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### Magnetic, Spectral, Thermal, and Electrical Properties of Coordination Polymers Derived From $\beta,\beta'$ -(2-Hydroxyl-5-Methylbenzoyl)-*p*-Divinylbenzene

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# MAGNETIC, SPECTRAL, THERMAL, AND ELECTRICAL PROPERTIES OF COORDINATION POLYMERS DERIVED FROM $\beta,\beta'$ -(2-HYDROXYL-5-METHYLBENZOYL)-*p*-DIVINYLBENZENE

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## ABSTRACT

Coordination polymers of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) have been prepared from  $\beta,\beta'$ -(2-hydroxyl-5-methylbenzoyl)-*p*-divinylbenzene. The analytical data are found to be consistent with 1:1 metal:ligand stoichiometry. Elemental analyses, magnetic, spectral (IR and electronic), thermal, and electrical properties of the coordination polymers have been studied, and probable structures are assigned to them. All of them are amorphous powders and insoluble in common organic solvents.

## INTRODUCTION

The interaction between metal ions and ligands may lead to the formation of coordination polymers in which the chelated metal ions are bridged by

ligand molecules [1, 2]. The formation of macromolecular chains may be expected for a ligand with two chelating sites which, for steric reasons, cannot interact with the same metal ion [3]. There are numerous reports [4-7] of the preparation of bisphenolic chelate polymers. Several amorphous and crystalline bisphenolic macromolecular chelates have been described [8-11]. They are usually obtained in the form of insoluble and infusible powders. It has been pointed out [12] that properly designed coordination polymers of transition metals should have semiconductive properties, and the formation of semiconductive coordination polymers has indeed been observed [13, 14].

This paper describes the preparation and properties of coordination polymers of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with the ligand  $\beta$ - $\beta'$ -(2-hydroxyl-5-methylbenzoyl)-*p*-divinylbenzene (HMBDB).

## EXPERIMENTAL

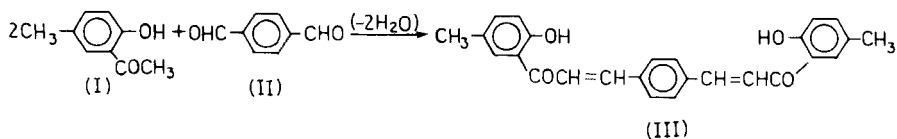
### Material

All the chemicals were obtained in chemically pure quality. They were used as such, except DMF, which was distilled before use.

### Preparation of the Ligand (HMBDB)

To a boiling solution of 2-hydroxyl-5-methylacetophenone (I) and terephthalaldehyde (II) in ethanol, 40% NaOH solution was slowly added with vigorous stirring. The mixture was stirred mechanically at room temperature for 3-4 h to obtain a red mass. It was decomposed with ice-cold concentrated hydrochloric acid. The separated yellow granular product was filtered off and washed with 10% sodium bicarbonate solution followed by water. Crystallization was effected by DMF to yield fine needle-like crystals of (III). Yield = 65%, mp = 245°C. Found: C, 78.71; H, 5.61%. Calculated for C<sub>26</sub>H<sub>22</sub>O<sub>4</sub>: C, 78.39; H, 5.53%.

The reaction taking place is as follows:



### Preparation of Polychelates

The coordination polymers were prepared by mixing a hot solution of metal acetate (0.01 mol) in dimethylformamide (DMF) with a solution of the ligand (HMBDB) (0.01 mol) in DMF. The resultant mixture was digested on a boiling-water bath for 5 h, whereby the product separated out. The colored products were filtered, washed thoroughly with DMF, hot water, and acetone, and then dried in a vacuum desiccator over calcium chloride. For the Fe(II) chelate, iron(II) acetylacetonate was used.

