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Synthesis, characterization and thermal studies of polychelates derived from 2-hydroxyacetophenone–thiourea–trioxane resin

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Abstract

Polychelates of copper(II), nickel(II), cobalt(II), manganese(II), zinc(II), oxovanadium(IV) and dioxouranium(VI) with 2-hydroxyacetophenone–thiourea–trioxane resin have been synthesized. Elemental analyses of the polychelates indicate 1:2 (metal:ligand) ratio. The structures of the polychelates have been assigned on the basis of their elemental analyses, IR and reflectance spectra and magnetic measurements. Thermal studies of polychelates have been carried out to determine their mode of decomposition, apparent activation energy and the order of each thermal reaction. Electrical conductivity behaviour of resin and its polychelates has also been studied.

INTRODUCTION

Attempts to prepare coordination polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. 2,4-Dihydroxyacetophenone [1], 8-hydroxyquinoline [2], salicylic acid [3] and 2,4-dihydroxypropiophenone [4] have been condensed with formaldehyde in an acidic medium to obtain polymeric ligands. Their polychelates have also been studied. Photodecomposable low density polyethylene composition was obtained by adding nonionic, organic soluble complexes of 2-hydroxy-4-methyl-acetophenone with iron, cobalt, nickel, copper, manganese, chromium and cerium in which the metal was converted to an easily photooxidizable form, in amounts to cause decomposition of the polymer after its specific lifetime [5]. The work described in the present communication deals with the synthesis, characterization and thermal studies of polychelates of copper(II), nickel(II), cobalt(II), manganese(II), zinc(II), oxovanadium(IV) and dioxouranium(VI) with 2-hydroxyacetophenone–thiourea–trioxane resin (HTT′).

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EXPERIMENTAL

Chemicals

All the chemicals used were of AnalaR grade. 2-Hydroxyacetophenone (b.p. 91°C) was prepared by a known method [6].

Synthesis of the polymeric ligand

The polymeric ligand 2-hydroxyacetophenone–thiourea–trioxane (HTT′) was synthesized by condensing 2-hydroxyacetophenone (0.1 mol), thiourea (0.1 mol) and trioxane (0.2 mol) in the presence of 2 M HCl as a catalyst at 100°C for 4 h as described earlier [7].

Synthesis of polychelates

Metal nitrate (0.1 mol) dissolved in DMF (20 ml) was added dropwise to the hot solution of polymeric ligand (0.2 mol) dissolved in DMF (20 ml) with constant stirring. The polychelate separated out on addition of a saturated solution of sodium acetate. The polychelate was digested for 1 h on a water-bath, filtered, washed with DMF and hot distilled water and dried at 60°C for 24 h. In the case of oxovanadium(IV) polychelate, vanadyl sulphate was used as the starting material.

Analytical methods

Microanalyses for carbon and hydrogen contents were carried out on a Carlo Erba elemental analyzer. Nitrogen was estimated by the Kjeldahl method and sulphur by the Carius method. Metal analyses were carried out by standard procedure [8]. Magnetic susceptibilities were determined by the Gouy method. The reflectance spectra were scanned on a Beckman DK-2A spectrophotometer using MgO as a reference at room temperature in the range 350–1300 nm. The IR spectra in the region 4000–400 cm^{-1} were recorded in the solid state (KBr pellets) on a Perkin Elmer 983 spectrophotometer. Thermal studies were done on a Du Pont thermal analyser-951 at a heating rate of 10°C min^{-1} in air, using 5–10 mg samples. For the electrical conductivity measurements a pellet of the polymer under study was prepared by pressing a finely powdered and dried sample under hydrostatic pressure at 20000 lbf in^{-2} for 2 min. A uniform thin layer of silver paste was applied to both sides of the pellet, providing electrical contacts. The average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed through the pellet holder for connections. The entire assembly was placed in a furnace. It was heated at a rate of 1°C min^{-1}. The resistance of the pellet was measured by a Hewlett Packard 4329-A high resistance meter.

RESULTS AND DISCUSSION

The analytical data of the resin and its polychelates are listed in Table 1. Elemental analyses showed that polychelates exhibit 1:2 metal to ligand stoichiometry. All the polychelates are coloured, amorphous in nature and insoluble in all common organic solvents.

Magnetic measurement studies

The magnetic moment of copper(II) polychelates is 1.93 BM corresponding to one unpaired electron. Nickel(II) polychelate shows a magnetic moment of 3.21 BM which is close to the range observed for octahedral stereochemistry [9]. The magnetic moment of cobalt(II) polychelate is found to be 4.52 BM indicating octahedral structure [10]. The magnetic moment of manganese(II) polychelate is 5.28 BM, which is slightly lower than expected on the basis of the spin-only value. This may be due to aerial oxidation of manganese(II) to manganese(III) during synthesis [11]. The magnetic moment of the oxovanadium(IV) polychelate (1.86 BM) is close to the spin-only value of 1.73 BM. Dioxouranium(IV) and zinc(II) polychelates, as expected, are diamagnetic in nature.

