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Thermal and electrical studies of some polychelates

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Abstract: Polychelates of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) with 4,4′-dihydroxy-3,3′-diacetylbiphenyl-dithioxamide (DDBDO) have been prepared. Their structures were determined by visible reflectance spectroscopy and magnetic measurements in conjunction with thermogravimetric and IR measurements. Elemental analysis indicates a 1:1 metal-ligand stoichiometry and the association of water molecules with the central metal. The decomposition temperature of the chelates is in the order Ni(II) > Fe(II) > Co(II) > Mn(II) > Cu(II). Thermal activation energies (E_a), calculated with the help of Freeman-Carroll and Sharp-Wentworth methods, are in agreement with each other. The polychelates were found to be semiconductive, and the activation energy obtained from semiconducting behavior follows the order Co(II) > Ni(II) > Fe(II) > Cu(II) > Mn(II). The probable structure, such as six coordinated octahedral for Mn(II) and Fe(II) polychelates and four coordinated square planar for Co(II), Ni(II), and Cu(II) polychelates, have been suggested.

Key words: Polychelates; decomposition temperature; thermal activation energy; IR measurements

Introduction

Polychelates having good thermal stability and catalytic activity have enhanced the development of polymeric materials either from polymeric or monomeric ligands. The first-row transition metals are characterized by their ability to form a wide range of coordination complexes, in which octahedral, tetrahedral, or square planar stereochemistry predominate. This inspired us to prepare a polymeric ligand, which would be able to form complexes with a variety of transition metals. In the present study, we report the synthesis and characterization of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) polychelates derived from 4,4′-dihydroxy-3,3′-diacetyl biphenyl-dithioxamide (DDBDO), its thermal degradation, and semiconducting behavior.

Experimental

All the metal acetates and chemicals used in the present work were of A.R. grade. All the solvents were used after double distillation.

Preparation of the ligand

The ligand (DDBDO) was prepared from the hydroxy ketone 4,4′-dihydroxy-3,3′-diacetyl biphenyl (DDABP) and dithiooxamide, as described below.

DDABP and dithiooxamide were dissolved separately in hot ethanol in stoichiometric proportion and were mixed and refluxed for 8 h. The mixture was cooled and an orange/yellow colored product precipitated. This was filtered off, washed with ethanol, and dried. It was insoluble in common organic solvents, but found to be soluble in DMF, DMSO, and H_2SO_4; M.P. 210 °C.

Preparation of chelates

Equimolar quantities of metal acetate and ligand DDBDO were dissolved separately in a minimum quantity of DMF and mixed. The reaction mixture was refluxed for 4–5 h. The colored products obtained with different metals were filtered off, washed throughly with first DMF, then ethanol, followed by acetone, and dried in a vacuum desiccator over $CaCl_2$. All the coordination polymers are dark-colored solids, insoluble in common organic solvents. Therefore, it was not possible to characterize their molecular weight by conventional methods.

Physical measurements

Magnetic susceptibility measurements were made on a Gouy balance at room temperature, using Hg [$CO(SCN)_4$] as calibrant. Pascal's constant was used for calculating diamagnetic corrections. Diffuse reflectance and IR spectra were recorded on a Carl-Zeiss spectrophotometer VSU-2P and Perkin-Elmer model 577 spectrophotometer, respectively. The thermogravimetric results, with heating rate 10 °C min^{-1}, were recorded on a TGS-2 TG analyzer connected to a TADS computer system (Perkin-Elmer) at RSIC, Nagpur. The electrical resistivities of the polychelates were measured over a wide range of temperature (304–515 K) in air by using a BPL-India Million Megohmmeter Model RM 160 MK IIIA at the Institute of Science, Nagpur.

Results and discussion

Characterization data are given in Table 1 and show that all the polychelates have the general formula $[\mathrm{ML}]_n$.