### Measurements

The metal contents in the chelate polymers were determined by volumetric (EDTA) and gravimetric analysis. Carbon and hydrogen contents were determined by the usual microanalytical methods. Diffuse reflectance spectra were measured on a Carl Zeiss spectrophotometer VSU-2P with MgO as reference. Magnetic measurements were made on a standard Gouy balance at room temperature with Hg[Co(NCS)<sub>4</sub>] as calibrant. IR spectra were recorded on a Specord-IR-75 spectrophotometer in the range of 4000 to 400 cm<sup>-1</sup>. Thermograms were scanned with a heating rate of 5°C/min in a platinum crucible. The electrical resistivity of the coordination polymers was measured over a wide range of temperature in air using a Million megohmmeter, Model RM 160 MK IIIA, BPL, India.

## RESULTS AND DISCUSSION

The reaction of 2-hydroxyl-5-methylacetophenone (I) and terephthalaldehyde (II) in the presence of concentrated alkali yields the  $\beta,\beta'$ -(2-hydroxyl-5-methylbenzoyl)-*p*-divinylbenzene (HMBDB) (III), the formulation of which is supported by analytical and spectral data. Its <sup>1</sup>H-NMR spectrum in DMSO-*d*<sub>6</sub> shows multiple signals at  $\delta$  7.20-8.00 ppm, which are due to aromatic protons, while the weak doublet signal at 6.75-6.95 ppm may be due to hydrogen-bonded protons of phenolic hydroxyl groups [15]. Intense signals at 2.20-2.50 ppm may be assigned to methyl protons, while the signal at 3.45 ppm may be assigned to protons of the -CH=CH- group [16]. Electronic absorption spectra of HMBDB in DMF display absorption bands at 260, 290, and 380 nm. The intense absorption band at 260 nm is characteristic of the  $\pi \rightarrow \pi^*$  transition of the -CH=CH- group, while the

TABLE 1. Analytical Data and Physical Properties

Chelate	Color	Analysis, %			MW <sup>b</sup>
		M	C	H	
$[\text{Cu-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}]_n$	Dark red	12.73 (12.82)	63.01 (62.96)	4.28 (4.84)	495.54
$[(\text{Ni-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]_n$	Yellow orange	11.24 (11.15)	59.82 (59.23)	5.48 (5.32)	526.71
$[(\text{Co-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]_n$	Buff	11.35 (11.18)	60.02 (59.21)	5.34 (5.31)	526.93
$[\text{Fe-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}]_n$	Red brown	11.20 (11.45)	64.09 (63.95)	4.65 (4.92)	487.85
$[\text{Mn-C}_{26}\text{H}_{20}\text{O}_4]_n$	Grey	12.09 (12.18)	68.85 (69.19)	4.48 (4.43)	450.93
$[(\text{Zn-C}_{26}\text{H}_{20}\text{O}_4) \cdot 5\text{H}_2\text{O}]_n$	White	12.02 (11.85)	57.05 (56.59)	5.69 (5.44)	551.37

<sup>a</sup>Theoretical values are given in parentheses.<sup>b</sup>Molecular weight of repeat unit estimated from elemental analysis.

band at 290 nm is due to the  $n \rightarrow \pi^*$  transition, which corresponds to the  $>C=O$  group. A broad absorption band near 380 nm may be assigned to extended conjugation due to the polar resonance forms [16].

The reaction of the ligand (HMBDB) with metal salts yielded amorphous complexes that were found to be quite stable in the atmosphere. The chelates in the present studies are described in Table 1.

All the chelates are colored and insoluble in common organic solvents. Hence, it was not possible to characterize them by conventional methods, like osmometry, viscometry, and conductometry. Elemental analysis (Table 1) showed that they exhibit 1:1 metal-to-ligand stoichiometry and also suggests the possibility of the association with water in all except the Mn(II)-chelate [17, 18]. This is reasonable since water allows the maximum coordination number of the metal ion to reach six [18-20].

The reflectance spectral and magnetic data are given in Table 2. The magnetic moment of copper(II) chelate polymer is 1.97 BM, very close to the spin-only value of 1.73 BM expected for one unpaired electron, which offers the possibility of octahedral symmetry [21]. The nickel(II) chelate polymer shows a magnetic moment of 3.08 BM, which is in agreement with that of Kohli et al. [22], suggesting octahedral geometry. The value for the cobalt(II) chelate, 5.29 BM reported here, may be due to the octahedral structure [23].

