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Coordination Polymers. VI. Physicochemical Studies on Chelate Polymers of 4,4'-(4,4'-Biphenylenebisazo)di(2-hydroxy Acetophenone)

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ABSTRACT

Dark colored Cr(III), Co(II), and Ni(II) polychelates of 4,4'-(4,4'-biphenylenebisazo)di(2-hydroxy acetophenone) have been prepared and characterized on the basis of their physicochemical properties. An octahedral stereochemistry was found for Cr(III) and Co(II) polychelates, while the Ni(II) polychelate is tetrahedral.

INTRODUCTION

Coordination polymers derived by polymerizing the monomeric bis-bidentate ligand through a metal ion are a subject of study in a limited number of schools. In the last few years our laboratory has studied such chelate polymers [1-5]. In this communication we report the synthesis of 4,4'-(4,4'-biphenylenebisazo)di(2-hydroxy acetophenone) and its polychelates with Cr(III), Co(II), and Ni(II). The stereochemis-

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try of each of them has been determined using their diffuse reflectance spectra, infrared spectra, magnetic moments, and conductivities.

EXPERIMENTAL

Materials

Benzidine obtained from Sisco Chem Industries was used after recrystallization from hot water. 2-Hydroxy acetophenone was prepared by Fries migration of phenylacetate using anhydrous aluminum chloride in the absence of solvent. Metal nitrates of Sarabhai M. Chemicals were used for polymerizing the monomeric ligand. N,N'-Dimethylformamide (DMF), also from Sarabhai M. Chemicals, was used after distillation. All other chemicals used were of reagent grade.

Preparation of the Ligand

A cold tetrazotized solution of benzidine (0.05 mol) was poured into a cold aqueous (150 mL) solution of 2-hydroxy acetophenone (0.05 mol) in sodium carbonate (23 g). The mixture was stirred for a period of about 4 h. The completion of the formation of an intermediate was tested with alkaline H acid. The same amount of the 2-hydroxy acetophenone dissolved in a minimum amount of NaOH solution was added to the above and stirred until the reaction was complete. The completion of the reaction was tested with alkaline β -naphthol. The isolated 4,4'-(4,4'-biphenylenebisazo)di(2-hydroxy acetophenone) was filtered and washed several times with hot water and then with a little alcohol. It was dried in an oven at 60°C. It is insoluble in almost all common organic solvents except nitrobenzene, THF, DMF, and pyridine.

Preparation of Polychelates

In the preparation of polychelates a hot ligand (0.005 mol) solution in DMF (~150 mL) was added to a metal (0.005 mol) solution prepared in minimum amount of DMF with constant stirring. To the hot reaction mixture, 1 g of sodium acetate was added and refluxed in an oil bath for ~2.5 h. The isolated polychelate was filtered and washed with hot DMF followed by hot water and finally with ethanol. The product was dried in an oven at 60°C.

Measurements

All structural studies were carried out at room temperature (30°C). Infrared spectra were recorded in KBr on a Carl-Zeiss UR-10 Spec-

trophotometer. The visible reflectance spectral data were obtained on a Beckman-DU spectrophotometer. Magnetic moments were determined by the Gouy method using a Sartorius semimicro Gouy balance. Carbon and hydrogen analyses were made on a Coleman C-H analyzer. The conductances were obtained using a Toshniwal digital conductometer. The metal content in each polymer was determined by independent gravimetric and volumetric methods.

RESULTS AND DISCUSSION

Analytical data (Table 1) suggest a 1:1 (metal:ligand stoichiometry for Ni(II) and Cr(III) polychelates while for the Co(II) polychelate it is 2:3. Because of the very poor solubilities of all the polychelates, their specific conductances have been measured (Table 1). Low values suggest their nonelectrolyte nature.

The ligand used contains four aromatic rings, while its polychelates contain several such rings. Because of this, the infrared spectra are difficult to interpret. However, the following tentative observations are made. The ligand and the polychelates show (Table 2) a medium broad band in the $3300\text{--}3400\text{ cm}^{-1}$ range which may be due to the ν_{OH} of the phenolic group. Such ligands are also found to contain hydrogen-bonded water to --N=N-- group of the ligand [6]. Therefore the observed frequency may also correspond to the ν_{OH} of such a hydrogen-bonded water molecular along with a phenolic ν_{OH} . The observed low energy shift of a band may be due to the presence of intramolecular or intermolecular hydrogen bonding [7]. Dissociation of the phenolic proton from the ligand during coordination could not be judged from these spectra because polychelates also contain water of coordination. At the same time, the water molecule associated with the ligand would have been retained in the polychelates.

