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Physicochemical Investigation on a Chelate Polymer

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ABSTRACT

Coordination polymers of Cu(II), Ni(II), Co(II), and Mn(II) with a poly-Schiff base derived from methylene bis-salicylaldehyde (MBSAL) and diamino diphenyl ether (DDE) have been prepared. Magnetic susceptibility, visible and IR spectra, and thermal and electrical conductivities of the chelates have been studied and probable structures assigned to the chelates.

INTRODUCTION

Synthesis of polymer-carrying azomethine groups on a polymer chain has been a subject of considerable interest. Recently, so-called poly-Schiff bases have been prepared, and the interesting behavior caused by their complexation with metal cations has been extensively investigated [1-4]. However, there are no reports on spectral and magnetic properties of the polychelates. Spectral, magnetic, thermal, and electrical properties of quadridentate ligand and its chelates are reported here. In certain cases it has been shown that the incorporation of an alternating aromatic molecule into a chain of metal ions, as in coordination polymers, produces materials which are electrical semiconductors [4-6]. The current study was undertaken with this in mind.

The prodigious growth of the published literature on Schiff-base complexes dictates certain limitations as far as spectral and magnetic investigations are concerned. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand which would be able to form complexes with a variety of transition metals and therefore have a large range of applications.

Coordination compounds of salicylaldehyde Schiff base have proven to be an excellent model system to study the enzymatic reactions of pyridoxal phosphate, because both of these systems effectively catalyze transamination and racemization reaction [7]. Of particular interest to us is the 5,5'-methylene bis-salicylaldehyde 4,4'-diaminodiphenyl ether [MBSAL-DDE].

The stereochemistry around the metal ion has been characterized from the diffuse reflectance spectra, IR spectra, magnetic moments, and thermogravimetric analysis. Band assignments consistent with this geometry can be made with reference to a Tanabe Sugano diagram. The decomposition temperature of the polymeric chelates is in the order

$$\mathrm{Co} > \mathrm{Mn} > \mathrm{Ni} > \mathrm{Cu}$$

while the thermal activation energy follows the order

$$\mathrm{Ni} > \mathrm{Co} > \mathrm{Mn} > \mathrm{Cu}$$

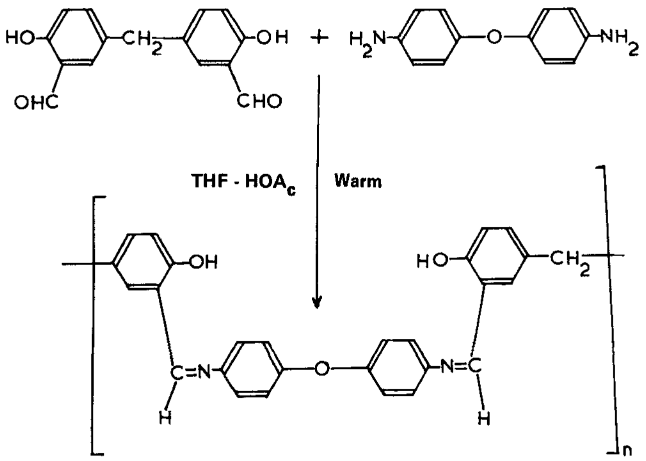
and the activation energy obtained from semiconducting behavior is in the order

$$\mathrm{Mn} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co}$$

Poly-Schiff base and its chelates are found to decompose between 350 and 600°C.

SYNTHESIS OF POLY-SCHIFF BASE AND ITS CHELATES

The poly-Schiff base (MBSAL DDE) was synthesized by the following method. A solution of MBSAL was prepared in tetrahydrofuran containing glacial acetic acid and that of DDM in a minimum quantity of glacial acetic acid. These two solutions were mixed in stoichiometric proportions and warmed on a water bath.