The iron(II) chelate polymer has a magnetic moment of 5.36 BM, which is lower than expected on the basis of a  $^5T_{2g}$  ground term for high-spin octahedral stereochemistry (5.5 BM). The lowering of the magnetic moment suggests the polymeric nature of the chelate [24]. Manganese(II) polychelate has 5.12 BM, lower than that expected on the basis of the spin-only value [25]. This may be due to spin exchange in the solid state of the complexes [26] or to air oxidation of Mn(II) to Mn(III) during preparation. However, some workers [27] explain this low magnetic moment on the basis of anti-ferromagnetic interaction between manganese(II) ions in the solid state. The zinc(II) chelate polymer is diamagnetic and may have a tetrahedral structure.

The diffuse reflectance spectrum of copper(II) chelate exhibits a medium band at  $10\,870\text{ cm}^{-1}$ , a broad band centered at  $15\,630\text{ cm}^{-1}$  associated with a shoulder at  $17\,240\text{ cm}^{-1}$ , and an intense broad band at  $21\,940\text{ cm}^{-1}$ . The band positions are in accordance with distorted octahedral geometry [28]. The broad band at  $15\,630\text{ cm}^{-1}$ , associated with a shoulder at  $17\,240\text{ cm}^{-1}$  in the spectrum, indicates distortion in the chelate. The nickel(II) polychelate shows bands at  $10\,145$ ,  $15\,630$ , and  $22\,220\text{ cm}^{-1}$ , similar to the spectrum expected for an octahedral spin-free nickel(II) complex [29]. The structure is further supported by the ratio of  $\nu_2/\nu_1$  which is 1.54, close to the value

TABLE 2. Electronic Spectral

Chelate	Energies, $\text{cm}^{-1}$	
	Observed	Calculated
$[\text{Cu-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}]_n$	10 870	—
	15 630	—
	17 240 <sup>(sh)</sup>	—
	21 940	—
$[(\text{Ni-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]_n$	10 145	10 145
	15 630	14 790
	22 220	23 060
$[(\text{Co-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}]_n$	9 800	—
	17 540	20 814
	20 620	—
$[\text{Fe-C}_{26}\text{H}_{20}\text{O}_4 \cdot 2\text{H}_2\text{O}]_n$	10 810	—
	16 660	—
	20 000	—
$[\text{Mn-C}_{26}\text{H}_{20}\text{O}_4]_n$	16 530	—
	20 410	—
	22 220	—
	23 520	—
$[(\text{Zn-C}_{26}\text{H}_{20}\text{O}_4) \cdot 5\text{H}_2\text{O}]_n$	—	—

<sup>a</sup><sub>sh</sub> = shoulder, C.T. = charge transfer complex.

Data and Magnetic Moment<sup>a</sup>

Assignments	Spectral parameters calculated	$\mu_{\text{eff}}$ , BM
${}^2B_{1g} \rightarrow {}^2A_{1g}$		1.97
${}^2B_{1g} \rightarrow {}^2B_{2g}$		
${}^2B_{1g} \rightarrow {}^2E_g$		
C.T.		
${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)\nu_1$	$\nu_2/\nu_1 = 1.54, B_{35} = 494.33 \text{ cm}^{-1}$	3.08
${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\nu_2$	$Dq = 1014.5 \text{ cm}^{-1}, \beta_{35} = 0.458$	
${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)\nu_3$	$\text{LFSE} = 34.79 \text{ kcal/mol}, \beta_{35}^\circ = 54.22\%$	
${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)\nu_1$	$\nu_2/\nu_1 = 1.79, B = 802.27 \text{ cm}^{-1}$	5.29
${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\nu_2$	$Dq = 1101.41 \text{ cm}^{-1}, \beta = 0.716$	
${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\nu_3$	$\text{LFSE} = 18.90 \text{ kcal/mol}, \beta^\circ = 28.37\%$	
${}^5T_{2g}(D) \rightarrow {}^5E_g$	$Dq = 1081 \text{ cm}^{-1}, B = 584.32 \text{ cm}^{-1}$	5.36
C.T.	$C = 2323.45 \text{ cm}^{-1}, \beta = 0.5512$	
C.T.	$\text{LFSE} = 12.35 \text{ kcal/mol}, \beta^\circ = 44.87\%$	
C.T.		5.12
${}^6A_1 \rightarrow {}^4T_1(G)$		
${}^6A_1 \rightarrow {}^4T_2(G)$		
${}^6A_1 \rightarrow {}^4A_1(G), {}^4E(G)$		
—		Diamagnetic



