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PHYSICOCHEMICAL STUDIES OF A FURFURAL COPOLYMER AND ITS POLYCHELATES

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INTRODUCTION

Copolymers like 8-hydroxyquinoline-furfural, 2,4-dihydroxyacetophenone-furfural, β -resorcylic acid-furfural, anthranilic acid-furfural, and salicylic acid-furfural are well-known polymeric ligands [1-4], and their ion-exchange properties have been reported. In the present paper, we report the preparation and characterization of β -resorcylic aldehyde-furfural (RAF) polymer and its polychelates with the bivalent metal ions Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , and Zn^{2+} .

EXPERIMENTAL

Materials

Furfural (SDS grade) was purified by distillation (bp 162°C) in the presence of 0.05% hydroquinone. All other chemicals used were of analytical grade. β -Resorcylic aldehyde was prepared in the laboratory [5].

Polymer Preparation

β -Resorcyaldehyde (β -RA) (5.52 g, 0.04 mol) and K_2CO_3 (0.165 g, 3% weight of β -RA) were mixed in 3 mL water, and freshly distilled furfural (3.84 g, 0.04 mol) was added with constant stirring. The mixture was heated at $120^\circ C$ for 6 h. The reaction mixture was poured into water and kept overnight. Next day the dark-brown solid was filtered and washed with a large amount of boiling water. It was dried at $60^\circ C$ for 24 h. The polymer was soluble in dimethylformamide, methyl ethyl ketone, dimethylsulfoxide, and pyridine. It did not melt up to $360^\circ C$. The yield was 4.5 g.

Preparation of Chelates

Stoichiometry proportions of RAF dissolved in a mixture of DMF and methanol (1:1) were added to a well-stirred solution of metal acetate in DMF-methanol (1:1). The precipitated metal chelates were filtered, washed with a mixture of DMF-methanol and hot water, and dried at $60^\circ C$ for 24 h.

Analysis (Table 1)

Elemental Analysis

The elemental analyses of polymer and polychelates were carried out on a Coleman C-H-N Analyzer. The metal content of the polychelates was determined by EDTA complexometric titration after decomposing the polychelates with a mixture of concentrated hydrochloric, perchloric, nitric, and sulfuric acid.

Molecular Weight Determination

The molecular weight (\bar{M}_n) of RAF polymer based on two phenolic hydroxyl groups in the repeat unit was determined by nonaqueous conductometric titration in pyridine against NaOMe in pyridine [6, 7] and by Hewlett Packard Vapor-Pressure Osmometry (VPO) in DMF at $70^\circ C$.

Spectral Measurement

The infrared spectra of polymer and polychelates were recorded on KBr pellets with a Perkin-Elmer 983 IR spectrophotometer. The diffusion electronic spectra of polychelates were scanned on a Beckman DU Spectrophotometer with MgO as the reference.

TABLE 1. Analytical and Thermal Data^a

Polymer samples	C, %	H, %	M, %	% Weight loss at temperature °C				
				100	200	300	400	500
RAF	66.1 (66.66)	3.6 (3.70)	—	—	1.0	15.0	61.0	87.0
[Cu(RAF) ₂] _n	58.1 (58.35)	2.7 (2.84)	12.2 (12.87)	—	1.5	50.0	76.0	76.0
[Ni(RAF) ₂ ·2H ₂ O] _n	54.7 (54.89)	3.1 (3.43)	10.7 (11.9)	—	4.5	23.0	84.0	84.0
[Co(RAF) ₂ ·H ₂ O] _n	56.6 (56.81)	3.0 (3.16)	10.9 (11.63)	1.0	3.5	21.5	79.0	79.0
[Mn(RAF) ₂ ·2H ₂ O] _n	55.0 (55.29)	3.3 (3.46)	10.1 (10.55)	—	6.5	23.0	82.5	82.5
[Zn(RAF) ₂] _n	57.8 (58.14)	2.6 (2.83)	12.8 (13.19)	—	22.0	22.0	78.0	89.0

^a Calculated values are shown in parentheses.

