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# Coordination Polymers. V. Spectral, Thermal, and Magnetic Properties of Polychelates Derived from 4,4′-Phenylylenebisazodisalicylic Acid

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## ABSTRACT

Polychelates of Cu(II), Ni(II), and Co(II) with 4,4'-phenylylenebisazodisalicylic acid have been prepared. All the polychelates are dark colored and insoluble in all common organic solvents. Octahedral structures are suggested on the basis of electronic spectral, infrared, magnetic susceptibility, and thermogravimetric analysis. A few ligand field parameters have been determined for the Ni(II) polychelate.

## INTRODUCTION

The demand for new polymeric materials with high thermal and chemical stability has stimulated research in many areas of polymer chemistry. Organic pigments are insoluble coordination complexes of organic compounds with metal ions, which are used in printing ink, plastics, rubbers, and protective and decorative coatings. This com-

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munication is in continuation with our previous work [1-4]. It describes the preparation and characterization of coordination polymers formed from 4,4'-phenylylenebisazodisalicylic acid and Cu(II), Ni(II), and Co(II).

## EXPERIMENTAL

### Materials

Salicylic acid and p-phenylenediamine were obtained from SD's Laboratory Chemical Industries. Metal chlorides from British Drug House, (India) Private Ltd., were used for the preparation of polychelates. Dimethylsulfoxide (DMSO) from Sarabhai M. Chemicals, Baroda, was used without further purification. All other chemicals used were of AnalaR grade.

### Preparation of the Ligand

A cold aqueous ethanolic tetrazotized solution of p-phenylenediamine (10 g) was poured into a cold solution of salicylic acid (13.8 g) in aqueous (100 mL) $Na_2CO_3$ (23 g). The reaction mixture was stirred for 3 h. When the coupling of the first mole of salicylic acid was completed, a second mole of it, dissolved in a minimum quantity of NaOH solution, was added to the reaction mixture and the stirring was continued until the reaction was complete (~2 h). The precipitated 4,4'-phenylylenebisazodisalicylic acid was filtered off, washed with water and then with alcohol, and dried in an oven at ~40°C.

### Preparation of Polychelates

Ligand and metal chloride solutions were prepared in DMSO. The ligand solution in slight excess over the metal:ligand ratio of 1:1 was added to the metal solution with constant stirring. About 1 g of sodium acetate was added to the hot reaction mixture. The resulting reaction mixture was then refluxed for 6 to 8 h. The precipitated polychelate was filtered, washed with hot DMSO followed by water, and then dried in an oven at 70°C.

### Measurements

Carbon and hydrogen were estimated by the usual microanalytical methods with a Coleman C-H analyzer. Infrared spectra were recorded using KBr pellets in the range 3600-400 $cm^{-1}$ using a Carl Zeiss UR-10 spectrophotometer. Electronic absorption spectra were studied in the solid state by employing a Beckman DU-spectrophotometer in the range 360-1300 nm. Magnetic measurements were done by Gouy's method using a Sartorius semimicro Gouy balance. Thermal analysis was done by heating the samples at the rate 10°C/min and recording the weight with increasing temperature. For establishing the composition, the metal content in each polychelate was determined by independent volumetric and gravimetric methods.

## RESULTS AND DISCUSSION

The polychelates are dark colored solids and insoluble in water and in most of the common organic solvents. Therefore it was not possible to characterize them by conventional methods. The analytical data (Table 1) suggest a $ML.3H_2O$ composition for all the polychelates.

The solution spectrum of the ligand in DMF shows a strong band at 25,641 $cm^{-1}$ and a shoulder at 23,255 $cm^{-1}$. The former band may be due to $\pi \rightarrow \pi^*$ transition and the latter may be due to $n \rightarrow \pi^*$ transition [5]. The high intensity of these bands and their large red shift compared to azobenzene may be attributed to extensive conjugation between the rings and –N=N– groups, resulting in the lowering of the $\pi^*$ orbital energy [6].

