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Chelate Polymers of Phenolic Resin

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ABSTRACT

Chelate polymers of the resin poly[3,5-(1-carboxy-2-hydroxy phenylene)ethylene] with such bivalent ions as copper, nickel, cobalt, zinc, manganese, and trivalent iron have been synthesized. They have been analyzed, and some of their properties have been determined. On the basis of these, a polymeric structure is assigned to the polychelates.

INTRODUCTION

Salicylic acid-formaldehyde (SFP), 8-hydroxyquinoline-formaldehyde (8-HQF), and salicylaldehyde-formaldehyde (SALFP) are well-known polymeric chelating agents [1-6]. Recently we have indicated that a resin such as poly[3,5-(1-carboxy-2-hydroxy phenylene)-ethylene] (CHPE), which was prepared by Friedel-Craft's condensation of 1,2-dichloroethane with salicylic acid in the presence of anhydrous aluminum chloride, may prove to be a more useful polymeric ligand [7] because of the large separation of the salicylic acid units in two successive repeating units. We report here on the polychelates of bivalent metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , and trivalent Fe^{3+} . The polychelates were characterized by elemental analyses, spectral (IR and electronic) data, and magnetic properties.

It is found that the polymeric metal chelates are thermally less stable than that of the polymeric ligand.

EXPERIMENTAL

All the chemicals used were of B.D.H. quality. The polychelates were synthesized by the following common method. Resin CHPE (3.28 g, 0.02 mol) was dissolved in 100 mL of ethanol and warmed on a water bath for 15 min. To this warm and clear solution was added an alcoholic solution of copper chloride (1.70 g, 0.01 mol) with constant stirring. Dilute aqueous ammonia was added dropwise to this mixture until there was complete precipitation. The suspension was digested for half an hour on a water bath and filtered. The solid was subsequently washed with boiling water to remove unreacted metal ions, acetone, and ethanol, and dried at 100°C.

Ni²⁺-polychelate. The amounts of the reactants used were CHPE 3.28 g (0.02 mol) and nickel chloride 2.37 g (0.01 mol). Nature of the polychelate: Light brown in color and insoluble in all common organic solvents. Yield, 2.0 g.

Co²⁺-polychelate. The amount of reactants used were CHPE 3.28 g (0.02 mol) and cobalt chloride 2.37 g (0.01 mol). Nature of the polychelate: Brown in color and insoluble in all common organic solvents. Yield, 3.5 g.

Zn²⁺-polychelate. The amount of reactants used were CHPE 3.28 g (0.02 mol) and zinc chloride 1.36 g (0.01 mol). Nature of the polychelate: Brown in color and insoluble in all common organic solvents. Yield, 1.0 g.

Mn²⁺-polychelate. The amount of reactants used were CHPE 3.28 g (0.02 mol) and manganese chloride 1.36 g (0.01 mol). Nature of the polychelate: Brown in color and insoluble in all common organic solvents. Yield, 3.5 g.

Fe³⁺-polychelate. The amount of reactants used were CHPE 4.92 g (0.03 mol) and ferric chloride 1.62 g (0.01 mol). Nature of the polychelate: Red in color and insoluble in common organic solvents. Yield, 4.8 g.

The metal content of the polychelates was estimated and presented in Table 1. Magnetic moments were determined using the Gouy method. Diamagnetic corrections were applied using Pascal's constants. The electronic spectra of polychelates were recorded on a Beckman Spectrophotometer using MgO as reference. The infrared spectra of polymer samples were recorded in KBr pellets on a Carl Zeiss Spectrophotometer. Thermograms were recorded on a Du Pont Thermal Analyzer 950.

