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Investigation of Stereochemistry of Coordination Polymers

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ABSTRACT

The stereochemistry of coordination polymers derived from Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) with bis(salicylaldehyde-5,5'-sulfone) and 1,8-diaminonaphthaline, is investigated. The polychelates are studied in terms of electrical, magnetic, spectral, and thermal properties. The mode of coordination in all compounds is in part determined by IR spectra. The polymeric ligand may act as a quadridentate.

INTRODUCTION

Coordination polymers having a one-dimensional metal atom chain have recently aroused great interest among chemists and physicists because of their good thermal and superior semiconducting behavior. Although polychelates from some poly-Schiff bases have been reported, the stereochemistry has not been characterized convincingly [1-3]. The metal complexes of the quadridentate salicylaldimine assume a variety of stereochemical forms, depending on the nature of metal ion and the number of bridging methylene groups between two imine nitrogen atoms [4]. In the present communication we report the polychelates of transition metal ions Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) formed by the mutual interaction of

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bis(salicylaldehyde-5,5'-sulfone) (SBSAL) with 1,8-diaminonaphthalin (DN). The polychelates are characterized by elemental analysis, magnetic, spectral (visible and IR), thermal, and electrical measurements. Bands assignments are made from a Tanabe Sugano diagram.

EXPERIMENTAL

Materials. All chemicals used were of either analytical grade or of Sarabhai Merk and were used without further purification.

Preparative method. SBSAL was synthesized by a known method [1]. Dialdehyde in stoichiometric proportion was added to a well-stirred solution of metal acetate and 1,8-diaminonaphthalin in absolute ethanol [2]. The resultant system was subjected to vigorous reflux for 8 h. The precipitated metal chelates were filtered, washed with hot water and ethanol, and dried under vacuum at 100°C for about 24 h.

Analysis. The metal percentage was determined by standard EDTA titration after decomposing the chelate with a mixture of analytical grade concentrated HCl, concentrated HNO_3, concentrated $HClO_4$, and a drop of concentrated H_2SO_4. The composition of the metal ion was confirmed by the gravimetric method. Carbon-hydrogen-nitrogen analysis was carried out on a Coleman C-H-N analyzer. Sulfur percentage was determined by the well-known Carius method.

Magnetic measurements. Magnetic measurements were made on a Sortorious semimicro Gouy balance at room temperature.

Spectral measurements. Electronic spectra were scanned on a Beckman Du Spectrophotometer. IR spectra were recorded on a Perkin-Elmer spectrophotometer in the range 4000-600 cm^{-1} by dispersing them in nujol mulls.

Electrical conductivity measurements. Electrical properties were studied by measuring the resistance of the preactivated pellets by a Hewlett-Packard 4329-A High Resistance meter under vacuum.

RESULTS AND DISCUSSION

The analytical data clearly show that the polychelates have the general formula $(ML)_n$. The elemental analyses are summarized in Table 1. Since the polychelates were insoluble in almost all common organic solvents, it was not possible to characterize them by known conventional methods. The magnetic moment of the copper(II) polychelate is 1.83 BM, which is very close to the spin-only value for one unpaired electron, suggesting that the orbital contribution is almost quenched by the crystalline field. The spectrum of the copper(II) chelate exhibits two bands in the normally expected region for square

TABLE 1. Elemental Analysis and Physical Properties of the Polychelates[a]

Polychelate	Color	C (%)	H (%)	N (%)	S (%)	Me (%)
[CuSBSAL DN] $CuC_{24}H_{14}O_4N_2S$	Green	57.74 (58.83)	2.64 (2.86)	5.30 (5.72)	6.30 (6.54)	12.36 (12.98)
[NiSBSAL DN $2H_2O$] $NiC_{24}H_{18}O_6N_2S$	Brown	54.77 (55.31)	3.30 (3.46)	5.05 (5.38)	5.95 (6.15)	11.54 (11.27)
[CoSBSAL DN $2H_2O$] $CoC_{24}H_{18}O_6N_2S$	Brown	56.99 (55.29)	3.35 (3.46)	5.15 (5.38)	5.89 (6.14)	11.57 (11.31)
[MnSBSAL DN $2H_2O$] $MnC_{28}H_{18}O_6N_2S$	Dirty green	54.95 (55.71)	3.35 (3.48)	5.20 (5.42)	5.98 (6.19)	10.88 (10.62)
[ZnSBSAL DN] $ZnC_{24}H_{14}O_4N_2S$	Brown	57.35 (58.61)	2.60 (2.85)	5.54 (5.70)	6.35 (6.51)	12.68 (13.30)

[a] Percent calculated values in parentheses.

TABLE 2. Observed and Calculated Electronic Transitions and Magnetic Moment of Polychelates in the Solid State

	Absorption maxima (cm^{-1})			
Polychelate	Observed	Calculated	Assignments	Magnetic moment (BM)
Copper	14,290	-	$^2B_{1g} \rightarrow {}^2A_{1g}$	
	17,240	-	$^2B_{1g} \rightarrow {}^2E_g$	1.85
	25,970	-	Charge transfer	
Nickel	8,621 10,990	8,621	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	
	14,710 16,670	14,371	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	3.48
	24,690	26,891	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
Cobalt	8,403	8,408	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	
	16,670	18,036	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	2.07
	21,740 24,690	21,750	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$	
Manganese	14,290	-	$^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$	
	17,240	-	$^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$	5.75
	21,280	-	$^6A_{1g} \rightarrow {}^4E_g.{}^4A_{2g}({}^4G)$	

planar copper(II) complexes [5]. According to Jørgensen [6], the ratio $\bar{\nu}_{Cu}/\bar{\nu}_{Ni} = 1.29$ suggests some distortion of the Cu(II) polychelate.