expected for a distorted octahedral structure [30]. The Racah parameter,  $B_{35}$ , and  $\nu_1$  and  $\nu_2$  are calculated by using the relation given in Refs. 29 and 31.

In the nickel(II) chelate, which has an octahedral geometry,  $\nu_1$  corresponds to  $10Dq$ , which is calculated by the literature method [29]. The  $\nu_1$  transition splits into two bands which are assigned to the transitions arising from the  ${}^3T_{2g}(F)$  term. The  $\nu_2$  transition is also found to split into two bands, arising from the splitting of the  ${}^3T_{1g}(F)$  term [30].

The spectral parameters in Table 2 were calculated by known methods [32-34]. The transitions observed at 9 800 and 20 620  $\text{cm}^{-1}$  for the cobalt(II) polymer may be assigned to distorted octahedral geometry (Table 2) [35]. The third transition,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ), is not clear. However, the shoulder merging in the  $\nu_3$  transition at 17 540  $\text{cm}^{-1}$  may be assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  ( $\nu_2$ ) transition. The  $\nu_3$  band of the cobalt(II) polychelate splits into shoulders, which makes the assignments very difficult [36]. It may be due to removal of the degeneracy of the  $T_{1g}(P)$  level either by spin-orbit coupling or by the presence of a low symmetry component in the ligand field [37]. The experimental value of  $\nu_2$  is lower than the calculated one, which also suggests lower symmetry for the cobalt(II) chelate polymer than that of the octahedral structure [35]. Therefore, it is concluded that the symmetry of cobalt(II) polychelate may be  $D_{4h}$ . In the  $D_{4h}$  symmetry, the  ${}^4T_{1g}(P)$  level splits into  ${}^4A_{2g}$  and  ${}^4E_g$  components [38]. Hence, the shoulder around 17 540  $\text{cm}^{-1}$  assigned to the  $\nu_2$  transition may also contain one of the components of the  $\nu_3$  transition, most likely the  ${}^4A_{2g}$  level.

The reflectance spectrum of iron(II) polychelate shows charge-transfer bands at 20 000 and 16 660  $\text{cm}^{-1}$ , while the absorption band at about 10 810  $\text{cm}^{-1}$  may be due to the d-d transition. The various crystal field parameters,  $Dq$ ,  $B$ ,  $C$ ,  $\beta$ , and  $\beta^\circ$ , were calculated by known relations [39]. In nickel(II), cobalt(II), and iron(II) chelate polymers, a reduction of the  $B$  value was observed upon chelation. This indicates that the radial displacement of the d electrons and, hence, the effective charge experienced by them is decreased. In other words, the decrease in  $B$  values suggests the partial covalent nature of the M-L bond [45].

The reflectance spectrum of the manganese(II) chelate shows three intense bands in the normally expected regions for tetrahedral stereochemistry [34] (Table 2).