TABLE 1. Metal Content, Magnetic Moment, and Electronic Transition Energies of Polychelates

Polychelate	M (%)	μ_{eff} B.M.	Transition energies (cm ⁻¹)	Assignment
Cu-CHPE ^a	15.60 (16.31) ^b	1.79	15,150 20,100	² E _g - ² E _{1g} Charge transfer
Ni-CHPE	15.50 (15.26)	3.33	9,400 15,380	³ T _{1g} (F) - ³ A _{2g} (F) ³ T _{1g} (F) - ³ A _{2g} (F)
Co-CHPE	15.50 (15.32)	4.72	22,990 8,696 15,380	³ T _{2g} (P) - ³ A _{2g} (F) ⁴ T _{2g} - ⁴ T _{1g} ⁴ A _{2g} - ⁴ T _{1g}
Mn-CHPE	14.45 (14.42)	5.25	21,050 13,790	⁴ T _{1g} - ⁴ T _{1g} ⁴ T _{1g} (⁴ G) - ⁶ A _{1g} (S)
Fe-CHPE	10.31 (10.25)	5.03	16,670 22,730	⁴ T _{2g} (⁴ G) - ⁶ A _{1g} (S) ⁴ E _g - ⁴ A _{1g} (⁴ G) - ⁶ A _{1g} (S)
Zn-CHPE	17.66 (16.70)	Diamagnetic	17,860 25,000	⁴ T _{2g} - ⁶ A _{1g} ⁴ E _g - ⁴ A _{1g} - ⁶ A _{1g}

^aCHPE = poly[3,5-(1-carboxy-2-hydroxy phenylene)ethylene].

^bCalculated.

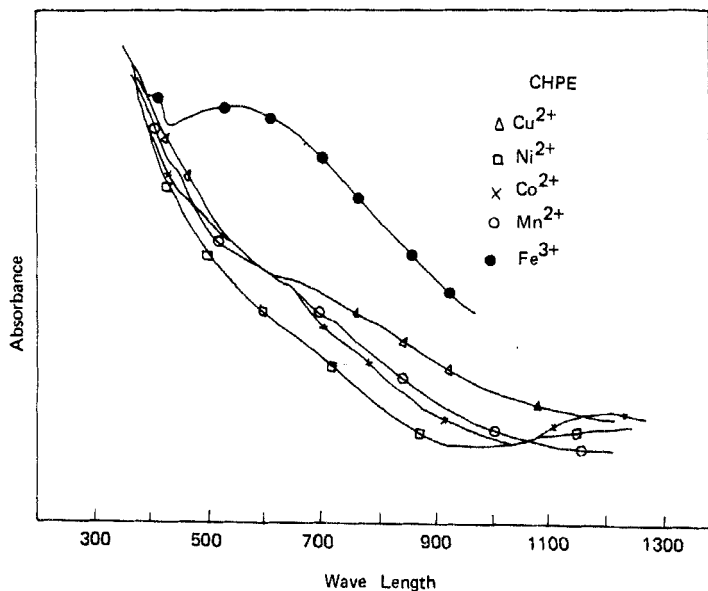


FIG. 1. Reflectance spectra of polychelates.

RESULTS AND DISCUSSION

Copper(II) polychelate exhibits a magnetic moment of 1.79 BM which is close to the "spin-only" value of 1.73 BM for one unpaired electron. The magnitude of the magnetic moment lends some support to a planar geometry [8]. The observed value of 3.33 BM for nickel(II) chelate suggests the paramagnetic nature in an octahedral configuration which is in good agreement, within the range of magnetic moment values (3.1-3.6 BM), proposed by Nyholm [9]. Figgis et al. [10] reported high-spin octahedral Co(II) complexes having magnetic moment values in the range of 4.7 to 5.6 BM. The value 4.72 BM for the Co(II) polychelate, lying within this range, favors an octahedral structure. The observed magnetic moment of 5.25 BM for Mn^{2+} polychelate is less than the "spin-only" value for five unpaired electrons. The lowering of the magnetic moment value may be due to the aerial oxidation of Mn(II)–Mn(III) during synthesis [11]. Fe(III) polychelate exhibits magnetic moment close to the range given elsewhere [8] for a low-spin octahedral configuration. Zn(II) was found to be diamagnetic as expected for its $3d^{10}$ configuration.