Methanol was added as a bad solvent to precipitate the poly-Schiff base. The solution was filtered, washed with methanol, water, and ether, and dried. The polychelates were found to be insoluble in almost all organic solvents. The molecular weight of the repeating unit was estimated from elemental analysis as shown in Table 1. The activation energies for semiconductor and thermal stability of the polychelates were determined from conductivity and TGA measurements.

RESULTS AND DISCUSSION

The magnetic moment of copper polychelate is 1.63 BM, which is very close to the spin-only value of 1.73 BM expected for one unpaired electron, which offers the possibility of either planar or octahedral symmetry.

Ni(II) polychelate shows a magnetic moment of 3.16 BM, suggesting its paramagnetic nature with octahedral stereochemistry. Goldberg et al. [8] reported a magnetic moment of 3.2 BM and assigned an octahedral structure. Dey et al. [9] observed μ_{eff} = 4.7-5.0 BM for manganese N,N'-ethylene bis(salicylideneiminato) dianion heterochelates and proposed an octahedral structure. The observed moment of 4.56 BM for an Mn-chelate is assigned to a distorted octahedral structure. The low value for the Co(II) complex (3.5 BM) reported here is similar to that reported by Calvin [10] for some Co(II) salicylaldehydrato derivatives. This value could be indicative of a mixture of tetrahedral (high spin) and planar (low spin) structures.

The electronic spectra provide the most detailed information about the electronic structure. Musker et al. [11] reported a copper complex with 1,5-diazocyclooctane which is extremely stable with planar

TABLE 1. Analytical Data and Other Physical Properties

		Elemental analysis						
		M		C		H		
Compound	Color	Found	Required	Found	Required	Found	Required	MW[a]
MBSAL DDE	Yellow	-	-	76.50	77.12	4.40	4.79	420
[CuMBSAL DDE] $2H_2O$	Brown	11.32	12.26	61.21	62.60	3.96	4.28	518
[NiMBSAL DDE $2H_2O$]	Green	10.06	11.44	61.80	63.19	4.06	4.32	513
[CoMBSAL DDE]	Brown	10.69	12.34	66.99	67.93	3.97	3.80	477
[MnMBSAL DDE]	Brown	10.32	11.60	68.48	68.50	3.70	3.83	473

[a] Molecular weight of repeating unit estimated from elemental analysis.

stereochemistry. The interest in the copper Schiff-base complexes has centered around their spectral and structural properties. Cu(Salen) was prepared, and it was found that the electronic spectra have been the subject of a number of investigations [12-14] in assigning the structure. In most cases the Cu(II) complex possesses only a single broad band, making the assignment of individual electronic transition difficult. We have observed three bands at 25,000, 16,130, and 14,710 cm^{-1} for the Cu(II) chelate. The broad band at 25,000 cm^{-1} is due to a charge transfer from ligand to metal ion. The other two bands are due to d-d transitions, which clearly indicate the planar stereochemistry. The Ni(II) chelate shows three absorptions in the visible region. Mishra et al. [15] synthesized the Ni(II) adduct from salicylaldehyde and 2,3-amino pyridine. The general pattern from their spectral data and the ν_2/ν_1 ratio (1.60) is in agreement with an octahedral symmetry, and we obtained 1.60 for the ν_2/ν_1 ratio. Rastogi and co-workers [16] studied the Ni(II) complexes of amino ligands and assigned an octahedral symmetry on the basis of spectral and magnetic observations. The position of the absorption band in diffuse reflectance spectra shows the possibility of distorted octahedral symmetry. The ν_1 band is split into two components at 9615 and 8475 cm^{-1} that are interpreted to the transition arising from the splitting of the ${}^3T_{2g}(F)$ in octahedral symmetry, descending to D_{4h} symmetry. The ν_2 band is also split into two components, 15,380 and 13,700 cm^{-1}, arising from ${}^3T_{1g}(F)$. The ν_3 band is observed at 25,970 cm^{-1} and is mixed with the charge transfer band.

