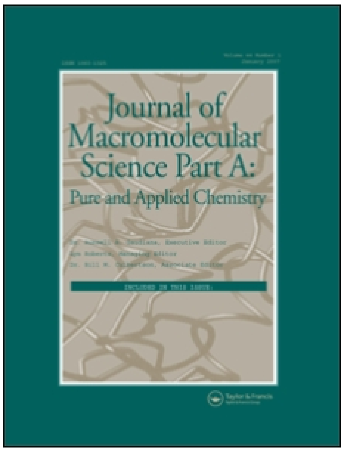

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Physicochemical Properties of Polyazomethine Polymers

M. N. Patel[a]; S. H. Patil[a]
[a] Department of Chemistry, Sardar Patel University Vallabh, Vidyanagar, India

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Physicochemical Properties of Polyazomethine Polymers

M. N. PATEL and S. H. PATIL

Department of Chemistry
Sardar Patel University
Vallabh Vidyanagar 388120, India

ABSTRACT

Polyazomethine chelate polymers of 3d transition metal ions have been prepared and characterized in terms of elemental analysis, magnetic moment, electronic spectra, infrared spectra, and thermal and electrical properties. All the polymers exhibit 1:1 stoichiometry and are insoluble in common organic solvents.

INTRODUCTION

Polymer science encompasses the efforts of the chemists basically interested in the fundamentals of chemical reactivity and macromolecular structure, the physicists and engineers primarily interested in the fundamentals of polymer properties, and the product designers interested in utilitarian applications. The three phases of study–structure, properties, and applications–and their interrelations represent successive development stages in a pattern of maturing knowledge about polymers. Many metal complexes had been shown to act as active homogeneous catalysts in the reaction of the hydrogenation [1], hydrosilation [2], hydroformylation [3], oxidative hydrolysis of olefins [4], and carbonylation of methanol [5]. Marvel et al. [6-8] reported on polymeric Schiff bases and their polychelates. The stereochemistry still needs to be investigated. The use of polymers requires new polymers containing inorganic components with superior thermal and electrical properties [9]. Coordination polymers are very similar in structure to the polynuclear cationic species [10]. Riederer and Sawodny recently reported [11, 12] polymeric Schiff base complexes and their ability to form addition compounds with neutral molecules, and investigated the behavior when used as stationary phase in molecular sieve gas chromatography. In certain cases it had been shown that the incorporation of alternating aromatic molecules into a chain of metal ions as in coordination polymers produced materials which were electrical semiconductor with good thermal stability, and the current investigation was undertaken with this in mind. The metal complexes of the quadridentate salicylaldimine assumed a variety of stereochemical forms [13] depending on the nature of the metal ion bonded and the number of bridging methylene groups between the two imine nitrogen atoms. The polychelates have been characterized in terms of elemental analyses, magnetic moment values, and visible and infrared spectra. A thermal and electrical study was also undertaken.

EXPERIMENTAL

Materials

Salicylaldehyde and glacial acetic acid were received from Sarabhai Merk and used after distillation under reduced pressure. Metal acetates (A.R.) and 1,8-diamino naphthaline (DN), Fluka AG, Buchs SG, were used.

Synthesis of Polychelates

Methylene bis-salicylaldehyde (MBSAL) was synthesized by a known method [6]. The polymeric chelates were synthesized by applying an alternate method. Dialdehyde in absolute ethanol was added slowly to a well-stirred ethanolic solution of methal-1,8-diaminonaphthalin in stoichiometric proportions. The resultant system was kept under vigorous reflux for 8 h. The dark, intense colored precipitates were filtered under suction; washed successively with ethanol, water, and ether; and dried at 110° for 24 h.

Analytical Estimations

The metal percentage was estimated by standard EDTA titration after decomposing the polychelates. Carbon-hydrogen-nitrogen analyses were made on a Coleman C-H-N analyzer.

Magnetic Measurements

Magnetic susceptibility was measured on a Sortorious semimicro Gouy balance. The fields were calculated by using a standard calibrant, mercury tetrathiocyanato cobalt, $Hg[Co(SCN)_4]$. Diamagnetic constants were calculated using Pascal's constants.