Magnetic Susceptibility

Magnetic susceptibility of the polychelates was determined by the Gouy method at room temperature using the relationship

$$\mu_{\text{eff}} = 2.83 \sqrt{\chi_M T} \quad (1)$$

Thermal Analysis

Thermograms of polymer and polychelates were scanned on a Du Pont Thermal Analyzer 951.

RESULTS AND DISCUSSION

The RAF polymer was soluble in DMF, MEK, DMSO, and pyridine. It was sparingly soluble in methanol, ethanol, and acetone. It did not melt up to 360°C. \bar{M}_n determined by VPO in DMF at 70°C was 1484 ± 50 , in good agreement with that obtained by conductometric titration, 1430 ± 50 .

Infrared

The broad infrared band at $3600\text{--}3100\text{ cm}^{-1}$ (Fig. 1) belongs to the stretching vibration of the OH group [8]. The bands at 2830 and 2930 cm^{-1} are due to the $-\text{CH}-$ bridge. The strong band around 1610 cm^{-1} is due to the stretch-

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ing vibration of the $-\text{C}=\text{O}$ group. The bands around 1360 , 1460 , and 1520 cm^{-1} are due to stretching vibrations of the aromatic skeleton. The bands around 1020 , 1080 , 1130 , 1170 , 1225 , and 1260 cm^{-1} are due to the $-\text{C}-\text{O}-\text{C}$ cyclic ether linkages and are characteristic of the furan ring [9]. The band around 905 cm^{-1} is due to the presence of isolated hydrogen in the phenol moiety of the polymer chains; that around 855 cm^{-1} is assigned to the 1,2,4,5-tetra-substituted phenyl ring (presence of isolated H on phenyl ring). Thus, on the basis of the IR spectral characteristics and the reactivity sites of the monomer, the structure at the top of page 215 is proposed. Elemental analysis indicates a 1:2 metal-ligand stoichiometry ratio (Table 1). Comparison of the infrared spectra of the ligand and its chelates (Fig. 1) leads to information about the structure of the polychelates. The bands at $3580\text{--}3220\text{ cm}^{-1}$ are due to the stretching vibration of the chelated $-\text{OH}$ group. The strong band at 1605 cm^{-1} is attributed to $\nu_{\text{C}=\text{O}}$. The lowering of this band is an indica-

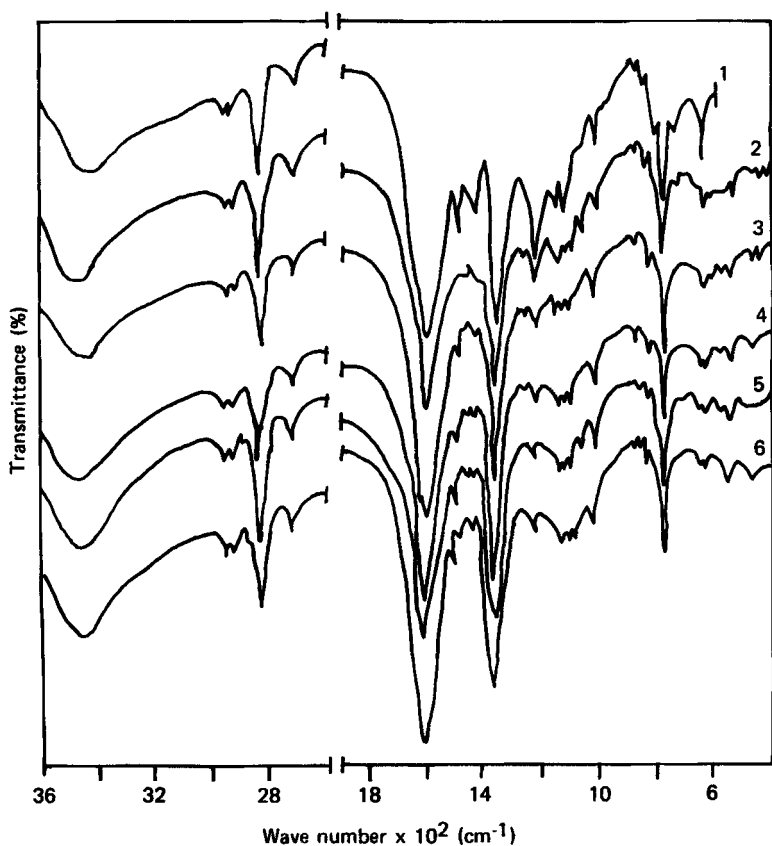
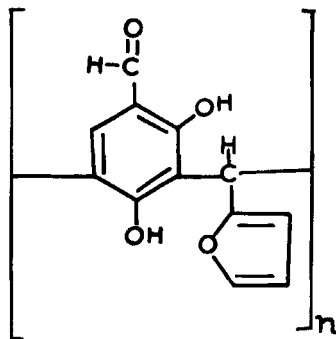


