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Magnetic, Spectral, Thermal, and Electrical Properties of Coordination Polymers Derived from Terpolymers

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Magnetic, Spectral, Thermal, and Electrical Properties of Coordination Polymers Derived from Terpolymers

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ABSTRACT

Coordination polymers of Cu(II), Ni(II), Co(II), zinc(II), chromium(III), iron(III), oxovanadium(IV), and dioxouranium(VI) with p-hydroxybenzoic acid (PHB)-thiourea (T)-trioxane (T) (PHBTT) polymer were prepared. The analytical data agree with 1:1 metal-ligand stoichiometry. Magnetic susceptibility, visible and IR spectra, and thermal and electrical conductivities of the chelates have been studied and probable structures assigned to the chelates.

INTRODUCTION

Metal complexes of sulfur donor ligands have received great attention during recent years because of their versatile use as antifungal and antibacterial agents [1]. Because transition metal complexes derived from polymers have occupied a central position in the development of coordination chemistry, this inspired us to prepare a polymeric chelating ligand which would be able to form complexes with a variety of transition metals. Salicylic acid has been used as a chelating agent for several transition metals [2]. However, no work

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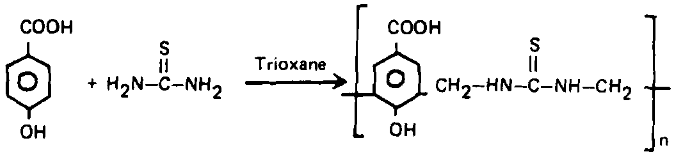
seems to have been reported on studies of chelates derived from a polymer containing p-hydroxybenzoic acid. This communication describes the preparation and characterization of chelates prepared from p-hydroxybenzoic acid-thiourea-trioxane (PHBTT) polymer [3].

The stereochemistry of the polychelates has been studied by diffuse reflectance spectra, infrared spectra, magnetic moment, and thermal analysis. The decomposition temperature of the polymeric chelates is in the order PHBTT > UO_2 > Ni > Zn, Fe > Cr, VO, Cu, Co, while the thermal activation energy follows the order PHBTT > Zn > Co > Cr > UO_2, VO > Fe > Cu, and the activation energy obtained from semiconducting behavior is in the order Co > UO_2 > PHBTT > VO > Fe > Ni > Cr > Cu > Zn.

EXPERIMENTAL

Material

PHBTT polymer was prepared as follows. A mixture of p-hydroxybenzoic acid and thiourea with trioxane in the ratio 1:1:2, respectively, was heated in the presence of 2 M HCl as catalyst in an oil-bath at 130 ± 2°C for 4 h [3]. The separated product was filtered, washed with hot water, and dried. The purification was effected by dissolving the product in 5% NaOH solution and reprecipitating it by 1:1 HCl solution. The reaction taking place is shown in I.



I

The polychelates were prepared by mixing a solution of metal nitrate in dimethylformamide (DMF) with the solution of PHBTT in DMF. To the resulting colored solution, concentrated solution of sodium acetate in DMF was added, whereby the product which separated out was digested, filtered, washed with DMF and hot water, and dried in an oven at 60°C. In the case of oxovanadium(IV) chelate, vanadyl sulfate was used. The polymeric ligand may act as a tridentate ligand. The structures of the complexes are indicated later.

Measurements

The magnetic susceptibility was determined at room temperature by the Gouy method. Diffuse reflectance and IR spectra were recorded on a Beckman DU and a Carl Zeiss UR-10 spectrophotometer, respectively. The electrical resistivity of the PHBTT and its polychelates was measured over a wide range of temperature in air using a Million Megohmmeter Model RM 160 MK III A, India. Thermograms were scanned on a Du Pont Thermal Analyzer 900.

RESULTS AND DISCUSSION

Elemental analysis (Table 1) showed that polychelates exhibit 1:1 metal to ligand stoichiometry, having the general formula $[ML]_n$, where ML is a dimeric species as shown in Structure II.

