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Coordination Polymers. VIII. Studies on Polymeric Metal Chelates of an Unsymmetrical Bis-bidentate Ligand

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ABSTRACT

The Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) polychelates of 4,4'-(4,4'-biphenylylenebisazo) salicylaldehyde-salicylic acid were prepared. The analytical data are found to be consistent with 1:1 (metal:ligand) stoichiometry. The polychelates were further characterized by conductivities, magnetic moment, as well as electronic and infrared spectral properties. All polychelates are found to have an octahedral stereochemistry.

INTRODUCTION

The development of routes to unsymmetrical mixed donor ligands is of interest, since such ligands may be useful in preparing synthetic analogs of the metal binding sites of zinc and copper proteins [1]. Several reports have been published of the preparation of polychelates from symmetrical bis-bidentate ligands. However, the literature

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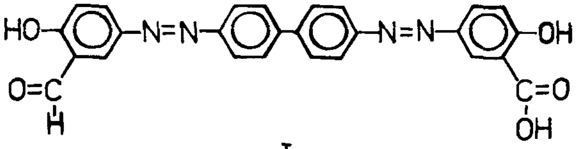
records no attempts of the preparation and characterization of polychelates from 4,4'-(4,4'-biphenylylenebisazo)salicylaldehyde-salicylic acid (I). In continuation of our earlier work [2-5], we here report the



I

preparation of polychelates of (I) with Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). An attempt has been made to derive the stereochemistry of these polychelates using elemental analyses, conductivities, and electronic and infrared spectral data in conjunction with the magnetic data.

EXPERIMENTAL

Salicylic acid and zinc chloride were obtained from British Drug House, India. All other chemicals were used as described earlier [3].

Preparation of the Polychelates

The ligand (I) was prepared by the literature method [6].

The ligand (I) (50 mmol, 80 mL DMF) was dissolved in DMF by refluxing. To the refluxed ligand solution, the ethanolic metal chloride solution (50 mmol, 5 mL) was added with constant stirring. Aqueous solutions of ferrous ammonium sulfate and zinc chloride were used for the preparation of Fe(II) and Zn(II) polychelates, respectively. To the resulting mixture, about 1 g sodium acetate was added, and the whole mixture was refluxed for ~2 h. The isolated solid was filtered, washed several times with hot water, followed by hot DMF, and finally with ethanol. The product was dried in an oven at 45°C.

All the physicochemical measurements were made as described earlier [3].

RESULTS AND DISCUSSION

All the polychelates are dark colored solids and insoluble in common organic solvents. It is not possible to characterize them by conventional methods due to their poor solubility, even in DMF. Therefore, the molar conductances could not be measured. However, low values of the specific conductances (Table 1) in DMF indicate the non-

TABLE 1. Analytical and Conductivity Data

Compound	Found (calculated), %				Specific conductance × 10^6 ohm^{-1} cm^2
	C	H	N	M	
$C_{26}H_{18}N_4O_5$	67.03 (66.95)	3.84 (3.86)	12.08 (12.01)	-	-
$Cr(C_{26}H_{14}N_4O_5)(Cl)(H_2O)^a$	54.09 (54.78)	3.20 (3.16)	10.13 (9.83)	9.15 (9.13)	2.7
$Mn(C_{26}H_{14}N_4O_5)(H_2O)_2$	56.58 (56.23)	3.97 (3.60)	10.06 (10.09)	10.04 (9.90)	2.9
$Fe(C_{26}H_{14}N_4O_5)(H_2O)_2$	56.68 (56.14)	3.50 (3.60)	10.37 (10.08)	9.90 (10.05)	4.5
$Co(C_{26}H_{14}N_4O_5)(H_2O)_2$	54.99 (55.84)	3.99 (3.58)	10.49 (10.02)	10.65 (10.54)	3.7
$Ni(C_{26}H_{14}N_4O_5)(H_2O)_2$	56.24 (55.86)	3.77 (3.54)	10.26 (10.02)	10.36 (10.50)	4.9
$Cu(C_{26}H_{14}N_4O_5)(H_2O)_2$	56.06 (55.36)	2.29 (2.67)	10.30 (9.94)	11.24 (11.30)	3.9
$Zn(C_{26}H_{14}N_4O_5)(H_2O)_2$	54.88 (55.20)	3.66 (3.54)	9.77 (9.91)	11.32 (11.56)	2.8

[a] Cl (%): calculated, 6.23; found, 5.95.

electrolytic behavior of the polychelates [2, 3]. Elemental analyses (Table 1) suggest a 1:1 stoichiometry for all the polychelates.