IR studies

On comparing the infrared spectra of a ligand and its polychelates, it is inferred that they are virtually identical. However, they show important differences. The presence of a strong band at about 1590 cm^{-1} in the ligand spectrum may be assigned to a C=N vibration. This band is shifted to lower frequency, indicating nitrogen coordination in the polymers. The shift of the band towards the low frequency region may suggest wider delocalization of the electronic charge in the newly formed chelate ring and strong bonding between –C=N group and metal ions on coordination [1]. The spectrum of the ligand shows a band around 3120 cm^{-1}, which may be assigned to –OH stretching. The existence of this band at higher frequency than desired (3275–3500 cm^{-1}) for phenolic OH frequency may be due to intramolecular hydrogen bonding, which is presumed to be formed between phenolic OH and amide nitrogen. On complexation, this band disappears, indicating the loss of phenolic OH hydrogen on coordination. The medium strong band at about 1220 cm^{-1} in the ligand may be given for the phenolic C–O vibration. On coordination, this band shows a marked shift towards higher frequency, indicating involvement of oxygen of phenolic C–O in bonding with a metal ion. The IR spectra of ligand show one sharp band at 830 cm^{-1}, which may be assigned to the –C=S group [2]. This has been found at the same position in the metal chelates with medium or nearly the same intensity. This observation may suggest that –C=S is free in the chelate, which indicates it does not take part in the chelate formation [3]. All polychelates exhibit very broad bands in the range 3200–3400 cm^{-1} and a weak band around

Table 1. Analytical, magnetic moment, and electronic spectra data

Compound	Elemental analysis found (calc.)%					μ_{eff} (B.M.)	Electronic band position cm^{-1}
	M	C	H	N	S		
DDBDO	–	61.58 (61.10)	4.23 (3.95)	8.34 (7.90)	18.13 (18.07)	–	–
$[\mathrm{Mn(II)(DDBDO)2H_2O}]_n$	12.34 (13.10)	48.54 (49.54)	3.59 (3.51)	6.29 (7.14)	14.38 (14.24)	5.92	23520 $6A_{1g} \rightarrow 4A_{1g}4E_g(G)$ 15621 $\rightarrow 4T_{2g}(G)$ 13153 $\rightarrow 4T_{1g}(G)$
$[\mathrm{Fe(II)\text{-}(DDBDO)2H_2O}]_n$	12.54 (13.41)	48.44 (49.10)	3.58 (3.64)	6.28 (6.19)	14.35 (14.42)	5.59	15621 C.T. $\left.\begin{array}{l}11624\\10980\end{array}\right\} 5T_{2g}(D) \rightarrow 5E_g$
$\{[\mathrm{CO(II)(DDBDO)}]\mathrm{2H_2O}\}_n$	13.12 (13.35)	48.11 (49.07)	3.56 (3.91)	6.23 (6.21)	14.25 (14.36)	2.47	$\left.\begin{array}{l}20830\\15190\end{array}\right\} 2A_{1g} \rightarrow 2E_g$ 12820 $\rightarrow 2B_{1g}$
$\{[\mathrm{Ni(II)\text{-}(DDBDO)}]\mathrm{H_2O}\}_n$	14.22 (14.25)	52.33 (53.04)	3.87 (3.97)	6.78 (7.01)	15.50 (15.60)	1.69	16120 $1A_{1g} \rightarrow 1B_{2g}$ 14280 $\rightarrow 1B_{1g}$
$\{[\mathrm{Cu(II)\text{-}(DDBDO)}]\mathrm{H_2O}\}_n$	14.09 (14.10)	47.62 (47.65)	3.52 (3.62)	6.17 (6.34)	14.11 (14.15)	1.71	15870 $2B_{1g} \rightarrow 2B_{2g}$ $\left.\begin{array}{l}12820\\11110\end{array}\right\} \rightarrow 2A_{1g}$

790 cm^{-1}, which may be assigned to ν_{OH} of water. The nature of the water molecules (coordinated or latticed) is confirmed by ■ (TG) analysis. In all the polychelates, the observed new band in the neighborhood of 530–600 cm^{-1} and 460–490 cm^{-1} may be identified as M–O and M–N stretching frequencies, respectively [4].

Reflectance studies

The spectrum of the Mn(II) polychelate exhibits three weak bands in the region normally expected for an Mn(II)-octahedral structure [5] (Table 1). The extremely low intensities of these bands are further indicative of octahedral geometry as a consequence of their doubly forbidden nature [6]. The observed magnetic moment of the Mn(II)-polychelate is 5.92 B.M. at room temperature, which is slightly greater than the spin-only value, but is within its limits for five unpaired electrons, indicating that the polymer is high-spin octahedral [7] (Fig. 3).

The Fe(II)-polychelate shows a doublet band in the 10 980–11 620 cm^{-1} region. The bands in this region are characteristic of Fe(II) high-spin octahedral complexes (Fig. 3). Cotton et al. [8] suggested a swan type of doublet band in six coordinated Fe(II). Complexes could be due to either John-Teller or D_4h distortion (Table 1).