The magnetic moment of copper polychelate is 1.62 BM which is very close to the spin-only value of 1.73 BM (Table 2) expected for one unpaired electron, which offers the possibility of octahedral symmetry [4]. Ni(II) polychelate shows a magnetic moment of 2.61 BM which is in agreement to that of Harris et al. [5], indicating the possibility of an octahedral or a distorted octahedral structure. The low value for the Co(II) complex, 4.33 BM reported here, may be due to polymeric octahedral structure [6].

Fe(III) polychelate exhibits a magnetic moment of 5.13 BM which is found to be lower than expected on the basis of spin-only value for five unpaired electrons (6.0 BM). The lowering of the magnetic moment suggests the polymeric nature of the chelate [7]. Cr (III) polychelate shows a magnetic moment of 3.56 BM which is close to the range (3.81-4.01 BM) required for high spin chromium complexes [8]. Such a lowering of the magnetic moment has been observed in binuclear complexes [9]. The magnetic moment 1.503 BM of the oxovanadium(IV) complex is lower than the spin-only value 1.73 BM. This lowering of the moment may perhaps be attributed to the binuclear nature of the complex [10-12]. Dioxouranium(VI) and Zn(II) chelates, as expected, are diamagnetic in nature.

The electronic spectra provide the most detailed information about the electronic structure. The diffuse reflectance spectra of the polymeric chelates were studied between 7,692 and 27,780 cm^{-1}. The Cu(II) complex possesses only a single broad band in the 13,100-18,700 cm^{-1} region, centered at 13,700 cm^{-1}, which may be due to the overlapping of the three transitions (Table 2) expected for a distorted octahedral structure [4]. The Ni(II) chelate shows bands at 9,390, 13,890, and 25,640 cm^{-1} which are assigned as given in Table 2. This spectrum is similar to that expected for an octahedral or distorted octahedral spin-free nickel(II) complex [13, 14]. The structure is also further confirmed by the ratio of ν_2/ν_1 which is 1.72, close to the value expected for the distorted octahedral structure [15].

The Racah parameter, B_{35}, is calculated using the relation [16]

$$B_{35} = \nu_2 + \nu_3 - \frac{3\nu_1}{15}$$

TABLE 1. Analytical Data and Other Physical Properties

Compound	Color	Elemental analysis						MW[a]
		M (%)		N (%)		S (%)		
		Found	Required	Found	Required	Found	Required	
PHBTT	Yellow	-	-	11.23	11.76	11.88	12.41	238.0
Cu PHBTT.2H_2O	Light green	18.84	18.93	7.91	8.34	9.01	9.53	335.5
Ni PHBTT.2H_2O	Pale yellow	16.92	17.75	8.092	8.46	9.12	9.67	330.7
Co PHBTT.2H_2O	Light pink	16.94	17.81	7.935	8.46	9.99	9.66	330.9
Zn PHBTT.2H_2O	Gray	18.65	19.37	8.87	8.29	8.981	9.49	337.4
Fe PHBTT.No_3.H_2O	Violet	14.89	15.01	10.12	11.29	8.05	8.61	371.8
Cr PHBTT.NO_3.H_2O	Green	14.92	14.12	10.66	11.41	7.98	8.696	368.0
UO_2 PHBTT.H_2O	Rosy red	44.68	45.45	5.87	5.34	5.41	6.103	524.3
VO PHBTT.H_2O	Green	15.61	15.87	9.22	8.72	9.23	9.97	320.9

[a] Molecular weight of repeating unit estimated from elemental analysis.

