Studies on Polyazomethine Chelate Polymers

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ABSTRACT

Poly-Schiff-base ligand (SBSAL-DDM) is synthesized by condens-
ing bis-salicylaldehyde 5,5'-sulfone with 4,4'-diaminodiphenyl
methane. The polychelates of Cu(II), Ni(II), Co(II), and Mn(II)
with poly-Schiff base have been isolated and analyzed. The
analytical data agree with 1:1 metal-ligand stoichiometry. The
polychelates are studied in terms of electrical, thermal, spec-
tral, and magnetic properties. A probable structure has been
proposed for the above polymers.

INTRODUCTION

The chelates from Schiff bases have long been of theoretical inter-
est because they seemed to early workers to be important in bonding.
Chemists have now reached general agreement to work on chelate
polymers and only a few workers continue to work in that area.
Marvel et al. [1, 2] is an outstanding exception and has done brilliant
work, especially on the reactions of polymeric Schiff bases. However,
there is a lacuna of stereochemistry of the polychelates derived from
polymeric Schiff bases with transition metal ions. Metal cluster
polychelates constitute an extremely interesting group of compounds
which is attracting interestingly wide attention both from those who
are interested in the theory of bonding and those who work in cataly-
sis [3, 4]. Because of its immense practical importance, physical

and chemical research on inorganic catalysts will certainly continue
at an accelerating rate. The reaction of bis-salicylaldehyde 5,5'-
sulfone [SBSAL] have been known [5, 6] with various diamines.
Looking to the poor literature data, it seems that there is some gap
in the study of spectral and magnetic investigations of polychelates
derived from polymeric Schiff bases. We report here polychelates
of transition metal ions formed by SBSAL with 4,4'-diaminodiphenyl
methane [DDM] along with their physicochemical properties. An
attempt is made in the present work to characterize these compounds
by elemental analysis, magnetic behavior, and spectral data. The
metal complexes of the quadridentate salicylaldimines assume a
variety of stereochemical forms [7-12] depending upon the nature of
the metal and the number of the bridging methylene groups between
the two nitrogen atoms. The stereochemistry of the polychelates is
studied from the diffuse reflectance spectra, infrared spectra,
magnetic moment, and thermal analysis. Bands assignments are
made from a Tanabe Sugano diagram.

EXPERIMENTAL

Material

SBSAL was synthesized by a known procedure [5]. DDM was re-
ceived from Merk-Schuchardt Co. The polymeric Schiff base was
prepared as described below.
SBSAL was dissolved in tetrahydrofuran containing glacial acetic
acid and DDM in minimum glacial acetic acid. These two solutions
in a stoichiometric ratio were mixed and warmed on a water bath.
The polymeric Schiff base was filtered and washed with methanol
and ether.
Methanol was used as a bad solvent to precipitate orange-yellow
polymeric Schiff base having 30-40% solubility in dimethylformamide.
The polychelates were prepared by adding a solution of metal
acetate in absolute ethanol to the dissolved part of the polymer in
dimethylformamide. It immediately gave an intensely colored com-
pound which was subjected for mechanical shaking for 6 d to complete
chelation and to lengthen the polychelate linkage. The polychelates
were found to be resistive toward common organic solvents. The
polymeric Schiff base may act as a quadridentate ligand and would be
expected to coordinate a metal ion as indicated below.

Measurements

The magnetic susceptibility was determined at room temperature
by the Gouy method. Diffuse reflectance and IR spectra were recorded
on a Beckman Du and a Carl Zeiss UR-10 spectrophotometer,

$$M = Cu^{2+}, Ni^{2+}, Co^{2+}, \text{ and } Mn^{2+}$$
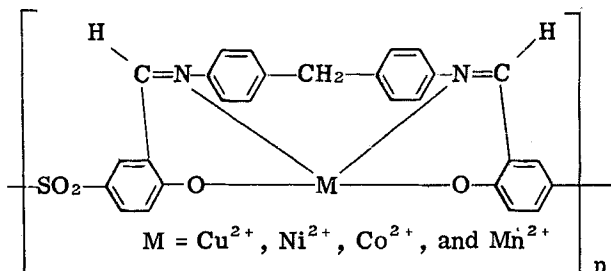
respectively. The electrical resistivity of the polychelates was measured over a wide range of temperature using a Hewlett-Packard 4329-A High Resistance Meter. Thermograms were scanned on a Du Pont Thermal Analyzer-900.