Crystal field parameters D_q, B, C (Racah inter electronic repulsion parameter), and β (Nephelauxetic ratio) have been determined by using the relationship g.

$$E(^5T_{2g} \rightarrow {^5E_g}) = 10\,D_q \qquad (1)$$

$$10\,D_q = \tfrac{5}{2}B + 4C$$

$$= 18.5\,B \quad (\because C = 4B) \text{ and}$$

$$\beta = \frac{B \text{ in the complex}}{B \text{ in the free ion}}\,.$$

B values for the free ion was taken to be 1060 cm^{-1} [7]. The values of crystal field parameters and nephelauxetic ratio are $D_q = 1098$ cm^{-1}, $B = 594$ cm^{-1}, $C = 2376$ cm^{-1}, and $\beta = 0.563$.

These values also favor tetragonally distorted octahedral geometry for the Fe(II)-polychelate, which is consistent with the results reported by Shah et al. [10]. In the present study, a reduction of

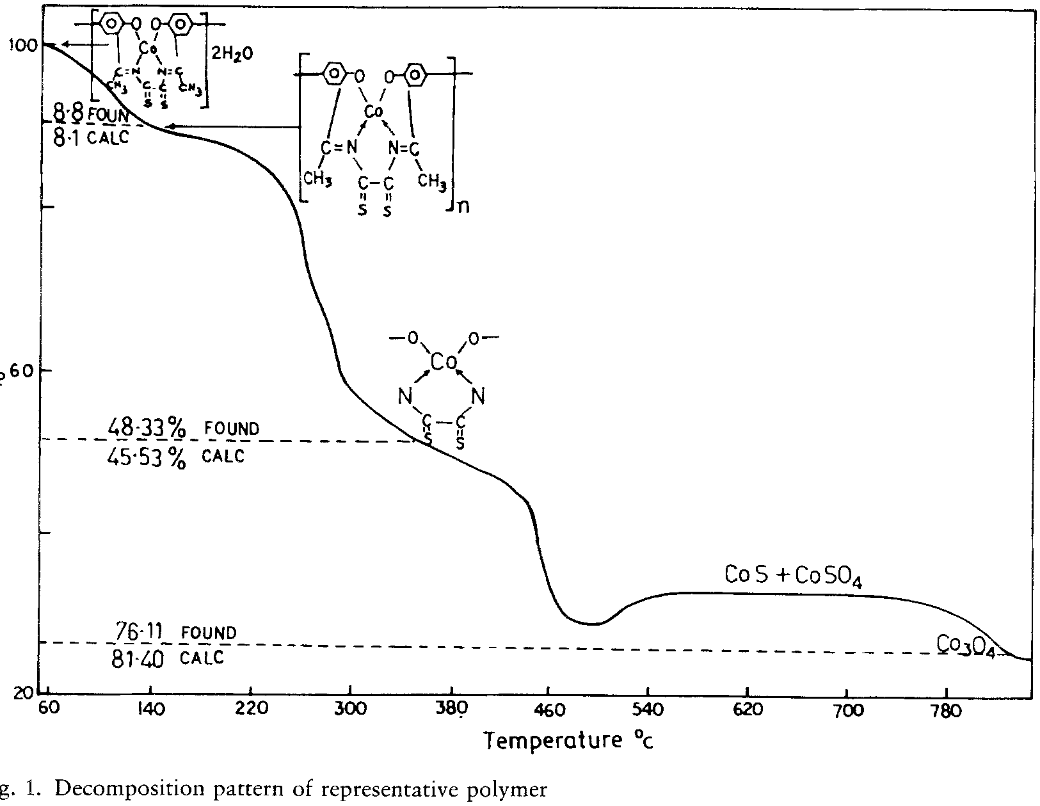

Fig. 1. Decomposition pattern of representative polymer

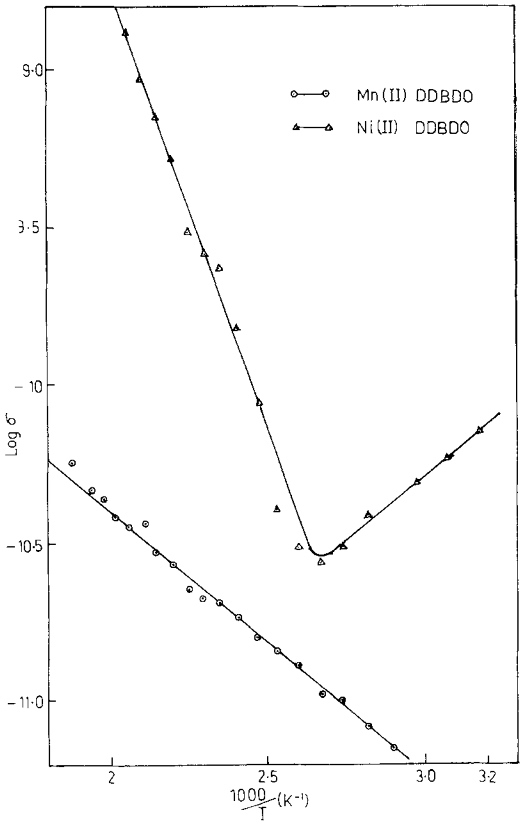

Fig. 2. Temperature dependence of log σ

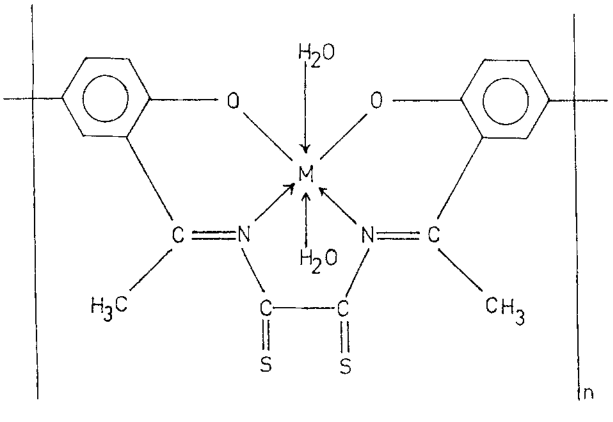

Fig. 3. M = Mn(II), Fe(II)

B value was observed upon chelation. This indicates that the small amount of the σ and π electron density on the metal may be transferred to the ligand. Such delocalization will increase the mean distance between d-electrons and thereby reduce B. In other words, a decrease in the B value suggests the partial covalent nature of the M–L bond [6].

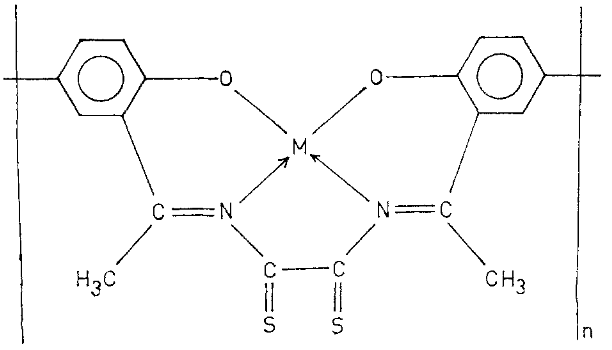

Fig. 4. M = Co(II), Ni(II), Cu(II)