TABLE 2. Electronic Spectral Data and Magnetic Moment

Compound	Energies (cm^{-1})		Assignment	u$_{eff}$ (BM)
	Observed	Calculated		
Cu PHBTT.2H$_2$O			$^2B_{1g} \rightarrow {}^2B_{2g}$	
	13,700	-	$^2B_{1g} \rightarrow {}^2E_g$	1.62
			$^2B_{1g} \rightarrow {}^2A_{1g}$	
Ni PHBTT.2H$_2$O	9,390	9,390.0	$^3A_{2g} \rightarrow {}^3T_{2g}(T)$	
	13,890	15,042.97	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	2.61
	25,640	24,486.97	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	
Co PHBTT.2H$_2$O	8,850	8,841	$^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)$	
		18,825	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	4.33
	19,360	19,342	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
Fe PHBTT.NO$_3$.H$_2$O	14,810	-	$^6A_{1g} \rightarrow {}^4T_{1g}$	5.134
	17,760	-	$^6A_{1g} \rightarrow {}^4T_{1g}$	
	21,700	-	$^6A_{1g} \rightarrow {}^4T_{1g}, {}^4E_g$	

(continued)

TABLE 2 (continued)

Compound	Energies (cm^{-1}) Observed	Energies (cm^{-1}) Calculated	Assignment	u_{eff} (BM)
Cr PHBTT.NO$_3$.H$_2$O	11,300	-	$^4A_{2g}(F) \rightarrow {}^2E_g$	
	17,480	-	$^4A_{2g}(F) \rightarrow {}^4T_{2g}$	3.56
	23,400		$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$	
VO PHBTT.H$_2$O	11,400	-	$^2B_2 \rightarrow {}^2E$	
	15,350	-	$^2B_2 \rightarrow {}^2B_1$	1.503
	25,050	-	$^2B_2 \rightarrow {}^2A_1$	

Transition energies ν_2 and ν_3 have been calculated [16] using the Racah parameter obtained from the above equation:

$$\nu_{2,3} = \tfrac{1}{2}(15B + 30\ Dq) \pm \tfrac{1}{2}[(15B - 10Dq)^2 + 12B \times 10\ Dq]^{\frac{1}{2}}$$

In nickel(II) polychelate having an octahedral geometry, the value of ν_1 corresponds to 10 Dq which is calculated using the equation [16]

$$\nu_1 = 10\ Dq = \tfrac{1}{3}(\nu_2 + \nu_3) - 5B$$

The ν_1 transition splits into two bands which are assigned to the transition arising from the splitting of the ${}^3T_{2g}(F)$. The ν_2 transition is also found to split into two bands arising from the splitting of ${}^3T_{1g}(F)$ [15]:

$$\begin{tikzcd}[row sep=small] & & {8{,}696\ \mathrm{cm}^{-1}} \\ {}^3A_{2g}(F) \arrow[r] & {}^3T_{2g}(F) = \nu_1 \arrow[ur] \arrow[dr] & \\ & & {10{,}000\ \mathrm{cm}^{-1}} \end{tikzcd}$$

$$\begin{tikzcd}[row sep=small] & & {13{,}160\ \mathrm{cm}^{-1}} \\ {}^3A_{2g}(F) \arrow[r] & {}^3T_{1g}(F) = \nu_2 \arrow[ur] \arrow[dr] & \\ & & {14{,}710\ \mathrm{cm}^{-1}} \end{tikzcd}$$

Various spectral parameters were calculated by known methods [15, 17]:

$\nu_2/\nu_1 = 1.72$ $\quad D_t = 149.0\ \mathrm{cm}^{-1}$

$Dq = 739.2\ \mathrm{cm}^{-1}$ $\quad Dq_{qv} = 739.2\ \mathrm{cm}^{-1}$

$D_S = 868.0\ \mathrm{cm}^{-1}$

$B_{35} = 757.33$ $\quad \beta_{35} = 0.7012,$

LFSE = 32.20 kcal/mol

In cobalt(II) polychelate the transitions observed at 8,850 and 19,360 cm^{-1} may be assigned to distorted octahedral geometry (Table 2) [18, 19]. The Racah parameter is calculated using the known relation [16]

$$B_{35} = \frac{1}{30}\left[-(2\nu_1 - \nu_3) \pm \{-\nu_1^{\,2} + \nu_3^{\,2} + \nu_1\nu_3\}^{\frac{1}{2}}\right]$$

$$\nu_2 = \tfrac{1}{2}[30\ \mathrm{Dq} - 15\mathrm{B}] + \tfrac{1}{2}[(10\mathrm{Dq} + 15\mathrm{B})^2 - 12\mathrm{B}10\mathrm{Dq}]^{\frac{1}{2}}$$

using observed ν_1 and ν_2. ν_2 at 18,825 cm^{-1} was calculated.