RESULTS AND DISCUSSION

The mode of coordination of the azomethine group in all polychelates is in part determined by the coordination number and geometry of the metal centers, and knowledge of these will aid in determining the possible coordination mode in all compounds. Additional information on the coordination modes of the azomethine group can be obtained from their IR spectra. The elemental analyses revealed that all polychelates exhibit 1:1 metal to ligand stoichiometry (Table 1) with the general formula $[ML]_n$.

The magnetic moment of copper polychelate is 1.86 B.M. It is in the expected range for copper(II) derivatives [13] involving square-planar stereochemistry. The excess of magnetic moment to spin only value (1.73 B.M.) might be due to orbital contribution. This finding is in agreement with structural information [14]. Nickel(II) polychelate shows a magnetic moment of 2.83 B.M. (Table 2) which is close to the spin-only value for two unpaired electrons. It is in agreement to that of Harris et al. [15], indicating the possibility of an octahedral or a distorted octahedral structure. Hariharan and Urbach [10] have reported cobalt(II) complexes with magnetic moment 4.33-5.52 B.M. and assigned tetrahedral stereochemistry. The anomously low value for cobalt(II) polychelate (4.05 B.M.) corresponds to those reported by Calvin [16] for some cobalt(II) salicylaldehydato derivatives. These values could be indicative of the presence of a mixture of high spin tetrahedral and low spin planar forms. Manganese(II) poly-chelate exhibits magnetic moment 5.51 B.M. found to be lower than that expected on the basis of spin-only value. The observed value is in agreement with that of Patel et al. [17]. The somewhat low value of magnetic moment may be due to spin exchange in the solid state of the complexes [18] or due to aerial oxidation of Mn(II)→Mn(III) during preparation. However, some workers [19, 20] explain this low magnetic moment on the basis of antiferromagnetic interaction between manganese(II) ions in solid state.

The electronic spectra provide the most detailed information about

TABLE 1. Characterization Data of Polychelates

Formula (MW)[a]	Color		Elemental analysis					
			M (%)	C (%)	H (%)	N (%)	S (%)
$C_{27}H_{20}O_4N_2S$ (468.53)	Yellow	Calc	–	69.21	3.87	5.97	6.84
		Found	–	70.20	3.52	5.59	6.59
$Cu-C_{27}H_{20}O_5N_2S$ (548.07)	Brown	Calc	11.59	59.17	3.67	5.11	5.84
		Found	10.34	59.67	3.47	4.80	5.30
$Ni-C_{27}H_{22}O_6N_2S$ (561.25)	Green	Calc	10.46	57.78	3.95	4.99	5.71
		Found	8.25	58.95	4.35	4.75	5.20
$Co-C_{27}H_{22}O_6N_2S$ (561.47)	Brown	Calc	10.49	57.75	3.95	4.98	5.71
		Found	8.67	60.23	3.94	4.33	5.15
$Mn-C_{27}H_{22}O_6N_2S$ (557.48)	Green	Calc	9.85	58.17	3.98	5.02	5.75
		Found	9.40	57.80	3.55	4.69	5.52

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

TABLE 2. Diffuse Reflectance Spectral Data and Magnetic Moments

Formula		Energies in cm⁻¹ and assignments			Charge transfer	μ_{eff} B.M.
Cu–$C_{27}H_{20}O_5N_2S$	Found	$^2B_{1g} \rightarrow {}^2A_{1g}$	$\rightarrow {}^2E_g$			1.86
		15,380	20,000		26,320	
Ni–$C_{27}H_{22}O_6N_2S$		$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$\rightarrow {}^3T_{1g}(F)$	$\rightarrow {}^3T_{1g}(P)$		2.83
	Calc	9,259	16,370		27,080	
	Found	9,259 / 10,870	14,710 / 16,130		26,320	
Co–$C_{27}H_{22}O_6N_2S$		$^4A_2 \rightarrow {}^4T_2(F)$	$\rightarrow {}^4T_1(F)$	$\rightarrow {}^4T_1(P)$		4.05
	Calc	3,831	6,675		18,870	
	Found	–	8,772		16,670	
Mn–$C_{27}H_{22}O_6N_2S$	Found	$^6A_1 \rightarrow {}^4T_{1g}(^4G)$	$\rightarrow {}^4T_2(^4G)$	$\rightarrow {}^4E_g, {}^4A_{1g}(^4G)$		5.51
		16,670	19,230	22,220		