The magnetic moment of the Fe(II) polychelate is 5.59 B.M. It is in the range expected for Fe(II) derivatives in high-spin octahedral geometry.

The diffuse reflectance spectrum of CO(II) polychelate exhibits two prominent bands, one of medium intensity at 12820 cm^{-1} and the other higher intensity band at 18200–20830 cm^{-1}, attributable to $2A_{1g} \rightarrow 2B_{1g}$ and $^2A_{1g} \rightarrow {}^2E_g$ transitions, respectively, in square planar geometry (II). The magnetic moment of this polychelate is found to be 2.47 B.M. (Table 1), which is well within the range (2.48–2.70 B.M.) expected for square planar Co(II) complexes [12, 13] (Fig. 4).

The reflectance spectra of Ni(II)-Polychelate show multiple bands around 15000–17000 cm^{-1}. The band at 14280 cm^{-1} and 16124 cm^{-1} may be assigned to $1A_{1g} \rightarrow 1B_{1g}$ and $1A_{1g} \rightarrow 1B_{2g}$ transitions, respectively [14]. Drago [15] and Holm [16] have suggested tetragonal or square planar geometry for Ni(II) complexes on the basis of similar spectral transition. The magnetic moment of Ni(II) polychelate is found to be 1.69 B.M. (Table 1), which is unusual and lower than spin-only value of two unpaired electrons. Holt et al. [17] and others [6, 18, 19] suggested that the partial paramagnetic moment of the Ni(II) complex may be attributed to the square planar tetrahedral equilibrium. Therefore, a square planar geometry can be suggested for Ni(II) chelate in the present case (Fig. 4).