Magnetic Moments

The Cr(III) polychelate shows a magnetic moment of 4.02 Bohr magnetons (μ_B), which is in the range required for an octahedral structure [7]. The Mn(II) polychelate had a magnetic moment of 5.76 μ_B, which is slightly lower than the spin-only value, but still within the range of an octahedral structure [8]. The Fe(II) polychelate had a high magnetic moment as high as 14 μ_B. The large value of the magnetic susceptibility indicates ferromagnetic behavior of the polychelate. The magnetic moment 5.14 μ_B of the Co(II) polychelate is in the range required for the high-spin octahedral structure [9]. The Ni(II) polychelate had a higher magnetic moment (3.9 μ_B). The magnetic moment of Cu(II) polychelate was 2.15 μ_B, which is in the expected range for a single unpaired electron. The Zn(II) polychelate is diamagnetic, as expected.

Electronic Spectra

The ligand shows a broad band centered around 21 052 cm^{-1} with a shoulder at 23 256 cm^{-1}. The former band may be due to a $n \rightarrow \pi^*$ transition, the latter to a $\pi \rightarrow \pi^*$ transition [10]. The high intensity of the bands and their large red shift compared to azobenzene may be attributed to the extensive conjugation of the ligand which results in lowering of the π^* orbital energy [11].

The diffuse reflectance spectrum of the Cr(III) polychelate shows shoulders at 12 500 and 16 000 cm^{-1} on a high-energy band at 23 255 cm^{-1}. The band at 12 500 cm^{-1} might be a spin-forbidden transition corresponding to the ${}^4A_{2g} \rightarrow {}^2E_g$ transition [12], while the band at 16 000 cm^{-1} may be assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (γ_1) transition in an octahedral stereochemistry [3]. The high-energy band may be a ligand band probably mixed with the charge-transfer process [13]. It is possible that a γ_2 transition would have been enveloped in the high-energy ligand band.

The reflectance spectrum of the Mn(II) polychelate shows bands at 15 150, 20 410, and 23 810 cm^{-1}. In an octahedral stereochemistry, the first two bands can be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transitions, respectively. The high-energy band may be the ligand band.

The diffuse reflectance spectrum of the Fe(II) polychelate shows bands at 23 810 and 18 519 as well as a weak shoulder at 13 071 cm^{-1}. The high-energy band may be a ligand band. The bands at 18 519 and 13 071 cm^{-1} may be attributed to the spin-allowed $^5T_{2g} \rightarrow {}^5E_g$ transition in an octahedral stereochemistry [14]. The pronounced doubling of this band may be ascribed to the presence of a low-symmetry component to the crystal field [15]. It is possible to obtain B = 707 cm^{-}1, β = 0.67, and C = 2 828 cm^{-1} [16]. The reduction in B suggests the partial covalent nature of the M–L bond [17].

The diffuse reflectance spectrum of the Co(II) polychelate exhibits bands at 8 333 and 22 730 cm^{-1}. The band at 8 333 cm^{-1} may be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ (γ_1) transition in an octahedral stereochemistry. The band at 22 730 cm^{-1} may be a ligand band. It is difficult to identify this band as a γ_3 band, as it would have enveloped with the ligand band.