Comparison of the IR spectra of the chelates and ligand (Fig. 1) revealed that the spectra of polymeric chelates do not significantly differ from each other, but they do differ from that of the ligand in some characteristic frequencies. All compounds contain three aromatic systems; hence, the region

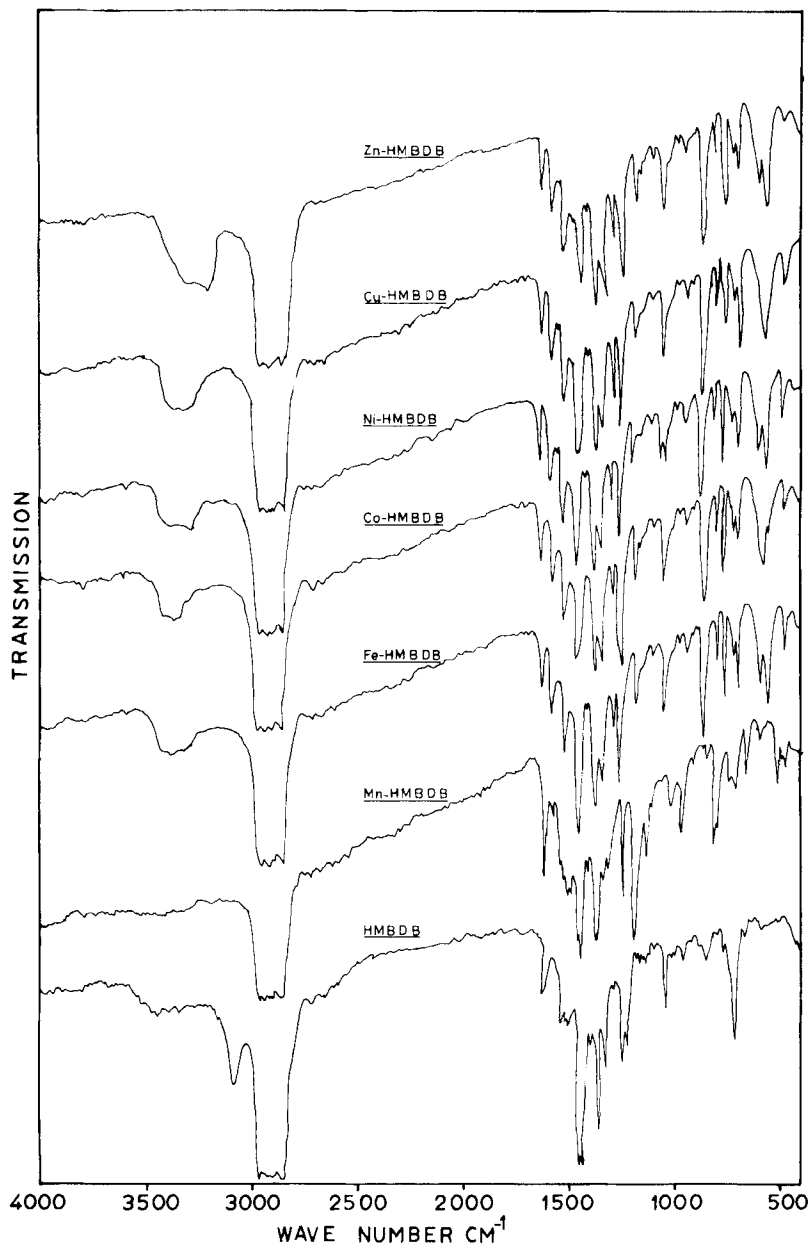


FIG. 1. Infrared spectra of the ligand and the chelate polymers.

characteristic of double bonds is comprised of several bands which overlap. This complicates the interpretation of the C=C stretching region. Even the out-of-plane bending region is difficult to interpret [18]. However, some observations follow.

1. The IR spectra (Fig. 1) of the ligand show a medium absorption band at  $3100\text{ cm}^{-1}$  which may be due to a hydrogen-bonded phenolic hydroxyl group [40]. This band is absent in the polychelates, indicating the dissociation of the phenolic proton on chelation. Moreover, the band at  $1250\text{ cm}^{-1}$ , due to C–O stretching in the ligand, has shifted to the  $1270\text{--}1280\text{ cm}^{-1}$  region, suggesting formation of an M–O bond by replacing the proton from the phenolic hydroxyl group of the ligand on chelation [41].