The diffuse reflectance spectra of all the polychelates show a high intense band in the region 22,220-20,830 $cm^{-1}$. This band may be due to a $n \rightarrow \pi^*$ transition of the ligand system. However, the large red

TABLE 1. Analytical Data

| | Elemental analysis found (calc) | | |
|---|---|---|---|
| Compound | Metal (%) | C (%) | H (%) |
| $C_{20}H_{14}N_4O_6H_2O$ | - | 57.00<br>(56.60) | 3.9<br>(3.77) |
| $[Cu(C_{20}H_{12}N_4O_6)(H_2O)_2.H_2O]$ | 12.20<br>(12.18) | 47.10<br>(46.02) | 4.03<br>(3.45) |
| $[Ni(C_{20}H_{12}N_4O_6)(H_2O)_2.H_2O]$ | 11.78<br>(11.36) | 47.78<br>(46.44) | 4.03<br>(3.48) |
| $[Co(C_{20}H_{12}N_4O_6)(H_2O)_2.H_2O]$ | 11.30<br>(11.40) | 47.48<br>(46.42) | 4.94<br>(3.48) |

shift observed as compared to the ligand band may be due to extended conjugation to the coordinated ligands through the metal ion.

The Cu(II) polychelate shows a broad band with some structures at 12,220, 12,990, and 13,890 $cm^{-1}$. This spectral pattern may well be due to distorted octahedral stereochemistry [7]. The $d^9$ configuration is highly John-Teller unstable, and the resulting tetragonal distortion ($D_4h$) leads to further splittings of the $E_g$ and $T_{2g}$ levels (of oh) into $B_{1g}$, $A_{1g}$ and $B_{2g}$, $E_g$ levels, respectively. Therefore the three bands observed might correspond to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions in a weakly distorted complex, respectively. The magnetic moment of the polychelate (1.8 B.M.) is consistent with the presence of a single unpaired electron.

The diffuse reflectance spectrum of Ni(II) polychelate shows bands at 25,000, 15,386, and 9524 $cm^{-1}$. The latter two bands may be safely assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(\nu_1)$ transitions, respectively, in an octahedral stereochemistry. The observed $\nu_2/\nu_1$ ratio (1.62) also confirms the octahedral structure for the Ni(II) polychelate. The former band may be due to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_3)$ mixed with the ligand $\pi \rightarrow \pi^*$ band. Due to the high intensity of this band, it is rather difficult to recognize it as a d-d transition. However, we have tried to calculate $\nu_3$ using the observed $\nu_1$ and $\nu_2$ values, following the ligand field theory of spin-allowed transitions [8]. The calculated $\nu_3$ (Table 2) fits well with the observed band and therefore it is assigned as $\nu_3$. Further, we have computed the important ligand field parameters $10D_q$, $B_{35}$, and $\beta_{35}$ [8]. An attempt has been made to obtain the value of λ using [9, 10]

$$\lambda = \frac{2.7 \times B^2{}_{35}}{10D_q} = -175 \text{ cm}^{-1}$$

$B_{35}$ used here was the value obtained from Method c. This is considerably lower than the free ion value. The room temperature magnetic moment of the polychelate is within the range required for octahedral stereochemistry. To correlate the spectral and magnetic properties, $\mu_{eff}$ was calculated by [11]

$$\mu_{eff}^{cal} = \mu_{eff}^{s.o.} \left(1 - \frac{4\lambda_{obs}}{10D_q}\right)$$

TABLE 2. Electronic Spectral Data and Calculated Transition Energies ($cm^{-1}$) of the Spin-Allowed Bands of Ni(II) Polychelate

| Method of calculation | Observed and calculated transition energies ($cm^{-1}$) $\nu_1$ | $\nu_2$ | $\nu_3$ | $B_{35}$ | $\beta_{35}$ |
|---|---|---|---|---|---|
| Experiment | 9,524 | 15,380 | 25,000 | - | - |
| a | $10D_q$ | Fitted | 25,374 | 812 | 0.751 |
| b | $10D_q$ | 15,296 | Fitted | 781 | 0.720 |
| c | $10D_q$ | 15,312 | 25,068 | 787 | 0.723 |

The calculated value (3.03 BM) is found to be in good agreement with the observed one (3.18 BM).

The diffuse reflectance spectrum of Co(II) polychelate shows three bands at 25,000, 22,730, and 8,696 $cm^{-1}$. The former two bands may be ligand $\pi \to \pi^*$ and $n \to \pi^*$ bands, respectively, and probably mixed with the charge transfer process [12]. The band at 8,696 $cm^{-1}$ may be assigned to the $^4T_{1g}(F) \to {}^4T_{2g}(F)$ ($\nu_1$) transition in an octahedral stereochemistry. The room temperature magnetic moment (4.5 BM) of the polychelate is slightly lower than the range required for high spin octahedral stereochemistry. This low magnetic moment may be due to the presence of a low symmetry component [13, 14].