The transitions are

$$\begin{tikzcd}
 & & 9{,}615\ \mathrm{cm}^{-1} \\
{}^3A_{2g} \arrow[r] & {}^3T_{2g}(F) = \nu_1 \arrow[ur] \arrow[dr] & \\
 & & 8{,}475\ \mathrm{cm}^{-1}
\end{tikzcd}$$

$$\begin{tikzcd}
 & & 15{,}380\ \mathrm{cm}^{-1} \\
{}^3A_{2g} \arrow[r] & {}^3T_{1g}(F) = \nu_2 \arrow[ur] \arrow[dr] & \\
 & & 13{,}700\ \mathrm{cm}^{-1}
\end{tikzcd}$$

$$\begin{tikzcd}
{}^3A_{2g} \arrow[r] & {}^3T_{1g}(P) = \nu_3 \arrow[r] & 25{,}970\ \mathrm{cm}^{-1}
\end{tikzcd}$$

The Racah parameter (B) is calculated by using [17]

$$B = \nu_2 + \nu_3 - 3\nu_1/15$$

Using the value of B, an attempt has been made to calculate the transition energies by the relation [17]

$$\nu_{2,3} = \tfrac{1}{2}(15B + 30Dq) \pm \tfrac{1}{2}[(15B - 10Dq)^2 + 12B \times 10Dq]^{1/2}$$

In Ni(II) polychelate with an octahedral symmetry, $\nu_1 = 10Dq$ which is calculated as

$$\nu_1 = 10Dq = \tfrac{1}{3}(\nu_2 + \nu_3) - 5B$$

Various spectral parameters were calculated by known methods [16, 18]:

$\nu_2/\nu_1 = 1.6$, $D_t = 130.3\ \text{cm}^{-1}$, $Dq^Z = 733.5\ \text{cm}^{-1}$

$D_s = 921.4\ \text{cm}^{-1}$, $B = 833.7$, $\beta = 0.772$

L.F.S.E. = 32.98 kcal/mol

Divalent manganese ion has a symmetrical half-filled $3d^5$ shell which causes the least perturbation to the shape irrespective of the preferred stereochemistry of a particular complex. Forster and Goodgame [19] studied the electronic spectra of $[Et_4N]_2[Mn(NCO)_4]$ in acetonitrile and assigned the group of three lowest energy bands as ${}^6A_1 \rightarrow {}^4T_1(G)$ at 20,000, ${}^6A_1 \rightarrow {}^4T_2(G)$ at 22,400, and ${}^6A_1 \rightarrow {}^4E, {}^4A_1(G)$ at 23,300 cm^{-1} by comparing the spectra of $[MnBr_4]^{2-}$ reported earlier [20]. Here, the Mn(II) polychelate exhibits absorption bands at 21,740 and 17,860 cm^{-1}. In addition, it shows absorption at 14,490 cm^{-1}, indicating a distorted octahedral geometry.

For the cobalt complex, transition energies ν_1 (= 10 Dq), ν_2, and ν_3 were calculated using known equations [17] and the results are summarized in Table 2. The bands at around 8,500 and 15,800 cm^{-1} are probably due to mixing of metal d functions with ligand functions. The ν_2 band is broad and exhibits a great deal of fine structure. The spectral results support the tetrahedral assignment (Fig. 1).

The bonding site has been confirmed by considering the IR spectra of the original polymer and those of the polychelates. C=N stretch in the poly-Schiff base occurs at 1610 cm^{-1} which shows either a positive shift [21] or a negative shift [22] on complexation. However, in some cases [23] there is no shift at all. In Cu(II) and Ni(II) polychelates the C=N stretch is shifted to a lower frequency while in the case of Co(II) and Mn(II) it is slightly shifted to higher frequency. The sharp, intense band observed at 1270 cm^{-1} in the ligand remained unshifted or shifted to a higher region. This is attributed to phenolic C–O vibrations, indicating the bonding of the ligand with metal ions through the phenolic oxygen. In Ni(II) the weak band at 1660 cm^{-1} indicates [24] the presence of coordinated water which is also confirmed from thermogravimetric analysis. In Cu(II) polychelate the