2. The strong  $1625\text{ cm}^{-1}$  band in the ligand may be attributed to  $>\text{C}=\text{O}$  stretching [39]. This band is shifted to a lower frequency,  $\sim 1605\text{ cm}^{-1}$ , in all the chelates, which indicates wider delocalization of the electronic charge in the chelate ring [42] and also coordination through the oxygen atom of the  $>\text{C}=\text{O}$  group of the ligand [35].

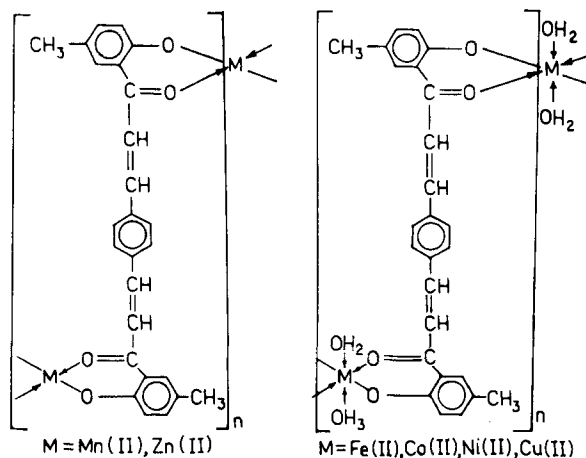
3. The new bands that appear at  $530\text{--}595\text{ cm}^{-1}$  in all the chelates are assignable to stretching frequencies of the M–O bond [35, 41].

4. In general, water of hydration absorbs at  $3300\text{--}3450\text{ cm}^{-1}$  [41]. The IR spectra show that all the chelate polymers, except that of manganese(II), contain water of hydration. The Cu(II), Ni(II), Co(II), and Fe(II) chelates exhibit weak bands at  $\sim 860$  and  $\sim 1590\text{ cm}^{-1}$ , which are ascribed to the rocking and bending vibrations of coordinated water, suggesting a six-coordinate structure for the chelate polymers [18, 19].

From what was stated above and in consideration of the position of potential donor atoms of the ligand, the polymeric structures shown at top of page 853 are proposed for the chelates.

Table 3 shows the loss of weight at different temperatures from HMBDB and its polychelates, calculated from the respective TGA curves. Thermal analysis confirms the presence of water molecules in all the chelates, except the Mn(II) chelate. Voges [43] reported that the thermal stability of the ligand is higher than that of polychelates because of hydrogen bonding. Our results also show that thermal stability at the half-decomposition temperature of HMBDB is more than that of the chelates, and the order of thermal stability is  $\text{HMBDB} > \text{Ni} > \text{Cu} > \text{Mn}, \text{Fe} > \text{Co}, \text{Zn}$ , which is comparable to the order  $\text{Ni} > \text{Cu} > \text{Co}$  observed by Goodwin and Bailar [44].

In general, water of hydration may be considered as either crystal of coordination water. According to Nikolaev et al. [45], water eliminated below



$150^{\circ}\text{C}$  can be considered as crystal water, and water eliminated above  $150^{\circ}\text{C}$  may be due to its coordination to the metal atom in chelates. In the present study, the removal of water from the complex is complete at nearly  $120^{\circ}\text{C}$  for the  $\text{Zn(II)}$  chelate. Similarly, the thermograms of the  $\text{Co(II)}$  and  $\text{Ni(II)}$  chelates also indicate removal of water ( $\sim 7\%$ ) at  $80\text{--}130^{\circ}\text{C}$ . This water is probably crystal water. The removal of water from the  $\text{Cu(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Co(II)}$ , and  $\text{Fe(II)}$  chelates above  $150^{\circ}\text{C}$  indicates the presence of coordinated water molecules. Most of the polychelates and ligands decompose in two stages [46]. The rate of degradation of the ligands and polychelates in the first stage is fast compared to the second stage. Decomposition is complete at about  $750^{\circ}\text{C}$  in all the chelates. The Broido method [47] was applied to the thermal data obtained to determine the energy of activation and the order of the reaction.

Semiconducting behavior was systematically developed by Brattain et al. [48]. Patel et al. [49] studied the electrical conductivity of chelate polymers, and an industrially useful semiconducting material has been reported [50].