Spectral Measurements

Visible spectra were measured on a Beckman Du Spectrophotometer using MgO as standard. Infrared spectra were scanned on a Perkin-Elmer spectrophotometer in a nujol mull.

Thermal Analysis

A Du Pont (thermal analyzer 900) thermogravimetric scanning balance operating in a pure dry carbon dioxide atmosphere was used.

Electrical Measurements

The pellets were prepared under a high tension hydraulic pressure of 12,000-15,000 lb and activated at 40° for 2 h before measurement. The electrical properties were studied by measuring the resistance of the pellets with a Hewlett-Packard 4329-A High Resistance meter under vacuum.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the elemental analyses and physical properties. The theoretical and experimental data are consistent with $[ML]_n$ stoichiometry.

The magnetic moment of copper(II) polychelate is 1.80 B.M. (Table 2) which is close to the spin only value (1.73 B.M.) for one unpaired electron. The magnitude of the magnetic moment value indicates the possibility of a square planar structure [14]. This finding is in agreement with available structural information [15]. Nickel(II) shows the paramagnetic nature because it exhibits a magnetic moment value of 3.13 B.M., consistent with distorted octahedral stereochemistry [16]. In fact, the magnetic moment value was usually found to lie between 2.9-3.3 B.M., while for tetragonally distorted nickel(II) complexes a magnetic moment greater than 3.3 B.M. would be expected. Cobalt(II) polychelate

TABLE 1. Analytical Data and Physical Properties of Polychelates

			Elemental analysis found/(calculated)				
No.	Compound	Color	M (%)	C (%)	H (%)	N (%)	Molecular weight[a]
1	[Cu MBSAL DN]	Dark green	14.11 (14.46)	68.04 (68.25)	3.50 (3.64)	6.35 (6.37)	439.54
2	[Ni MBSAL DN $2H_2O$]	Green	10.73 (12.47)	62.43 (63.73)	3.40 (4.25)	5.40 (5.95)	470.71
3	[Co MBSAL DN $2H_2O$]	Brown	12.21 (12.51)	63.21 (63.70)	3.49 (4.25)	5.70 (5.95)	470.93
4	[Mn MBSAL DN $2H_2O$]	Brown	11.45 (11.76)	62.33 (64.25)	3.22 (4.28)	5.85 (6.00)	466.94
5	[Zn MBSAL DN]	Brown	15.12 (14.81)	68.01 (67.97)	3.16 (3.62)	6.07 (6.34)	441.38

[a] Estimated from elemental analysis.

TABLE 2. Magnetic Moments and Spectral Data of Polychelates

No.	Compound	Magnetic moment, B.M.	Transition energies (cm^{-1}) Observed	Calculated	Assignments
1	[Cu MBSAL DN]	1.80	14,290	-	$^2B_{1g} \longrightarrow {}^2A_{1g}$
			17,860	-	$^2B_{1g} \longrightarrow {}^2E_g$
			22,220	-	Charge transfer
2	[Ni MBSAL DN $2H_2O$]	3.13	8,772 11,110	8772	$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$
			12,990 16,130	14646	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$
			24,690	26176	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$
3	[Co MBSAL DN $2H_2O$]	2.17	9,259	9265	$^4T_{1g} \longrightarrow {}^4T_{2g}(F)$
			17,540	20160	$^4T_{1g} \longrightarrow {}^4A_{2g}(F)$
			23,260	23270	$^4T_{1g} \longrightarrow {}^4T_{1g}(P)$
4	[Mn MBSAL DN $2H_2O$]	5.99	14,710	-	$^6A_{1g} \longrightarrow {}^4T_{1g}(^4G)$
			17,240	-	$^6A_{1g} \longrightarrow {}^4T_{2g}(^4G)$
			23,260	-	$^6A_{1g} \longrightarrow {}^4E_g.{}^4A_{1g}(^4G)$

shows μ_{eff} = 2.17 B.M., a much too low value for an octahedral bivalent cobalt complex, thus suggesting either a square planar or a low spin octahedral geometry [17]. The observed room temperature magnetic moment for manganese(II) polychelate of 5.99 B.M. corresponds to five unpaired electrons (spin only value 5.92 B.M.) in an octahedral environment [18]. Zinc(II) was found to be diamagnetic from its expected $3d^{10}$ configuration.