The electronic spectra of Cu(II) show a broad band at $15,150\text{ cm}^{-1}$ which is characteristic of Cu(II) in planar geometry [12]. Ni(II) polychelate exhibits three less resolved bands in the normally expected

TABLE 2. Infrared Spectral Data in cm^{-1}

CHPE	Cu(II)	Ni(II)	Co(II)	Zn(II)	Mn(II)	Fe(III)	Assignment
-	475 (bw)	500 (bw)	440 (sh)	430 (w)	440 (w)	450 (w)	O-M
-	550 (b)	585 (b)	570 (b)	535 (w)	540 (w)	560 (w)	C-O-M
850 (s)	835 (m)	840 (w)	780 (s)	835 (s)	840 (s)	850 (s)	Isolated H
1230 (s)	1150 (w)	1150 (w)	1150 (w)	1160 (w)	1145 (m)	1160 (w)	C-O
1300 (m)	1250 (m)	1250 (w)	1250 (s)	1255 (s)	1255 (s)	1250 (s)	O-H
1470 (s)	1410 (s)	1440 (m)	1450 (s)	1465 (s)	1435 (s)	1400 (s)	C=C
1667 (s)	1615 (s)	1615 (s)	1600 (s)	1615 (s)	1595 (s)	1610 (s)	C=O
2955 (w)	2980 (b)	2970 (b)	2980 (b)	2920 (b)	2950 (b)	2915 (b)	Phenolic OH

TABLE 3. Decomposition Data at Various Temperatures

Polymer	% Weight loss at temperature (°C) of							
	100	200	300	400	500	600	650	700
CHPE	0	4	40	50	60	65	67	67
Cu-CHPE	4	9	23	35	47	62	68	72
Ni-CHPE	6	12	18	28	49	72	74	74
Co-CHPE	8	12	20	33	50	71	76	76
Zn-CHPE	4	7	14	24	38	58	67	-
Mn-CHPE	7	12	19	31	52	70	76	80
Fe-CHPE	6	12	19	36	50	60	65	70

position for octahedral structure [13]. These bands may be assigned as

$${}^3T_{2g}(F) \rightarrow {}^3A_{2g}(F) \quad \nu_1 \quad 22,990 \text{ cm}^{-1}$$

$${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F) \quad \nu_2 \quad 15,380 \text{ cm}^{-1}$$

$${}^3T_{1g}(P) \rightarrow {}^3A_{2g}(F) \quad \nu_3 \quad 9,400 \text{ cm}^{-1}$$

In Co(II) polychelate the transitions observed at 8,696, 15,380, and 21,050 may be assigned to the octahedral structure. The observed positions for absorption bands of Mn(II) polychelate clearly indicate [12] its octahedral nature. Fe(III) polychelate exhibits two maxima at 17,880 and 25,000 cm^{-1} , thus confirming an octahedral environment [14]. The electronic spectra are shown in Fig. 1. The results of important bands with assignments are given in Table 1.

In the polychelates, the bands observed around 460 and 550 cm^{-1} correspond to the M-O and M-O-C vibrations, respectively, and suggest that the phenolic and carboxy groups are involved in bond formation with metal ions. The C=O stretching frequency in resin observed at 1670 cm^{-1} is lowered by 55 to 75 cm^{-1} in all polychelates which suggests C=O→M coordination [15]. Bands around 800, 1150, 1250, and 1430 cm^{-1} correspond to an isolated hydrogen atom, C-O vibration, O-H vibration, and C=C skeletal vibration, respectively. The important infrared bands are given in Table 2.

The thermal decomposition of the polychelates took place in two stages [2]. The first stage terminates around 400°C, followed by the major step of decomposition. The rate of decomposition of the

polychelate is more than that of parent polymer, suggesting that there may be powerful intramolecular hydrogen bonding [16]. Such hydrogen bonding favors the reduction in the thermal stability of polychelates compared to the parent polymer. It seems that metal ions accelerate the decomposition of polychelates. In copper and iron polychelates the decomposition occurred at a lower temperature which may be due to the oxidation of the polymer by the catalytic action of these metal ions [1] (Table 3).

In view of the above discussion, we propose a polymeric structure for metal chelates.

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