The ligand shows two strong bands at 1640 and 1600 cm^{-1} . These bands may be safely assigned to $\nu_{\text{C=O}}$ and $\nu_{\text{N=N}}$, respectively. On coordination, the former band shows a larger positive shift, suggesting oxygen coordination of the ketonic group.

A strong ligand band at 1300 cm^{-1} may be due to in-plane bending O-H vibration [8]. All polychelates show this band, thus confirming the presence of water in the chelated molecule. A strong phenolic C-O vibration band, present at 1125 cm^{-1} in the ligand, is observed at higher energy in all the polychelates. This suggests oxygen coordination of the phenolic OH [9].

The diffuse reflectance spectrum of the ligand shows a strong absorption band at $22,222\text{ cm}^{-1}$ with a shoulder at $25,641\text{ cm}^{-1}$. The ligand shows a continuous decrease in absorption up to $14,285\text{ cm}^{-1}$, after which there is practically no absorption. The former band may be due to a $n \rightarrow \pi^*$ transition, while the latter may be assigned to a $\pi \rightarrow \pi^*$

TABLE 1. Analytical and Conductivity Data

Compound	Elemental analysis found (calc) (%)			Specific conductivity $\times 10^6$ mho/cm
	C	H	M	
$C_{28}H_{22}O_4N_4$	71.31 (70.29)	3.62 (3.94)	-	-
$[Cr(C_{28}H_{20}O_4N_4)(CH_3COO)_2 \cdot H_2O]$	56.05 (55.48)	3.20 (3.62)	8.5 (8.6)	9.4
$[Co_2(C_{28}H_{20}O_4N_4)_3 \cdot 4H_2O]$	61.87 (62.30)	4.75 (4.57)	7.42 (7.63)	7.5
$[Ni(C_{28}H_{20}O_4N_4)_2 \cdot H_2O]$	60.01 (60.79)	3.06 (3.92)	10.11 (10.62)	6.8

TABLE 2. Infrared Spectral Data^a

Compound	Cr(III)	Co(II)	Ni(II)
3440 mbr	3475 mbr	3480 mbr	3300 mbr
1640 ss	1696 msh	1674 ws	1684 ws
1600 ss	1600 ss	1600 ss	1600 ss
1300 ss	1284 ms	1290 ms	1290 ms
1125 ss	1132 mbr	1130 ss	1136 ws

^ass = strong sharp, ms = medium sharp, ws = weak sharp, wbr = weak broad, msh = medium shoulder, mbr = medium broad.

transition [10]. The large high energy shift compared to azobenzene may be due to the presence of extensive conjugation in the ligand [11].

The Cr(III) polychelate shows a strong band at 25,641 cm⁻¹ and shoulders at 21,739 and 16,000 cm⁻¹ in its diffuse reflectance spectrum. The first band may be due to ligand absorption in this region. However, the second band shows a low energy shift, which may be due to a ⁴A_{2g} - ⁴T_{1g} transition admixed with the ligand transition for an octahedral stereochemistry of the Cr(III) polychelate. The low energy band may be due to a ⁴A_{2g} - ⁴T_{2g} transition. Its magnetic moment (3.78 BM) corresponds to the spin-only value [12].

The spectrum of Co(II) polychelate shows very strong absorption at a higher energy and then a continuously decreasing intensity. However, there is some indication of structures at 8,474 and 12,195 cm⁻¹. It is concluded that ligand absorption has influenced the d-d bands. The observed weak shoulders may be assigned to ⁴T_{1g} - ⁴T_{2g} and ⁴T_{1g} - ²E_g transitions, respectively. The observed magnetic moment (3.6 BM) is abnormally lower than required. The absence of low temperature magnetic moments is difficult to explain. However, spin-orbit coupling interaction would play an important role in an abnormal result [13].

The Ni(II) polychelate shows a large bathochromic shift to the high energy bands 22,727 and 21,276 cm⁻¹, which may be due to an extensive conjugation extending through Ni(II). The bands at 20,408, 16,129 and 9,524 cm⁻¹ may be assigned to the ³T_{1g}(F) - ¹T₂, ⁻³T₁(P), and ⁻³A₂ transitions, respectively, for a tetrahedral structure [14]. The observed magnetic moment (3.90 BM) is in the required range [15].

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