D.H., were used after distillation. Metal chlorides (B.D.H.) were used for the preparation of polychelates. Absolute ethanol obtained from Alembic Co. Ltd., was directly used without further purification.

Preparation of the Ligand

5,5'-Methylene-bis-salicylaldehyde was prepared by the method of Marvel et al. [1]. The Schiff base (mp 142°C) was obtained by refluxing the ethanolic mixture for 2 h on a water-bath. The mixture was obtained by mixing the ethanolic solution of the bis-aldehyde and aniline in a 1:2 mole ratio. After cooling, the isolated solid was filtered and washed with ethanol. The product was recrystallized from ethanol.

Preparation of Polychelates

The requisite amounts of metal and ligand were dissolved separately in minimum amounts of ethanol. The ligand solution in slight excess over the metal:ligand ratio of 1:1 was added to the metal solution with constant stirring. To the clear, refluxed solution, about 3 g of sodium acetate was added. The mixture was refluxed for 4 h. The precipitated solid was filtered and washed several times with hot water and finally with hot ethanol. The products were dried at 80°C. They were found to be insoluble in all common organic solvents. They showed some solubility in DMF.

Measurements

All measurements were made at room temperature. The conductivities of polychelates in DMF were measured using the Konduktoskop

Metrohm Herisau (Switzerland) conductometer and conductivity cell. Magnetic measurements were made on a Sartorious semimicro Gouy balance. The diffuse reflectance measurements were made on a Beckman-DU spectrophotometer. The infrared spectra were recorded on a Perkin-Elmer spectrophotometer in a Nujol mull. The thermogravimetric analysis was recorded on a DuPont (U.S.A.) analyzer.

For establishing the composition, the metal content in each polychelate was determined by independent gravimetric and volumetric methods. Carbon-nitrogen-hydrogen analyses were made on a University (India) C–H–N analyzer. The water contents of Co(II) and Ni(II) polychelates were estimated from the thermograms.

RESULTS AND DISCUSSION

The elemental analyses of the polychelates, given in Table 1, suggest 1:1 (metal:ligand) stoichiometry. The molar conductivities of Cu(II), Ni(II), and Co(II) polychelates in DMF are found to be 15, 4, and 7 ohm^{-1} cm^2 mol^{-1}, respectively. These are lower than the reported range for 1:1 electrolytes in this solvent. Thus the polychelates appear to be nonelectrolytes.

The infrared spectral data are given in Table 2. The ligand shows a medium broad band in the region 3275-3500 cm^{-1} which may be assigned to phenolic OH stretching. The stretching frequency for the free OH usually occurs at 3600 cm^{-1} [3]. The observed shifting to the low energy side might be because of the presence of intramolecular hydrogen bonding [3]. This band disappears in the spectra of polychelates. However, a weak band present in the spectra of Ni(II) and

TABLE 1. Elemental Analysis of the Polychelates

	Analysis (%)[a]			
Compound	C	H	N	M
$C_{27}H_{22}O_2N_2$	80.20 (79.78)	5.38 (5.46)	6.82 (6.89)	
$[Cu(C_{27}H_{20}O_2N_2)]$	62.28 (64.34)	5.02 (4.80)	5.42 (5.56)	12.82 (12.61)
$[Ni(C_{27}H_{20}O_2N_2)(H_2O)_2]$	62.58 (64.96)	4.93 (4.80)	5.81 (5.61)	12.10 (11.76)
$[Co(C_{27}H_{20}O_2N_2)].H_2O$	68.22 (67.36)	4.32 (4.61)	5.92 (5.82)	12.58 (12.24)

[a] Theoretical values in parentheses.

TABLE 2. Infrared Data in cm^{-1} [a]

Bis-aniline of 5,5'-methylene-bis-salicylaldehyde	Cu(II)	Ni(II)	Co(II)
3400 m,vbr	-	3350 w,vbr	3400 w,vbr
1618 vs,vs	1592 s,br	1600 sh	1608 s,s
1315 m,s	-	1300 sh	1300 sh
1280 s,s	1280 w,s	1275 sh	1285 w,br

[a] vs, vs = very strong, very sharp; s,s = strong, sharp; w,s = weak, sharp; m,vbr = medium, very broad; w,vbr = weak, very broad; sh = shoulder.

Co(II) polychelates indicates the presence of water molecules. A strong band at 1315 cm^{-1} in the ligand may be assigned to phenolic OH deformation vibrations [4]. This band is found to be absent in the spectra of polychelates. This indicates the loss of the phenolic proton on coordination. The presence of a very strong band at 1618 cm^{-1} in the ligand spectra may be assigned to the C=N stretching vibration [5]. The polychelates show this vibration at lower energy, indicating nitrogen coordination. The ligand shows a very strong band at 1280 cm^{-1} which may be assigned to the phenolic C–O vibration [5]. This band does not show a marked shift on chelation, indicating that this frequency is not as sensitive to the chelation [5].

The reflectance spectral and magnetic data are given in Table 3. The Cu(II) polychelate shows three bands at 14,700, 19,080, and 24,390 cm^{-1} which may be assigned to square planar stereochemistry [6]. The first two bands presumably involve the $^2A_{2g} \longleftarrow {}^2B_{2g}$ (14,700 cm^{-1}) and $^2E_g \longleftarrow {}^2B_{2g}$ (14,700 cm^{-1}) transitions. The third band may be charge transfer in origin. Jorgensen has used the ratio $\bar{\nu}_{Cu}/\bar{\nu}_{Ni}$ of the wavenumber of the principal band of a Cu(II) complex to the first spin-allowed band of the high-spin octahedral Ni(II) complex, with the same ligands, as a measure of tetragonality of the Cu(II) complexes [7]. The ratio obtained, 1.47, shows some distortion. The observed magnetic moment is very close to the spin-only value.