TABLE 2. Electronic Spectral Data and Magnetic Moment

Compound	Energies (cm^{-1})		Assignment	μ_{eff} (BM)
	Observed	Calculated		
[Cu MBSAL DDE] $2H_2O$	14,710	-	$^2B_{1g} \rightarrow {}^2A_{1g}$	1.63
	16,130	-	$^2B_{1g} \rightarrow {}^2E_g$	
	25,000	-	Charge transfer	
[Ni MBSAL DDE $2H_2O$]	9,615	9,614	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	3.16
	15,380	15,565	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	
	25,970	25,784	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
[Co MBSAL DDE]	-	4,513	$^4A_2 \rightarrow {}^4T_2(F)$	3.50
	8,333	7,731	$^4A_2 \rightarrow {}^4T_1(F)$	
	15,870	16,473	$^4A_2 \rightarrow {}^4T_1(P)$	
[Mn MBSAL DDE]	17,860	-	$^6A_1 \rightarrow {}^4T_1(G)$	4.56
	21,740	-	$^6A_1 \rightarrow {}^4T_2(G)$	

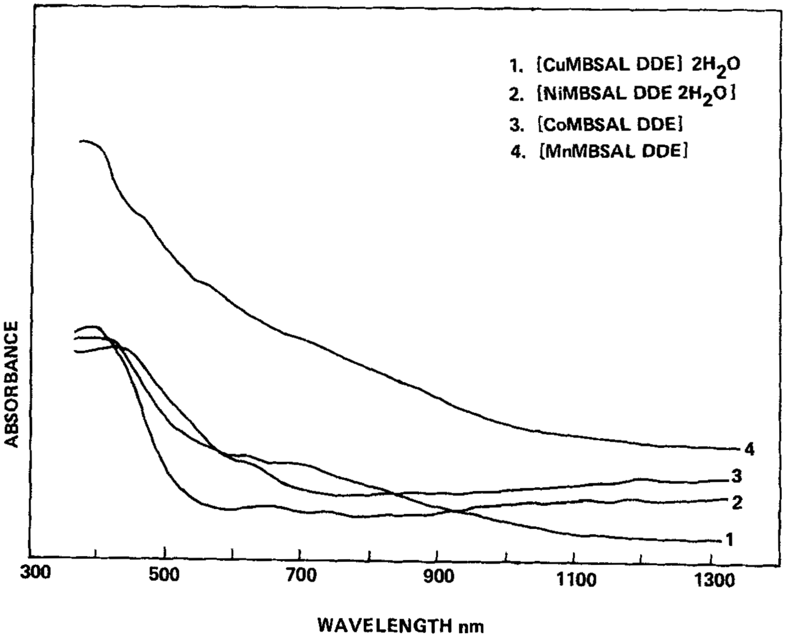


FIG. 1. Electronic spectra of polychelates.

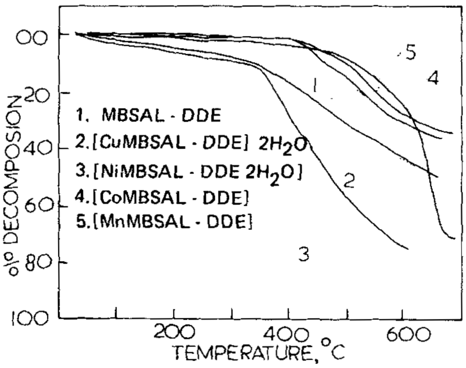


FIG. 2. TGA curves in air at 10°C/min heating rate for polymeric ligand and its polychelates.