The diffuse reflectance spectrum of the Ni(II) polychelate shows a broad band at 8 333 and a weak band at 15 385 cm^{-1}. It also shows ligand bands at 22 222 and 25 000 cm^{-1}. The former two bands may be assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ (γ_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (γ_2) transitions in an octahedral stereochemistry [18]. The γ_1 band is found to be unsymmetrical and shows structure at 9 303 cm^{-1}. The γ_2 band also shows some sign of splitting, with a weak band at 13 890 cm^{-1}. The splitting of γ_1 and γ_2 bands suggests the presence of tetragonal distortion in the polychelate [19]. The observed γ_2/γ_1 (1.85) is greater than required [18], which also indicates the presence of distortion [18].

Considering the effective D_4h symmetry for the polychelate, the most probable assignments for the split components can be made as follows [19-21]:

$^3B_{1g} \rightarrow {}^3E_g$	8 333 cm^{-1}
$^3B_{1g} \rightarrow {}^3B_{2g}$	9 303 cm^{-1}
$^3B_{1g} \rightarrow {}^3A_{2g}(F)$	13 890 cm^{-1}
$^3B_{1g} \rightarrow {}^3E_g(F)$	15 385 cm^{-1}

From the amount of splitting in γ_1 band, the degree of distortion is estimated (D_t = 111 cm^{-1}), and from the splitting of γ_2 band, D_s = 817 cm^{-1} [22, 23]. Using the observed value DQ^{XY} (930 cm^{-1}), $D_q^{\,z}$ = 1 124 cm^{-1} can be calculated [19, 24]. Examination of these values suggests a stronger ligand field in the XY-plane than along the Z-axis [25].

For this polychelate, DS = 5 717 cm^{-1}, DT = 1 503 cm^{-1}, DQ = 23 801 cm^{-1}, DQ^{XY} = 25 579 cm^{-1}, and DQ^{Z} = 20 245 cm^{-1} have been determined [26, 27]. The ratio DT/DQ suggests small distortion from the idealized cubic symmetry [25].

The diffuse reflectance spectrum of the Cu(II) polychelate shows weak bands at 15 150, 13 158, and 10 362 cm^{-1} on the tail of the ligand bands which presumably involve the d-d transitions [28]. The polychelate may have a tetragonally distorted octahedral structure [29]. The d^9 configuration is highly unstable, and the resulting tetragonal distortion leads to a further splitting of the octahedral (e.g., T_{2g}) levels. The observed three bands at 10 362, 13 158, and 15 150 cm^{-1} may be assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively [30].

Infrared Spectra

Although infrared studies are employed increasingly in investigations of the complexes, such studies have been strictly empirical and have proved of little use in solving stereochemical problems. In the present work, an attempt has been made to understand the mode of coordination of metal ion with the ligand system. Due to the presence of several aromatic rings and different coordinating sites in the ligand, it is rather difficult to derive any definite conclusion on the bonding sites in the polychelates. However, some stray findings are indicated here, and tentative assignments have been made.

1) The IR spectra of the ligand display a broad and medium band in the region 2800-3560 cm^{-1}, which is attributed to phenolic γ_{OH} and hydrogen-bonded –COOH group. γ_{OH} usually occurs at 3 600 cm^{-1} [31]. The observed shift to the low-energy side may be due to intramolecular or intermolecular hydrogen bonding [31]. In the spectra of all the polychelates, this band is less broad than that of the ligand, indicating the absence of hydrogen bonding in the polychelates and participation of phenolic OH in the coordination [32]. In the IR spectra of all the polychelates, the peak due to phenolic OH may be assumed to be engulfed in the broad trough due to coordinated water.

2) A strong band at 1 643 cm^{-1} observed in the spectrum of the ligand may be assigned to $\gamma_{C=O}$ of the carboxylic group as well as that of $\gamma_{C=O}$ of the aldehyde group [33-35]. This band shifts to lower frequency in the region 1575-1630 cm^{-1} in the spectra of the polychelates, indicating ionization of the –COOH group and coordination through the COO^- group as well as the carbonyl group of the aldehyde [33-35].

3) A characteristic absorption of intermediate intensity is found at 1 112 cm^{-1} in the spectrum of the ligand, which may be assigned to the

C–O vibration of the hydrogen-bonded ring system of the ligand [36]. On chelation, this band shows a small positive shift, indicating coordination through oxygen [37].

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