the stereochemistry of complexes. Srivastava et al. [21] reported
the evidence for square planar copper(II) complexes as (i) the value
of magnetic moment lie within the range 1.72-1.89 B.M., and (ii) the
complexes show a single sharp absorption band around 700 nm,
arises due to $t_{2g} \rightarrow e_g$ transitions. The broad band observed might be
due to unresolved transitions expected for copper(II) square planar
complexes. The intense band observed at 26,320 cm^{-1} may be assigned
due to charge transfer or intraligand transition [21] while the two
bands at 20,000 and 15,380 cm^{-1} may be due to d-d transition (Table 2).
The diffuse reflectance spectrum of nickel(II) polychelate is similar
to that expected for an octahedral or distorted octahedral spin-free
nickel(II) complex [22-24]. The positions of these transitions are
consistent with those of octahedral, essentially distorted structure
[25].

The Racah parameter, B_{35}, is calculated using the known relation
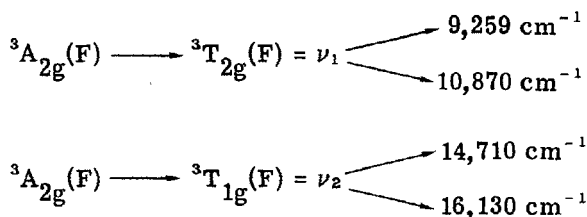[26]

$$B_{35} = \nu_2 + \nu_3 - 3\nu_1/15$$

Transition energies ν_2 and ν_3 are calculated [26] using the Racah
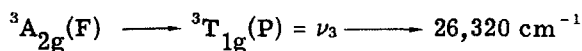parameter obtained from the above equation.

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

In nickel(II) polychelate having octahedral geometry, the value of ν_1
corresponds to 10Dq which is calculated using the known equation
[26]

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

The ν_1 transition is found to split into two bands which are assigned
to the transition arising from the splitting of the $^3T_{2g}(F)$. The ν_2
transition is also split into two bands arising from the splitting of
$^3T_{1g}(F)$ [25]. The ν_3 band is observed at the expected position. The
transitions are

$$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F) = \nu_1 \begin{cases} 9{,}259 \text{ cm}^{-1} \\ 10{,}870 \text{ cm}^{-1} \end{cases}$$

$$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F) = \nu_2 \begin{cases} 14{,}710 \text{ cm}^{-1} \\ 16{,}130 \text{ cm}^{-1} \end{cases}$$

$$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P) = \nu_3 \longrightarrow 26,320 \text{ cm}^{-1}$$

An attempt has been made to compute the repulsion parameter using the splitting values ν_1 and ν_2 by known methods [25, 27].

B_{35} = 978.2, β_{35} = 0.9057,   Dt = 184.1 cm^{-1}

Dq = 764.8 cm^{-1},   Dq$_{av}$ = 764.8 cm^{-1},   Ds = 805 cm^{-1}

ν_2 / ν_1 = 1.74 and LFSE = 31.76 kcal/mol

In cobalt(II) polychelate the transition observed at 8,772 and 16,670 cm^{-1} may best be assigned to tetrahedral geometry (Table 2) which is in good agreement [10]. The band at 25,970 cm^{-1} may arise due to charge transfer and internal ligand transitions [28]. However, some workers reported this band to be due to tetragonal distortion [29, 30]. The Racah parameter is calculated using known relation [26]

$$B_{35} = \frac{1}{510} [7(\nu_2 + \nu_3) \pm \{49(\nu_2 + \nu_3)^2 + 680(\nu_2 - \nu_3)^2 \}^{1/2}]$$

The transition energies ν_1, ν_2, and ν_3 have been calculated [26] using the known relation given for nickel(II) polychelate. The values of B_{35}, β_{35} [26], and LFSE are found to be 859.8, 0.7678, and 13.15 kcal/mol, respectively.