TGA data (Table 3) indicate that the ligand as well as all the polychelates decompose in a gradual manner rather than with the sharp decomposition observed earlier [15]. Here all the polychelates show residues not conforming to the corresponding metal oxides, even at 800°C, indicating that the composition of the organic moiety remains incomplete even at this temperature. The ligand loses 4.76% weight at 120°C, which corresponds to the presence of one water molecule in the ligand [2]. The association of water molecule with the ligand may be due to hydrogen bonding to the azo group [16]. The Cu(II), Ni(II), and Co(II) polychelates show weight losses of 11.4, 10.7, and 10.4%, respectively, at 160°C. This may be attributed to the loss of three water molecules per repeating unit of polychelate.

An attempt has been made to determine the bonding site in polychelates. Because of the presence of several aromatic rings in the ligand and polychelates, it is rather difficult to derive definite conclusions on the bonding sites due to the presence of $\nu_{C=C}$. However, some important stray findings are given below:

1. The infrared spectrum of the ligand shows a strong absorption band at ~3400 $cm^{-1}$ which may be due to coupling of the stretching

TABLE 3. Thermogravimetric Analysis Data

| Temperature (°C) | Weight loss of ligand (%) | Percentage of weight loss of | | |
|---|---|---|---|---|
| | | Cu | Ni | Co |
| 80 | 0.79 | 2.0 | 2.30 | 1.48 |
| 100 | 3.18 | 6.07 | 4.6 | 4.45 |
| 120 | 4.76 | 7.38 | 6.87 | 5.93 |
| 140 | 5.55 | 10.07 | 8.4 | 8.15 |
| 160 | 7.94 | 11.41 | 10.7 | 10.37 |
| 180 | 8.73 | 12.08 | 13.74 | 12.59 |
| 200 | 10.32 | 12.76 | 15.27 | 15.55 |
| 300 | 26.19 | 29.53 | 34.36 | 20.74 |
| 400 | 30.15 | 35.57 | 35.12 | 35.55 |
| 500 | 37.30 | 42.95 | 43.52 | 40.74 |
| 600 | 46.03 | 48.32 | 50.40 | 47.41 |
| 700 | 55.55 | 56.38 | 63.30 | 57.04 |
| 800 | 65.87 | 63.22 | 68.70 | 65.92 |

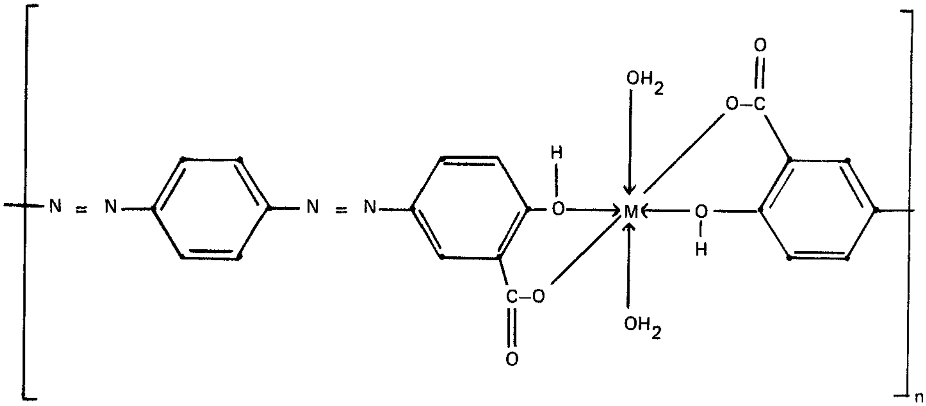
vibrations of the phenolic and carboxylic hydroxyl groups as well as that of the hydroxyl group of the water molecule associated with the ligand. $\nu_{OH}$ usually occurs at 3600 $cm^{-1}$. The observed shift to the low energy side might be due to the presence of intramolecular or intermolecular hydrogen bonding [17]. However, because such a band is observed in the spectra of all the polychelates, the presence of water molecules is confirmed.

2. The ligand shows a broad band centered around 1300 $cm^{-1}$ which may be assigned to the in-plane bending vibration of O–H [18]. All the polychelates also show this band, which confirms the presence of water.

3. It is rather difficult to assign the band due to $\nu_{N=N}$ as it can be confused with the band due to $\nu_{C=O}$. Therefore, the very strong band at ~1605 $cm^{-1}$ may be due to $\nu_{N=N}$ or $\nu_{C=O}$.

4. The weak band at 1095 $cm^{-1}$ may be attributed to C–O vibrations of the ligand. This band does not show a marked shift in the spectra of polychelates, indicating that this frequency is not sensitive to chelation [19].

The polymeric chain may be straight, and the following general structure may be given for the chelate polymers.



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