Reflectance spectral data for the Ni(II) polychelate show three bands in their normally expected regions for Ni(II) octahedral. These bands may be assigned as follows:

ν_1: $^3T_{2g} \longleftarrow {}^3A_{2g}$ 10,000 cm^{-1}

TABLE 3. Color, Magnetic, Spectral, and Thermal Data

Compound	Color	Magnetic moment (B.M.)	Decomposition temperature (°C)	Transition energies (cm^{-1})	Energy of activation, E* (kcal/mol)		Order of reaction n	
					Freeman-Anderson	Broido	Freeman-Anderson	Broido
$C_{27}H_{22}O_2N_2$	Yellow	-	280	-	21.19	18.71	2.34	2
$[Cu(C_{27}H_{20}O_2N_2)]$	Brown	1.85	300	24390 14700 19080	17.11	13.33	2.60	2
$[Ni(C_{27}H_2O\ O_2N_2)(H_2O)_2]$	Green	3.08	376	10000 15380 25640	17.50	17.50	2.20	2
$[Co(C_{27}H_{20}O_2N_2)].H_2O$	Reddish brown	4.66	397	7692 16130	15.62	21.05	2.56	2

ν_2: $^3T_{1g} \longleftarrow {}^3A_{2g}$ 15,380 cm^{-1}

ν_3: $^3T_{1g}(P) \longleftarrow {}^3A_{2g}$ 25,640 cm^{-1}

These data are utilized to compute the important ligand field parameters, 10 Dq, B_{35}, and λ using ligand field theory of spin allowed transitions in a d^8 configuration as discussed by Konig [8]. The results are given in Table 4. The γ_2 band shows some sign of splitting. This may be attributed to the spin-forbidden transition occurring due to spin-orbit coupling to $^1E(D)$, laying close to $^3T_{1g}(F)$ [9]. An attempt has been made to obtain approximate value of λ using, $= 2.7 \times B_{35}{}^2/10\,Dq$ [10]. The B_{35} used here was the average of the B_{35} values obtained in Table 4. Its value was found to be 145. This is lower than the free ion value. The ratio ν_2/ν_1 (1.54) lies in the range required for octahedral Ni(II) complexes [11]. Among the different numerical procedures used for band fitting, the best fit was observed by Method (b). The magnetic moment of the polychelate is within the range required for octahedral stereochemistry. To correlate spectral and magnetic properties, μ_{eff} was calculated by $\mu^{cal}_{eff} = \mu^{s.o.}_{eff}$ $(1 - 4\lambda 0/10\,Dq)$ [12]. The calculated value (3.18) is found to be in agreement with the observed value.

The reflectance spectrum for the Co(II) polychelate shows two general regions of absorption, one around 7692 cm^{-1} in the near IR region and the other at 16,130 cm^{-1} in the visible region. They may correspond to $^4T_1 \longleftarrow {}^4A_2(\nu_2)$ and $^4T_1 \longleftarrow {}^4A_2(\nu_3)$ transitions, suggesting tetrahedral stereochemistry for the Co(II) polychelate. The low energy ν_1 band usually occurs in the region 3000-5000 cm^{-1}. Because of instrumental limitations, it was not possible to obtain the ν_1 band. However, we have calculated ν_1, using observed bands and the theory of spin-allowed transitions for the d^7 tetrahedral [8]. The calculated ν_1 along with the observed bands were used to predict the positions of ν_2 or ν_3. Ligand field parameters were also calculated and are shown in Table 4. The results are encouraging. The magnetic moment of the complex falls within the required range for tetrahedral Co(II).

From an examination of the TG thermogram for the Ni(II) polychelate, the presence of 2 mol of water per mole of the polychelate is shown. It loses 7.8% of its weight at 300°C, which corresponds to the above. The thermogram for the Co(II) polychelate shows a 3.8% loss at 200°C. This weight loss corresponds to the presence of 1 mol of water per mole of polychelate. The thermal stability order

TABLE 4. Electronic Spectral Data and Calculated Transition Energies (in cm^{-1}) of Spin-Allowed Bands in Octahedral Ni(II) and Tetrahedral Co(II) Chelates

Compound	Method of calculation	Observed and calculated transition energies (in cm^{-1})			B_{35}	β_{35}	$\partial \nu$
		ν_1	ν_2	ν_3			
$[Ni(C_{27}H_{20}O_2N_2(H_2O)_2]$	Experimental	10000	15380	25640	-	-	-
	(a)	10 Dq	Fitted	33215	616.0	0.570	+7575
	(b)	10 Dq	15403	Fitted	769.8	0.712	+23
	(c)	10 Dq	16530	24490	734.7	0.680	±150
	(d)	10 Dq	16268	25902	817.8	0.757	+888
$[Co(C_{27}H_{20}O_2N_2)].H_2O$	Experimental	-	7692	16130			
	(e)	4259	Fitted	Fitted	743.2	0.6881	
	(c)	10 Dq	7734	16182	743.2	0.6881	±52
	(d)	10 Dq	7578	16848	776.6	0.719	-14

Co(II) > Ni(II) > Cu(II) was derived from the decomposition temperatures (Table 3) calculated from the TG thermograms. This is in agreement with the most commonly observed order [13]. It was also possible to calculate the energy of activation and the order of reaction for all the polychelates using Freeman-Anderson's and Broido's method [14]. The results are given in Table 3.

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