Our conductivity measurements were made over a wide range of temperatures. Typical plots of  $\log \sigma$  vs  $1/T$  are shown in Fig. 2. Values of  $\sigma_0$ , which provides a measure of carrier mobility and of the energy of activation of electrical conductance  $E_a$ , are calculated from the expression  $\sigma = \sigma_0 \exp(-E_a/RT)$  [49] and are summarized in Table 4, while Fig. 2 depicts the effect of temperature on the electrical conductivity of the chelates. The following conclusions can be drawn:

TABLE 3. Thermogravimetric Analysis of HMBDB and Its Polychelates<sup>a</sup>

Compound	$D_H$ , °C	Wt% loss at temperature, °C										First decomposition stage			Second decomposition stage		
		100	200	300	400	500	600	700	Temperature range, °C		$E^*$	$n$	Temperature range, °C		$E^*$	$n$	
HMBDB	500	—	—	5.0	33.0	45.0	82.0	100	260-360	—	—	—	380-560	6.11	1		
Cu-HMBDB	430	—	4.0	30.0	42.0	53.0	60.0	83	180-280	6.92	1	300-680	3.14	1			
Ni-HMBDB	440	6	14.5	15.5	20.0	63.0	77.0	84	80-300	1.83	1	400-720	3.36	1			
Co-HMBDB	350	1	14.0	23.0	61.0	67.5	74.0	85.5	100-320	3.66	1	360-700	2.46	1			
Fe-HMBDB	400	—	1.0	7.5	25.0	68.0	70.0	82	180-400	10.82	1	420-740	4.71	1			
Mn-HMBDB	400	—	—	4.0	30.0	65.0	75.0	83	200-400	14.26	1	420-640	3.57	1			
Zn-HMBDB	350	5	16.0	25.0	57.0	63.0	70.0	83	180-360	3.05	1	380-720	2.12	1			

<sup>a</sup> $D_H$  = Half-decomposition temperature.  $E^*$  = Activation energy of thermal decomposition in kcal/mol.  $n$  = Order of decomposition reaction.