The electronic spectrum of the Cu(II)-polychelate shows two bands in the region normally expected for square planar Cu(II) complexes [20] (Table 1). These bands may be due to a d–d transition, which suggests square planar geometry [21]. The broadness of the band around 11110–12824 cm^{-1} may be an indication of lower symmetry. Their room temperature magnetic moment is 1.71 B.M., which also supports a square planar geometry [12] (Fig. 4). The observed magnetic moment is very close to the spin-only value, suggesting that the orbital contribution is almost quenched by the crystal field [22].

Thermal studies

The thermal degradation study of coordination polymers has become a subject of recent interest. The thermal behavior of a polymer in air at different temperatures provides information of practical importance. The procedural decomposition temperature of the polychelates is given in Table 2. The presence of coordinated water molecules, which is suggested from the IR spectra, is confirmed by the TG data. From the TG curve (Fig. 1), it can be seen that there are three distinct stages in the degradation process. In the first stage for the Mn(II) and Fe(II) polychelates, the loss near 160–240 °C is 9.60% and 10.20%, respectively. These weight losses correspond to two coordinated water molecules per repeating unit of polychelate [23]. The Co(II), Ni(II), and Cu(II) polychelates show weight losses at 110–140 °C equal to 8.80%, 4.50%, and 4.70%, respectively; these weight losses correspond to two, one, and one lattice water molecules, respectively [2]. In the second stage, there is further weight loss. Ultimately, the polymers decompose at 800 °C, leaving behind a residue corresponding to the formation of metal oxides in air [24]. In all the chelates, the rate of decomposition in the first stage is rapid compared to the second stage. The observed weight loss is a little higher than that required. This may be due to some other chain degradation reactions involved in pyrolysis of the polychelates [24]. The thermal activation energy was calculated by employing both the Freeman-Carroll [25] and Sharp-Wentworth [26] methods. The comparable values are summarized in Table 2. In all the DDBDO polychelates except the Fe(II) polychelate, it is observed that there is a slight increase in the weight of residue after 370 °C. Such type of results have been obtained by Sceney et al. [27, 28] and suggest that the increase in weight is due to the oxidation of Cu_2S to CuO and $CuSO_4$.

Electrical studies

Semiconduction of **metallic** compounds is of current interest. Some work on the semiconducting properties of chelate polymers has been reported from this laboratory [1, 29].

Conductivity measurements were made over a wide range of temperature using pelleted material. The electrical conductivity σ was found to vary exponentially with the absolute temperature at higher temperature according to the relationship

Table 2. Thermal and electrical data

Compound	Decomposition Temp °C	Activation energy FC (kJ/mole)SW		Electrical conductivity $\sigma^{\Omega^{-1}}\text{cm}^{-1}(T\ ^\circ\text{K})$ (324, 374 and 514 °K)	E_a (ev)
Mn-DDBDO	250	29.74	31.88	5.011×10^{-12} 1.047×10^{-11} 4.665×10^{-11}	0.163
Fc-DDBDO	270	21.25	22.97	4.168×10^{-9} 5.623×10^{-8} 1.064×10^{-7}	0.314
Co-DDBDO	260	23.30	22.30	6.108×10^{-10} 1.780×10^{-9} 8.900×10^{-8}	0.642
Ni-DDBDO	325	22.92	16.98	6.160×10^{-11} 2.730×10^{-11} 5.460×10^{-9}	0.543
Cu-DDBDO	220	22.97	23.55	7.923×10^{-7} 3.671×10^{-6} 1.101×10^{-5}	0.193

[30]

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right), \tag{2}$$

where E_a is the activation energy of the semiconductor and σ_0 is a constant. This relationship was not obtained at lower temperature. The values of σ at room temperature and in the temperature range 324–514 K and E_a are given in Table 2.

It can be seen from the plots (Fig. 2) that there are two distinct regions. In the low temperature region, the slopes of plots have small values and the polymers present extrinsic conduction. In the high temperature region, a linear dependence of log $\sigma = F(1/T)$ was observed. In this temperature domain, the polymers present intrinsic conduction [30]. There is an anomalous electrical conductance change with temperature in Ni(II), Co(II), and Fe(II)-polychelates; i.e., above room temperature to nearly 85 °C, the conductance decreases as temperature increases and after 85 °C the conductance increases with temperature. The initial trend is typical of metallic conduction, while the latter part of behavior is a characteristic of semiconduction. The metal-metal interaction may be responsible for anomalous behavior of these polychelates [31]. From the analysis of our results, it can be assumed that the difference in the electrical properties of the polymers studied are determined mainly by their chemical structure [32].

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