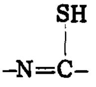
The transition energies ν_1, ν_2, and ν_3 have been calculated using calculated ν_2 [16], and the values of B_{35}, β_{35} and LFSE are

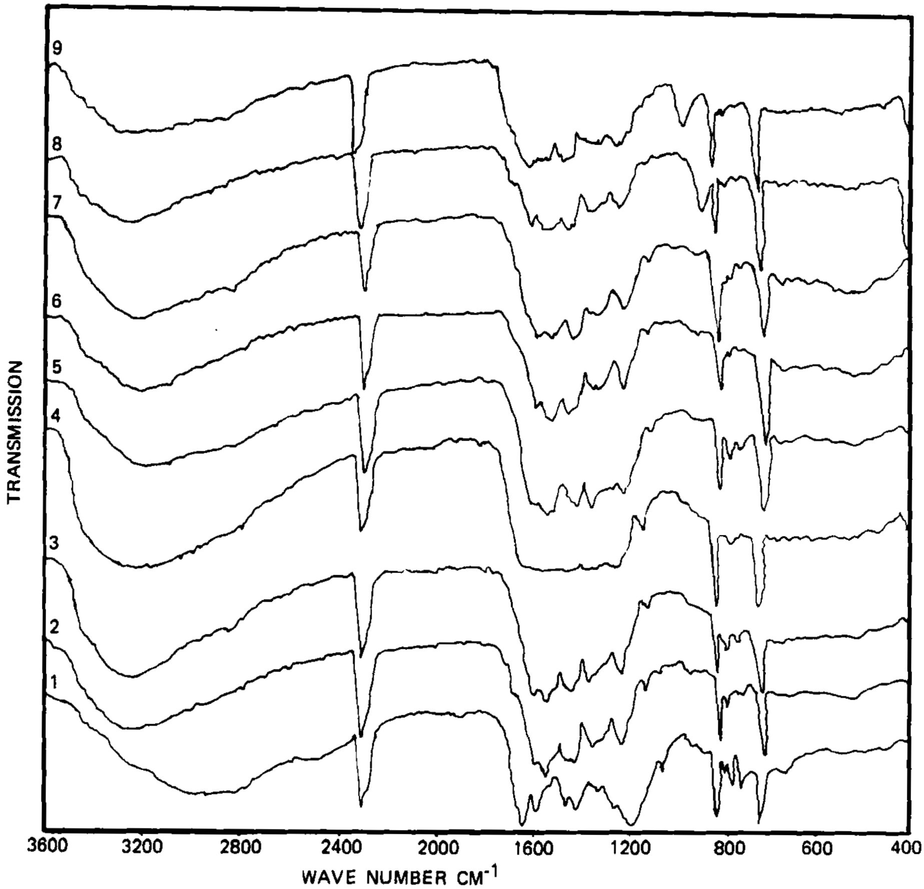
$B_{35} = 776.02$, $\beta_{35} = 0.693$, LFSE = 17.11 kcal/mol

Iron(III) chelate shows bands at 14,810, 17,760 and 21,700 cm^{-1} which may be assigned to the transition given in Table 2 for an octahedral structure [20]. In chromium(III) polychelate the transitions observed at 11,300, 17,480, and 23,400 cm^{-1} may best be assigned to an octahedral geometry [21]. The lowest energy transition is spin forbidden due to $^4A_{2g}(F) \rightarrow {}^2Eg$, the lowest energy spin allowed band is $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (17,480 cm^{-1}) and the other band is due to the transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (Table 2).

Oxovanadium(IV) chelate exhibits three transitions at 11,400, 15,350, and 25,050 cm^{-1}. These bands are not well resolved and appear as weak bands except for the band at 25,050 cm^{-1}. However, the positions of these bands are inconsistent with distorted octahedral oxovanadium(IV) complexes [22].