FIG. 1. Infrared spectra. 1: RAF. 2: Cu^{2+} polychelate. 3: Ni^{2+} polychelate. 4: Co^{2+} polychelate. 5: Mn^{2+} polychelate. 6: Zn^{2+} polychelate.

TABLE 2. Magnetic Moment and Electronic Transition Energies of Polychelates

Polychelates	μ_{eff} , BM	Transition energies, cm^{-1}	Assignment
$[\text{Cu}(\text{RAF})_2]_n$	2.0	15 504	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$
		23 529	Charge transfer
$[\text{Ni}(\text{RAF})_2 \cdot 2\text{H}_2\text{O}]_n$	3.12	9 216	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$
		15 625	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$
		23 256	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$
$[\text{Co}(\text{RAF})_2 \cdot \text{H}_2\text{O}]_n$	4.55	8 889	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$
		16 260	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$
		23 809	Charge transfer
$[\text{Mn}(\text{RAF})_2 \cdot 2\text{H}_2\text{O}]_n$	5.68	15 267	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$
		18 182	${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$
		23 529	${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{T}_{1g}({}^4\text{G})$
$[\text{Zn}(\text{RAF})_2]_n$	Diamagnetic	—	—

tion of coordination through the oxygen of the aldehyde group. The band around 480 and 550 corresponds to the $\nu_{\text{M-O}}$ vibration [10].

Magnetic Moment

The magnetic moment of the Cu(II) polychelate is 2.0 Bohr magneton (Table 2), which is very close to the spin-only value for one unpaired electron, indicating square planer symmetry. The slightly excess value of the magnetic moment might be due to orbital contributions [11, 12]. The spectrum of the copper(II) chelate exhibits two bands in the region expected for square planar copper(II).

The Ni(II) polychelate shows a magnetic moment of 3.12 BM, in the expected range of 2.8-3.3 BM for octahedral stereochemistry [13]. The electronic spectrum of nickel(II) show three bands in the region expected for

octahedral geometry [14]. The ν_2/ν_1 ratio of 1.69 also lies in the expected range for regular octahedral complexes [15].

The Co(II) polychelate has a magnetic moment of 4.55 BM in agreement with cobalt (II) in tetrahedral structures [16]. The electronic spectra show three bands in the region expected for tetrahedral geometry [17].

The magnetic moment value of the manganese(II) polychelate (5.68 BM) and the band positions in the visible region are typical for Mn(II) with octahedral geometry. The low magnetic moment of the spin-only value (5.92 BM) may be due to air oxidation of Mn(II) to Mn(III) during synthesis [18]. The Zn(II) polychelate is found to be diamagnetic as expected from its $3d^{10}$ configuration.

Thermal Analysis

The weight loss of Co(II) chelate at 100-125°C of 3.5% (Table 1) shows that the Co(II) chelate has one lattice water molecule. The Ni(II) and Mn(II) chelates weight loss due to the coordinated water molecules occurred at 200-250°C.

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