The Ni(II) polychelate shows a magnetic moment 3.48 BM in the range quite typical of nickel(II) with a high-spin configuration in an octahedral, essentially distorted environment. The electronic spectra of nickel(II) show some novel features of interest. The ν_1 and ν_2 transitions are found to be split, which is an indication of nickel(II) in a distorted octahedral symmetry. Various parameters [7, 8] are computed as shown in Tables 2 and 3.

The Co(II) polychelate shows a magnetic moment of 2.07 BM which is in agreement with cobalt(II) in a square planar structure [9], but the reflectance spectrum is characteristic of an octahedral structure

TABLE 3. Spectral Parameters for Nickel(II) and Cobalt(II) Polychelates

Polychelate	B	β	ν_2/ν_1	D_s	D_t	D_q	Dq_{av}	LFSE (kcal/mol)
Nickel	1033.2	0.9566	1.97	1149.3	270.8	625.2	625.2	29.57
Cobalt	970.8	0.8667	-	-	-	-	-	14.47

[10]. Although it is difficult to assign a definite structure on the basis of the positions of these bands alone, it appears that the field around the cobalt(II) ion has a strong tetragonal character which manifests itself in the splitting of the orbitally degenerate term; viz., $^4T_{1g}$ in octahedral symmetry. The evidence in support of the tetragonal character comes from the magnetic moment value, a much too low value for an octahedral bivalent cobalt complex [10]. The magnetic moment value of the manganese(II) polychelate (5.75 BM) and the band's positions in the visible region are typical for Mn(II) with an octahedral geometry. The low magnetic moment of the spin only value (5.92 BM) may be due to air oxidation of Mn(II)→Mn(III) during synthesis [11]. The Zn(II) polychelate is found to be diamagnetic from its expected $3d^{10}$ configuration.

Many of the characteristic frequencies of the double bonds occur in the region of the C–O and C–C stretching mode, so that the occurrence of an absorption band at a specific frequency cannot alone be taken as evidence for the presence of a certain type of double bond. It was not possible to compare the magnitude of depletion upon complexation in the –C=N– stretch because the poly-Schiff base could not be isolated in the solid state. The strong band at 1645-1595 cm^{-1} may be assigned to the –C=N– stretching vibration [12]. Cobalt(II), nickel(II), and manganese(II) polychelates exhibit characteristic bands of a coordinated water molecule at 1565 cm^{-1} [13]. The strong band at ~1290 cm^{-1} may be assigned [14] to the phenolic C–O vibration. The bands due to bridging, –SO_2– were observed at 1180, 1140, 1115, and 1085 cm^{-1}, which is in good agreement with those reported by Schrieber [15].

The decomposition temperatures for the polychelates are given in Table 4 and reveal the following thermal stability order: Zn > Ni > Co > Mn > Cu. The amount of water molecules (lattice or coordinated confirmed from IR spectra) was determined by considering the decomposition residue at ~200°. It was possible to evaluate the thermal energy of activation by employing the Freeman-Anderson's method [16]. By comparing the magnitude of decomposition reported [2], it was concluded that polychelates of polymeric Schiff bases with aromatic diamines exhibit better thermal stability than those of

TABLE 4. Thermal and Electrical Data of Polychelates

Polychelate	Decomposition temperature (°C)	Thermal activation energy (kcal/mol)	σ at room temperature ($ohm^{-1} cm^{-1}$)	σ_0 ($ohm^{-1} cm^{-1}$)	E_a (eV)
Copper	271	11.45	1.57×10^{-10}	2.75×10^{-11}	0.063
Nickel	315	14.29	5.83×10^{-11}	2.09×10^{-11}	0.057
Cobalt	308	17.19	9.54×10^{-11}	2.75×10^{-11}	0.033
Manganese	301	16.15	5.47×10^{-11}	1.45×10^{-11}	0.041
Zinc	332	22.48	1.38×10^{-11}	3.63×10^{-11}	0.034

aliphatic diamines. The decomposition temperature and activation energy are given in Table 4.

All polychelates show interesting semiconducting properties. Technically important semiconducting material was reported by Dewar et al. [17] and Terent've [18]. It was found that the logarithm of electrical resistivity (ρ) for a polymer is a linear function of the temperature reciprocal. The activation energy (E_a) and specific conductivity of the polychelates were evaluated using the relation $\sigma = \sigma_0 \exp (E_a/kT)$, where σ is the conductivity at T° K, σ_0 is the specific conductivity, and k is the Boltzman constant. E_a, σ_0, and room temperature electrical resistivity are given in Table 4. The low value of electrical conductivity may be due to 1) the low molecular weight which results in low conjugation or 2) the undesirable morphology which may occur when the polychelate is pressed into a hard brittle pellet. On the other hand, a large number of π-electrons may be responsible for the low magnitude of activation energy.

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