The infrared spectra of PHBTT and its metal chelates are given in Fig. 1.

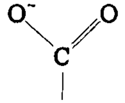
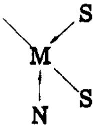
The IR spectra of all polychelates are similar to that of the ligand but are found to be comparable with each other which suggests some difference from the polymeric ligand. The bands in the regions 2800-3300, 1400-1550, 1200-1340, and 700-800 cm^{-1} suggest the presence of methylene bridges in the PHBTT polymer [23]. The IR spectra of the ligand show strong absorptions between 2900-3300 cm^{-1} (also attributed to $-CH_2$ bridges) and a medium intensity band at 2640 cm^{-1} which may be attributed to ν-OH with hydrogen bonding. Moreover, spectra show –NH stretching vibrations in the region 3200-3400 cm^{-1}. The sharp strong band at 1620 cm^{-1} in the PHBTT due to C=N stretch shifts to lower frequencies at ~1600 cm^{-1} in the complexes showing coordination through the nitrogen atom of  $-\mathrm{N}{=}\overset{\mathrm{SH}}{\overset{|}{\mathrm{C}}}-$ [20]. The strong band at 860 cm^{-1} may be very safely assigned to C=S stretch [9]. The weak band observed at 2380 cm^{-1} is due to the presence of a thioenolic form of the ligand even in the free PHBTT [24]. However, this ν-SH band disappears in complexes, showing that the M–S band

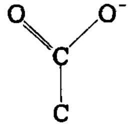


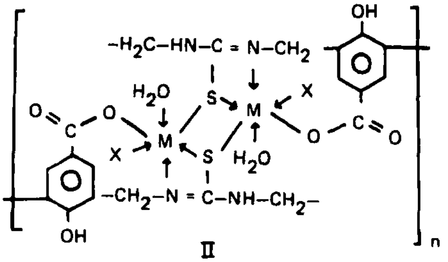
1. PHBTT. 2.[CuPHBTT $2H_2O$] 3.[NiPHBTT $2H_2O$] 4.[CoPHBTT $2H_2O$] 5.[ZnPHBTT $2H_2O$]
6.[FePHBTT NO_3H_2O] 7.[CrPHBTT NO_3H_2O] 8.[UO_2PHBTT]H_2O 9.[VOPHBTT H_2O]

FIG. 1. Infrared spectra of polymeric ligand and its polychelates.

is formed due to deprotonation of the –SH group. Besides, a strong and sharp band is observed at 780 cm^{-1} in the ligand and has been attributed to the coupled bands of ν(C–S) and ν(C–N) [24]. On coordination with metal complexes this band shifts to a lower frequency region and appears at ~750 cm^{-1}, clearly implying the coordination of the sulfur and nitrogen atoms. Therefore, it is obvious that thioenolization is more favored during complex formation. A medium band due to νC=O of the carboxylic acid group observed at 1636 cm^{-1} in PHBTT shifts to lower frequency in all the chelates, indicating coordination through the COO^- group [25]. The sharp, intense band observed at 1272 cm^{-1} in the ligand may be due to the phenolic C–O stretching vibration [26]. On chelation, this band remains unshifted which clearly indicates the noninvolvement of phenolic oxygen in bond formation [27]. Additional bonds appear in the case of Fe(III) and Cr(III) chelates at ~1500, 1280, 1030, and 940 cm^{-1} which can be attributed to the coordinated NO_3^- group [28]. All polychelates except dioxouranium(VI) polychelate exhibit weak bonds at ~780 and 1580 cm^{-1} which are attributed to coordinated water [29], confirming a six-coordinated structure. In oxovanadium(IV) and dioxouranium(VI) complexes, sharp bands at ~ 965 and ~925 cm^{-1}, respectively, are assigned to the νV=O and νU=O modes [30, 31].

Spectral evidence suggests that the complexes may have any one of the following structures (II or III). The major difference between Structures II and III is the mode of coordination of O^- in the  moiety. Also, in Structure II the two water molecules are not in the plane containing the  fragment while for Structure II, oxygen of one of the water molecules is in the said plane. This water molecule (in Structure III) probably coordinates in such a way as to keep its two H-atoms not in the said plane to minimize the steric interaction with the phenyl ring atoms.