TABLE 3. Results of Thermogravimetric Analysis

Compound	DP	T_d^a	Species volatized	% weight loss at temperature						Ea (kcal/mol)
				100	200	300	400	500	600	
MBSAL DDE	414	-	-	0	0	0	1.9	14.4	30.6	20.04
[CuMBSAL DDE]$2H_2O$	348	250	$2H_2O$	2.1	5.3	8.2	17.5	31.6	43.8	14.97
[Ni MBSAL DDE $2H_2O$]	350	250	$2H_2O$	3.0	6.0	9.0	28.6	56.8	73.6	8.75
[Co MBSAL DDE]	600	-	-	0.3	0.7	2.1	3.7	8.0	25.0	23.03
[Mn MBSAL DDE]	462	-	-	0	0	0.5	1.6	9.8	27.5	17.51

[a] From first significant weight loss to beginning of plateau.

TABLE 4. Electrical Data of Poly-Schiff Base and Its Polychelates

Compound	Conductivity at room temperature, σ (ohm^{-1} cm^{-1} $\times 10^{11}$)	Specific conductivity, σ_0 (ohm^{-1} cm^{-1})	E_a (eV)
MBSAL DDE	1.52	3.31×10^{-12}	0.036
[Cu MBSAL DDE]$2H_2O$	1.46	2.51×10^{-12}	0.047
[NiMBSAL DDE $2H_2O$]	1.57	3.16×10^{-12}	0.040
[CoMBSAL DDE]	10.35	2.51×10^{-11}	0.030
[MnMBSAL DDE]	27.62	2.09×10^{-11}	0.062

presence of water is attributed to its lattice nature. The bands around 1250 and 1150 cm^{-1} are assigned to Ph–O–Ph from the reported frequencies by Barnes et al. [25] and Lecomte [26] (Fig. 2).

Aromatic backbone units are much more widely stable than aliphatic one, and they have significantly higher melting temperatures. Poly-Schiff base and its polychelates have higher thermal stabilities. Pittman [27] noted an interesting point regarding chelated polymers: that the greater thermal stability of uncomplexed polyimine polymer than of chelated polymers may be due to hydrogen bonding. Marvel et al. [1] reported thermal stability of poly-Schiff bases derived from various 5,5'-methylene-bis-salicylaldehydes. They observed the heat stability of polychelates to be in the order

Ni > Co > Cu

However, the order observed by Goodwin et al. [3] is

Ni > Cu > Co

The order of decomposition of polychelates at 300°C in air is (Table 3)

Mn > Co > Cu > Ni

The water molecule (lattice or coordinated) was calculated by taking the amount of residue at 250°. The activation energy was calculated in kcal/mole as in Table 4.

The first systematic investigation of semiconductors was by Brattain and Garrett [28]. Eley [29] reported that the conductivity of some of the phthalocyanines varies exponentially with the reciprocal of the temperature, as in the case for many inorganic semiconductors. A considerable stimulus in the study of organic semiconductors was afforded by the publication of Szent-Gyorgyi [30] in which it was suggested that the transfer of π-electrons from molecule to molecule may play an important role in the fundamental physical processes of living organisms. The recent interest in semiconductor surfaces has arisen from the numerous problems encountered in understanding their properties which are controlled by surface treatment and ambience.

The relationship between temperature and resistivity was obtained at compaction pressures between 12,000 and 15,000. The measurements were carried out from room temperature to 150° C. It was found that the negative logarithm of conductivity for the polymers is a linear function of the reciprocal of temperature under the range of study. The activation energy and specific conductivity of semiconductors were obtained by using the relation

$$\sigma = \sigma_0 \exp [E_a/kT]$$

where E_a is the activation energy of semiconductor and k is the Boltzmann constant. The slope and the intercept of the plot give the activation energy and specific conductivity respectively. The electrical conductivity at room temperature decreases in the order

$$\mathrm{Mn} > \mathrm{Co} > \mathrm{Ni} > \mathrm{Cu}$$

while the activation energy declines as

$$\mathrm{Mn} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co}$$

which is in agreement with reported results [6].

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