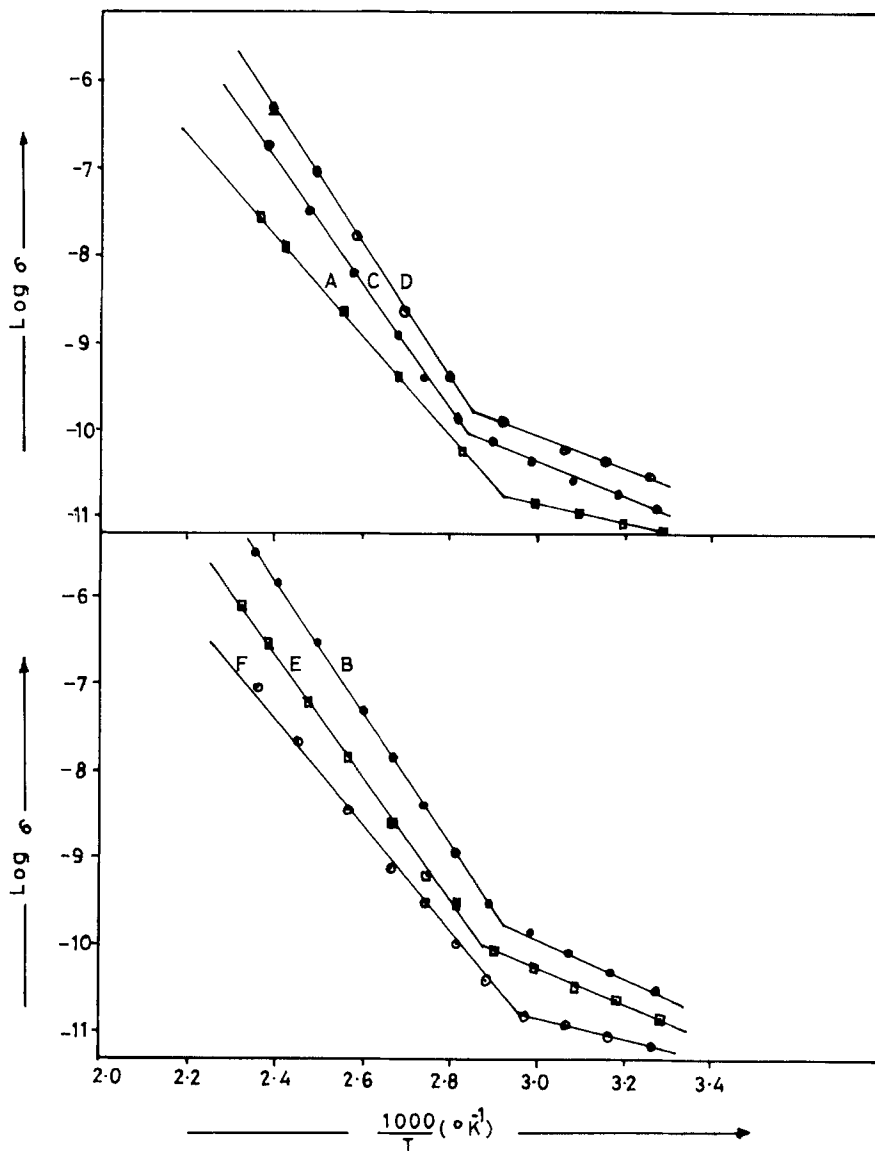


FIG. 2. Arrhenius plots for the electrical conductance. Chelate polymers of: A, Mn; B, Fe; C, Co, D, Ni; E, Cu; F, Zn.

TABLE 4. Electrical Properties of the Coordination Polymers<sup>a</sup>

Compound	$\sigma$ , (ohm·cm) <sup>-1</sup>	$T$ , °K	$T_c$ , °K	$E_a$ , eV	$\sigma_0$ , (ohm·cm) <sup>-1</sup>
Cu-HMBDB	$1.58 \times 10^{-11}$	304	344	1.38	$1.02 \times 10^{10}$
	$6.45 \times 10^{-8}$	404			
Ni-HMBDB	$3.59 \times 10^{-11}$	304	340	1.54	$1.83 \times 10^{12}$
	$9.46 \times 10^{-8}$	402			
Co-HMBDB	$1.38 \times 10^{-11}$	304	345	1.40	$1.02 \times 10^{10}$
	$3.61 \times 10^{-8}$	404			
Fe-HMBDB	$3.53 \times 10^{-11}$	304	342	1.50	$1.54 \times 10^{12}$
	$3.12 \times 10^{-7}$	404			
Mn-HMBDB	$8.10 \times 10^{-12}$	303	338	1.13	$7.47 \times 10^5$
	$2.50 \times 10^{-9}$	393			
Zn-HMBDB	$7.25 \times 10^{-12}$	304	334	1.19	$1.70 \times 10^7$
	$2.52 \times 10^{-8}$	404			

<sup>a</sup> $\sigma$  = Electrical conductivity at temperature  $T$ .  $T_c$  = The temperature at which the polymers have intrinsic conduction.

1. In general, the two slopes observed have lower activation energies in the lower-temperature region. This agrees well with the observations of Spiratos et al [13] that the activation energy approaches higher values at high temperatures, suggesting intrinsic conduction, while that at lower temperatures has much lower values and is due to extrinsic conduction.

2. The coordination polymers have electrical conductivities in the range  $7.25 \times 10^{-12}$  to  $3.59 \times 10^{-11}$  (ohm·cm)<sup>-1</sup> at room temperature.

3. The activation energy of electrical conduction and  $\sigma_0$  values were evaluated from the high-temperature part of the curves. The activation energies decline in the order Ni > Fe > Co > Cu > Zn > Mn, which is in partial agreement with the order given in Refs. 49 and 51.

4. The electrical conductivity at room temperature of chelate polymers increases in the order Zn < Mn < Co < Cu < Fe < Ni, consistent with the reportings of Patel and Manavalan [49].

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