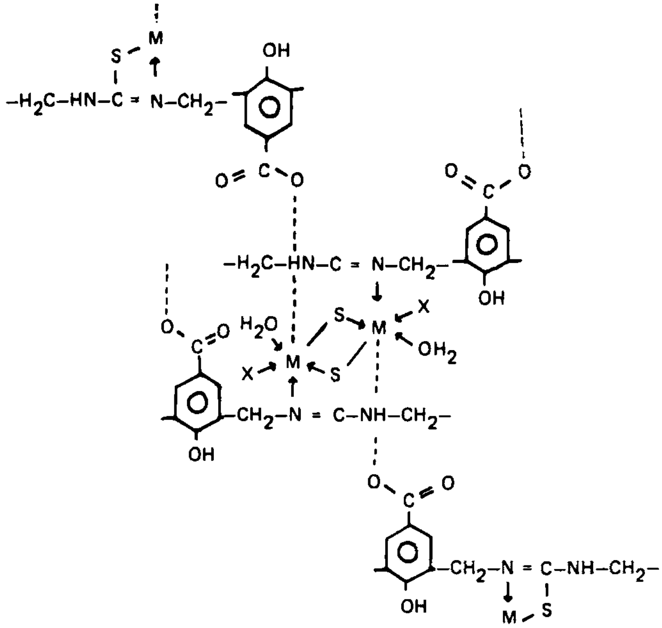
The  moiety may have a rotation around C–C bond such that the two oxygens are not planar with the ring (Structure III). This O^- may bind to a metal ion of another layer, thereby forming a cross-linked polymer and thus satisfying the octahedral environment around



II

X = H_2O when M = Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}

X = NO_3^- when M = Fe^{3+} and Cr^{3+}



III

the metal ions. However, it is not possible to say conclusively from spectral data alone which of these structures is present. Considering the fact that the presence of an eight-member ring in the molecule (Structure II) imposes a certain instability in it, we would prefer Structure III to Structure II.

Table 3 shows the loss of weight at different temperatures of PHBTT and its polychelates, calculated from the respective thermogravimetric analysis curves. Thermal analysis confirms the presence of water molecules in all the chelates. Voger [32], has reported that the thermal stability of polymer is higher than that of the polychelates because of hydrogen bonding. Our results also show that PHBTT is more stable than that of chelates, and the order of stability is in the order PHBTT > UO_2 > Ni > Zn, Fe > Cr, Cu, Co, VO.

This order of stability is comparable to the order Ni > Cu > Co observed by Goodwin and Bailar [33].

In general, the water of hydration may be considered either as crystal or coordination water. According to Nikolaev et al. [34], water eliminating below 150°C can be considered as crystal water and water eliminated above 150°C may be due to coordination to the metal ion. In the present study in the case of the dioxouranium(VI) complex, at 160°C the removal of water from the complex is completed. The water is probably crystal water. The removal of water above 150°C in the case of other polymeric chelates indicates the

TABLE 3. Results of Thermogravimetric Analysis

Compound	DP	Species volatized	% weight loss at temperature (°C)						Order of reaction		E_a (kcal/mol)
									n = 1	n = 2	
			100	200	300	400	500	600	Temperature (°C)		
PHBTT	245		2.5	5.5	21.5	37.5	52.5	80.5	500-700	220-500	10.8
Cu PHBTT.$2H_2O$	120	$2H_2O$	3.5	11.5	29.0	45.5	60.0	80.0	220-620	600-220	4.2
Ni PHBTT.$2H_2O$	165	$2H_2O$	4.5	12.5	24.0	57.5	66.0	84.5	300-560	40-160	9.1
Co PHBTT.$2H_2O$	125	$2H_2O$	4.5	13.0	22.0	52.0	65.5	90.0	280-620	60-180	10.8
Zn PHBTT.$2H_2O$	150	$2H_2O$	3.5	7.0	27.0	47.0	76.0	82.5	250-640	60-220	6.2
Fe PHBTT.NO_3.H_2O	120	H_2O	4.0	8.0	25.4	42.5	58.0	81.0	220-520	40-140	7.12
Cr PHBTT.NO_3.H_2O	120	H_2O	2.5	8.5	15.5	32.0	61.5	63.5	280-580	40-280	5.82
UO_2 PHBTT.H_2O	180	H_2O	1.5	5.5	12.5	34.0	50.0	59.5	270-600	40-280	6.42
VO PHBTT.H_2O	125	H_2O	3.0	11.0	26.0	48.0	68.5	85.0	280-560	40-220	6.12