The manganese(II) polychelate shows some novel features of interest, and exhibits the transition sextet—quartet. The ground term for manganese(II) is $^6A_1(S)$ and exhibits two absorption maxima, one at 20,830 cm^{-1}, which may arise due to $^6A_1(S) \rightarrow {}^4T_2(G)$ transition, and another at 15,380 cm^{-1}, assigned [31] as $^6A_1(S) \rightarrow {}^4T_1(G)$.

Although much information is available in the literature concerning the IR spectra of imines, less is known about IR absorption by polymeric azomethines and polychelates. The IR spectra of all polychelates are very similar to the ligand but are found to be comparable with each other which suggests a definite difference from that of ligand. Coordination through the azomethine group causes a small depletion (Fig. 1) in the electron density in the $-C=N$ π-bond, resulting in a small negative shift [32]. Polymeric Schiff base exhibits a medium band at 1285 cm^{-1} which may be assigned to the phenolic C–O stretching vibration [33]. On chelation, this band is raised to a higher wavenumber, indicating that oxygen is involved in bonding [34]. However, some workers reported this small shift to be due to insensitivity of this frequency toward chelation [33]. The four bands of different intensity observed in the region 1090-1180 cm^{-1} may be due to S=O
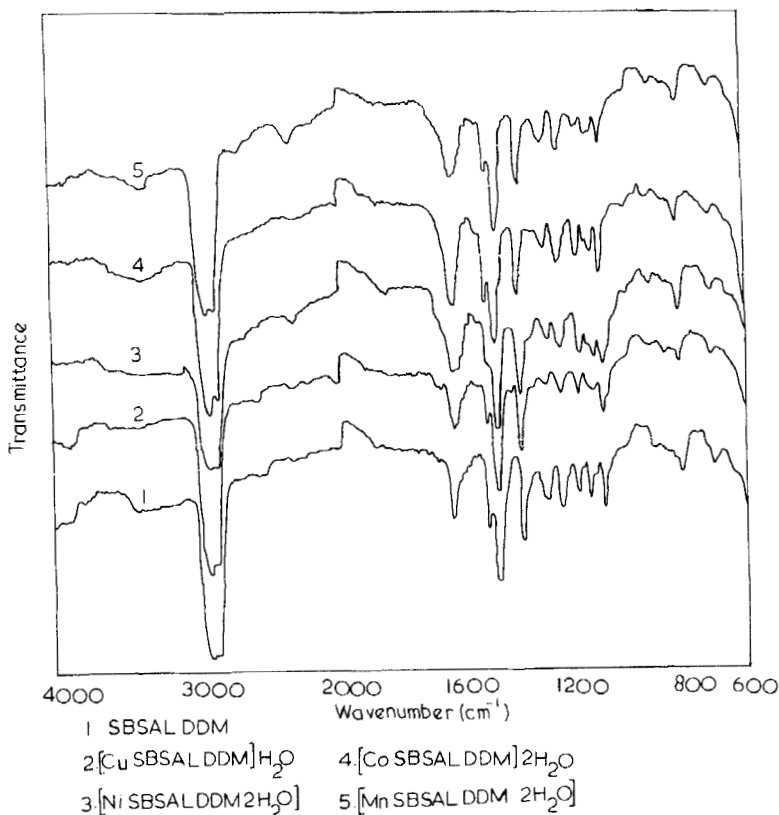
FIG. 1. Infrared spectra of SBSAL-DDM and polychelates.

stretching vibrations which are in agreement with those of Schrieber
[35] and Herzberg [36]. Nickel(II) polychelate exhibits weak bands at
775 and 1560 cm^{-1} while manganese(II) has a band at 1650 cm^{-1}.
These are attributed [37] to coordinated water, confirming a six co-
ordinate structure.