A study of diffuse reflectance spectra in combination with magnetic and infrared spectral study provides the most important information about stereochemistry. Many authors reported [19] copper(II) planar complexes on the basis that they possess a single broad band in the region of 10,000-20,000 cm^{-1}, thus making the assignment of individual transitions difficult. The single broad band observed might be due to the unresolved transitions expected for square planar copper(II) complexes [20]. The diffuse reflectance spectra of Cu-MBSAL-DN exhibits three transition band as

$^2A_{1g} \longleftarrow {}^2B_{1g}$ 14,290 cm^{-1}

$^2E_g \longleftarrow {}^2B_{1g}$ 17,860 cm^{-1}

The band observed at 22,220 cm^{-1} may be assigned to intraligand transition. The visible spectra of nickel(II) polychelate show some novel features of interest. From the splitting of $^3T_{2g}(F)$ and $^3T_{1g}(F)$ the corresponding transitions ν_1 and ν_2 were also found to split, which is one of the signs of nickel(II) in distortion from octahedral geometry [16]. The difference of $[(\nu_3 - \nu_2)_{calc} - (\nu_3 - \nu_2)_{obs}]$ corresponds to the measure of tetragonal distortion. From the nature of splitting, an attempt has been made to compute the new crystal field parameters, D_s and D_t, needed to describe the energy levels of tetragonal molecules. Another parameter, the crystal field radial integral (Dq), has been evaluated and is given in Table 3. Racah's parameter (B_{35}), the nephelauxetic ratio (β_{35}), the ligand field stabilization energy, and the ν_2/ν_1 ratio were calculated by reported relations [21, 22] and are summarized in Table 3. The cobalt(II) polychelate absorptions at 9,259, 11,630, 12,820, 17,540, and 23,260 cm^{-1} have been related to octahedral geometry [23]. Although it is difficult to assign a definite structure for cobalt(II) polychelate on the basis of the position 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 terms, viz., $^4T_{1g}$ and $^4T_{2g}$ in an octahedral environment. The evidence

TABLE 3. Spectral Parameters of Ni(II) and Co(II) Polychelates

No.	Compound	B	β	ν_2/ν_1	LFSE (kcal/mol)	D_s (cm^{-1})	D_t (cm^{-1})	D_q (cm^{-1})	$D_{q_{av}}$ (cm^{-1})
1	[Ni MBSAL DN $2H_2O$]	967	0.8954	1.84	30.09	1737	267.3	643.3	643.4
2	[Co MBSAL DN $2H_2O$]	1021	0.9107	-	15.89	-	-	-	-

from the magnetic moment value supports the tetragonal character (Table 2). Using the observed ν_1 and ν_3, the electronic parameter was calculated by the known [21] relations

$$B_{35} = \frac{1}{30}\left[-(2\nu_1 - \nu_3) \pm \{-\nu_1^2 + \nu_3^2 + \nu_1\nu_3\}^{1/2}\right]$$

and

$$10Dq = 2\nu_1 - \nu_3 + 15B$$

The transition energies ν_1, ν_2, and ν_3 have been also evaluated. Ligand field stabilization energy was calculated and found to be in the range expected for an octahedral structure. Manganese(II) polychelate (electronic configuration $3d^5$) is exceptional in that no spin-allowed transition is to be expected since the ^6S ground state is not significantly split by the field and all excited states are of lower multiplicity. It follows that only very weak absorption, corresponding to the sextet-quartet transition, is to be expected. Manganese(II) polychelate exhibits three weak absorptions:

$^4T_{1g}(^4G) \longleftarrow {}^6A_{1g}(^6S)$ 14,710 cm^{-1}

$^4T_{2g}(^4G) \longleftarrow {}^6A_{1g}(^6S)$ 17,240 cm^{-1}

$^4A_{1g}.{}^4E_g(^4G) \longleftarrow {}^6A_{1g}(^6S)$ 23,260 cm^{-1}

The above finding is in agreement with that of Mn(II) ion in a distorted octahedral environment [24].