TABLE 4. Electrical Data of Polymer and Its Polychelates

	Electrical conductivity		Specific conductivity		
Compound	σ (Ω^{-1} cm^{-1})	(T)	σ_0 (Ω^{-1} cm^{-1})	(T)	E_a (eV)
PHBTT	3.66×10^{-12}	(308)	1.81×10^{9}	(308)	1.267
	2.47×10^{-11}	(373)	2.69×10^{7}	(373)	
Cu PHBTT.2H_2O	5.01×10^{-12}	(308)	3.2×10^{-1}	(308)	0.663
	2.702×10^{-10}	(423)	2.60×10^{-3}	(423)	
Ni PHBTT.2H_2O	1.76×10^{-10}	(308)	2.88×10^{11}	(308)	1.042
	6.04×10^{-12}	(513)	3.71×10^{2}	(513)	
Co PHBTT.2H_2O	6.9×10^{-12}	(308)	2.51×10^{11}	(308)	1.410
	6.81×10^{-12}	(513)	1.86×10^{3}	(513)	
Zn PHBTT.2H_2O	5.1×10^{-12}	(308)	1.71×10^{-3}	(308)	0.585
	7.48×10^{-10}	(443)	3.2×10^{3}	(443)	
Fe PHBTT.NO_3.H_2O	6.7×10^{-12}	(308)	7.94×10^{7}	(308)	1.155
	6.22×10^{-11}	(463)	3.51×10^{1}	(463)	
Cr PHBTT.NO_3.H_2O	2.27×10^{-11}	(308)	1.31×10^{4}	(308)	0.905
	1.41×10^{-10}	(453)	0.16×10^{1}	(453)	
UO_2 PHBTT.H_2O	1.85×10^{-12}	(308)	1.8×10^{11}	(308)	1.409
	1.96×10^{-11}	(433)	3.23×10^{6}	(433)	
VO PHBTT.H_2O	1.99×10^{-12}	(308)	8.9×10^{7}	(308)	1.205
	1.41×10^{-10}	(423)	8.91×10^{3}	(423)	

presence of coordinated water molecules. The thermal activation energy was calculated by using the Broido method [35], and the values are summarized in Table 4.

Semiconducting behavior was systematically developed by Brattain et al. [36]. Pekaln and Kotosonov have studied the electrical conductivity of phenol-formaldehyde resin [37]. An industrially useful semiconducting material has been reported [38].

The measurements were made over a wide range of temperature.

The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relationship

$$\sigma = \sigma_0 \exp \left[-\frac{E_a}{RT} \right]$$

where E_a is the activation energy of the semiconductor and σ_0 is a constant. At higher temperature the above equation seems to hold good, and a linear relationship has been observed when the logarithm of the conductivity was plotted against the reciprocal of the absolute temperature. At lower temperature there is a deviation, and the linear relation has not been observed. The values of σ and σ_0 at room temperature and in the temperature range 373-513 K and E_a are given in Table 4.

The electrical conductivity at room temperature is in the order (Table 4) Ni > Fe > Cu > Co. The activation energy increases in the order Co > UO_2 > PHBTT > VO > Fe > Ni > Cr > Cu > Zn which is in partial agreement with the order [39]. The results indicate that electrical conductivity of metal chelates is slightly higher than that of PHBTT, which may be due to the incorporation of metal in the PHBTT which increases the ionization tendency [40].

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