None of the polychelates and poly-Schiff base showed any sign of
decomposition below 329°C. Thermal decomposition data are sum-
marized in Table 3. Stivala et al. [38] reported the steric course and
resonance energy responsible for the relative thermal stabilities.
Goodwin et al. [6] observed the given thermal stability order for the
polychelates as Ni > Cu > Co which is in agreement with the obser-
vation reported by Marvel et al. [5]. We have observed the change in
order in thermal stability at 200°C which remains unchanged up to
600°C as Cu > Mn > Ni > Co. This might be due to an aromatic
diamine or a bridging methylene group in diamine. The magnitude

TABLE 3. Results of Thermogravimetric Analysis

| Formula | DP | $T_d{}^a$ | Species volatized | % Weight loss at temperature | | | | | | E_a (kcal/mol) |
				100	200	300	400	500	600	
$C_{27}H_{20}O_4N_2S$	329			4.7	5.5	6.6	17.7	28.7	36.6	11.52
Cu–$C_{27}H_{20}O_5N_2S$	375	~200	H_2O	1.7	3.1	5.5	9.8	21.8	29.6	15.44
Ni–$C_{27}H_{22}O_6N_2S$	384	~200	$2H_2O$	3.9	6.3	8.3	19.0	83.7	83.7	–
Co–$C_{27}H_{22}O_6N_2S$	410	~200	$2H_2O$	4.3	6.5	8.5	20.8	84.5	88.0	–
Mn–$C_{27}H_{22}O_6N_2S$	417	~300	$2H_2O$	4.0	5.7	7.8	10.6	25.7	37.9	17.04

TABLE 4. Electrical Data of Polymers

Formula	Conductivity at room temperature (σ ohm^{-1} cm^{-1})	Specific conductivity (σ ohm^{-1} cm^{-1})	E_a (eV)
$C_{27}H_{20}O_4N_2S$	30.03×10^{-12}	1.905×10^{-12}	0.1
$Cu-C_{27}H_{20}O_5N_2S$	2.99×10^{-11}	6.76×10^{-12}	0.037
$Ni-C_{27}H_{22}O_6N_2S$	1.07×10^{-10}	3.80×10^{-11}	0.033
$Co-C_{27}H_{22}O_6N_2S$	1.48×10^{-10}	3.16×10^{-11}	0.040
$Mn-C_{27}H_{22}O_6N_2S$	2.89×10^{-10}	2.239×10^{-11}	0.060

of water molecule (lattice or coordinated, confirmed from IR) was calculated by taking the residue of decomposition at ~200-300°C. The thermal activation energy was calculated by employing the Freeman and Anderson method and the values are summarized in Table 4. Comparing the results of decomposition with Goodwin et al. [6], it is concluded that polychelates derived from polymeric Schiff base with aromatic diamine exhibit better thermal stability than those with aliphatic diamine.

Semiconducting behavior was systematically developed by Brattain et al. [39]. Carbajal investigated the electric properties of the squaric acid copper [40] semiconductive coordination polymers which are prepared by various methods. Technically useful semiconducting material was reported by Dewar et al. [41] and Terentev [42].

The relationship between measured temperature and resistivity was determined at compaction pressure between 12,000-15,000. The measurements were made over a range of temperature from room temperature to approximately 150°C, employing silver paste in volatile solvent on both sides of the pellets. It was found that the logarithm of electrical conductivity or resistivity for a polymer is a linear function of temperature reciprocal in the range under study. The activation energy of all polychelates was calculated from the plots of the logarithm of electrical conductivity (σ) versus the reciprocal of temperature in °K [43]. The activation energy, E_a, and specific conductivity of the semiconductor were calculated by using the relation

$$\sigma = \sigma_0 \exp\left[-E_a/KT\right]$$

where σ is conductivity at T °K, σ_0 is a constant, and K is the Boltzman constant. The slopes of the logarithm of conductivity against the

reciprocal of temperature in °K were accurately determined using the least square method and corresponds to the activation energy. The magnitude of activation energy depends on the number of π electrons present in the semiconducting material. The more the number of π bonds, the lower the magnitude of activation energy and vice versa. Generally, polymeric chelates containing aromatic nuclei in the backbone exhibit a lower activation energy than those with aliphatic systems. The electrical conductivity at room temperature declines in the order (Table 4) Mn > Co > Ni > Cu.

A similar trend was observed by Patel and Patil [17]. D'Sa et al. [44] reported an increase in conductivity order which is exactly reversed. A similar observation was reported by Vozzhennikov et al. [45]. The activation energy decreases in the order Reagent > Mn > Co > Cu > Ni, which is in partial agreement [42].

ACKNOWLEDGMENT

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