The important infrared bands along with their assignments are given in Table 4. The infrared spectra of the polychelates showed general features similar to each other. The strong band observed around 1590-1625 cm^{-1} may be assigned [25] to the depleted –C=N– stretch. It is not possible to compare the magnitude of depletion in –C=N– stretch because the poly-Schiff base could not be isolated in the solid state. The band due to the bridging methylene group was expected [26] at 2900 cm^{-1} and is merged with the nujol peak. The strong band at ~1270 cm^{-1} may be assigned [27] to the phenolic C–O stretch. Ni(II), Co(II), and Mn(II) polychelates exhibit a peak due to coordinated water [28, 29] at ~1640 to 1600 cm^{-1} which is confirmed by a weak broad band in the near-infrared region. The important infrared frequencies are given in Table 4. Many of the

TABLE 4. Important Infrared Frequencies (cm^{-1}) of Polychelates[a]

No.	Compound	$\nu_{(C=N)}$	$\nu_{(C-O)}$	$\nu_{(H_2O)}$
1	[Cu MBSAL DN]	1590 m	1265 w	3600-3100 w, br
2	[Ni MBSAL DN $2H_2O$]	1620 m	1265 w	3560-3180 w, br 1640 w
3	[Co MBSAL DN $2H_2O$]	1625 m	1270 w	3560-3120 m, br 1600 w
4	[Mn MBSAL DN $2H_2O$]	1625 m	1270 w	3510-3150 w, br 1600 w
5	[Zn MBSAL DN]	1600 m	1270 w	3740-3070 m, br

[a] Abbreviations: m = medium, w = weak, br = broad.

TABLE 5. Thermal and Electrical Data of Polychelates

No.	Compound	Decomposition temperature (°C)	Thermal activation energy (ΔE, kcal/mol)	Electrical conductivity at room temperature ($ohm^{-1}cm^{-1}$)	σ_0 ($ohm^{-1}cm^{-1}$)	E_a (eV)
1	[Cu MBSAL DN]	402	15.49	2.00×10^{-11}	1.59×10^{-12}	0.073
2	[Ni MBSAL DN $2H_2O$]	376	13.56	1.39×10^{-11}	3.02×10^{-12}	0.10
3	[Co MBSAL DN $2H_2O$]	371	19.73	9.61×10^{-11}	1.82×10^{-11}	0.038
4	[Mn MBSAL DN $2H_2O$]	381	11.45	5.51×10^{-11}	3.98×10^{-12}	0.066
5	[Zn MBSAL DN]	340	21.09	6.23×10^{-11}	2.19×10^{-11}	0.029

characteristic frequencies of the double bonds occur in the C–O and C–C stretching mode region 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.

THERMAL PROPERTIES

Thermogravimetric analysis (TGA) is widely used as a method to investigate the thermal decomposition of polymer and to determine such kinetic parameters as activation energy. The course of thermal decomposition in a carbon dioxide medium of the polychelates presented was typical. All polychelates decomposed in two stages into volatile product with increasing temperature. The first occurred at 250° C and accounted for the loss of water. The remainder of the polymer decomposed in the second stage at ~340-402 °C. All aromatic polymers were found to exhibit a good magnitude of thermal activation energy (E_a) of the decomposition process as obtained from thermograms. Ozawa [30] determined the activation energy through the TGA curves by changing the heating rate. The first state of decomposition of a polychelate corresponds to volatization of two kinds of water molecules. Adsorbed water molecules are evolved up to 110° while coordinated water molecules are released in the range of 200-250° C. The thermal energy of activation was calculated by employing the Anderson-Freeman method [31]. The thermal decomposition data are presented in Table 5.

ELECTRICAL PROPERTIES

The electrical resistivity (ρ) of the polymers was calculated by the reported relation. Plots of $\log_{10} \rho$ against reciprocal temperature are linear. The low electrical conductivity value may be attributed to 1) the low molecular weight, due to which the extent of conjugation becomes low, of 2) an undesirable morphology that may occur when the sample is pressed into a hard, brittle pellet. Due to weak forces between adjacent coordinating sites, there is little electronic coupling and electrons find it difficult to jump from one molecule to another. Many of these materials have been amorphous powders; the lack of ordered structure in such a material has the effect of scattering electrons when they try to flow through it and so lowers the conductivity. Dewar and Talati [32] reported on polychelates derived from dioxime with bivalent metal ions and showed the formation of d_π-p_π bonding. The low magnitude of activation energy (Table 5) may be due to the presence of a large number of π-electrons.

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