Diffuse reflectance spectral studies

The diffuse reflectance spectrum of copper(II) polychelate possesses only a single broad band in the region 13 000–17 500 cm^{-1}, centered at 14 700 cm^{-1}, which may be due to overlapping of the three transitions, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ expected for a distorted octahedral structure [12]. The nickel(II) polychelates show three bands at 10 050, 16 260 and 24 691 cm^{-1} which may be assigned as $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively for distorted octahedral structure [13]. The ν_2/ν_1 ratio is 1.62 which lies in the range required for an octahedral chelate [14]. The cobalt(II) polychelate shows three transitions at 8264, 16 949 and 20 408 cm^{-1} attributed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively for distorted octahedral geometry [15]. The reflectance spectrum of manganese(II) polychelate shows three weak bands at 16 000; 20 833 and 25 974 cm^{-1} which may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$ and $^6A_{1g} \rightarrow {}^4E_g \cdot {}^4A_{1g}(^4G)$ transitions respectively, for octahedral stereochemistry [16]. Oxovanadium(IV) chelate exhibits three bands at 25 641, 15 748 and 11 236 cm^{-1} which may be assigned to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$, and $^2B_2 \rightarrow {}^2A_1$ transitions, respectively, for distorted octahedral geometry [17].

TABLE 1

Physical and analytical data of polymeric ligand and its polychelates

Compound [a]	Colour	Analyses [b] (%)					Molecular mass [c] (g mol^{-1})
		C	H	N	S	M	
HTT′	Yellow	55.66 (55.92)	5.10 (5.12)	11.69 (11.86)	13.13 (13.57)		236.3
[Cu(HTT′)$_2$]	Light green	49.02 (49.47)	5.44 (5.46)	10.29 (10.49)	11.68 (12.01)	11.56 (11.90)	534.1
[Ni(HTT′)$_2$]	Brown	49.51 (49.93)	4.59 (4.62)	10.44 (10.62)	11.84 (12.12)	10.91 (11.09)	529.3
[Co(HTT′)$_2$]	Light grey	49.38 (49.90)	4.60 (4.62)	10.46 (10.62)	11.79 (12.11)	10.86 (11.13)	529.5
[Mn(HTT′)$_2$]	Brown	49.98 (50.28)	4.62 (4.66)	10.47 (10.70)	11.76 (12.20)	10.28 (10.45)	525.5
[Zn(HTT′)$_2$]	Yellowish White	48.69 (49.31)	4.54 (4.57)	10.18 (10.49)	11.58 (11.97)	12.11 (12.20)	535.9
[VO(HTT′)$_2$]	Green	48.73 (49.16)	4.54 (4.55)	10.11 (10.46)	11.52 (11.93)	9.32 (9.48)	537.5
[UO$_2$(HTT′)$_2$]	Brick red	35.41 (35.68)	3.28 (3.30)	7.31 (7.59)	8.41 (8.66)	32.01 (32.14)	740.6

[a] HTT′ = 2-Hydroxyacetophenone–thiourea–trioxane resin.

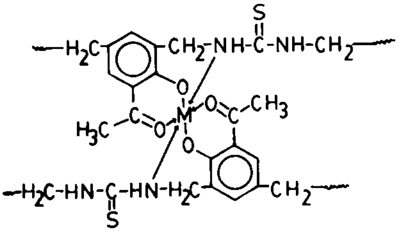
[b] Values in parentheses are calculated.

[c] Molecular mass of repeating unit estimated from elemental analyses.

Infrared spectral study

A comparison of the IR spectra of ligand and its polychelates shows that the weaker broad band at 2600–2700 cm^{-1} in the ligand due to the intramolecular H bond, disappears from the spectra of polychelates. This indicates the replacement of hydrogen of the phenolic OH group by metal ions [18]. The band at 1270 cm^{-1} in ligand due to ν(C–O(H)) vibrations increases by 10 cm^{-1} on chelate formation confirming coordination through the phenolic OH group. The thioamide bands I and II at 1540 and 1500 cm^{-1} respectively in the ligand have been found to be shifted to higher wavenumber by 5–20 cm^{-1} in polychelates. This observation unequivocally supports coordination through nitrogen atom [19]. The lowering of the ν(C=O) band by 10–15 cm^{-1} in polychelates suggests coordination of metal ions through oxygen of carbonyl group. The consistent appearance of the ν(C=S) band in both ligand and polychelates rules out the involvement of sulphur in coordination. In oxovanadium(IV) and dioxouranium(VI) polychelates, strong bands at 960 and 920 cm^{-1} are assigned ν(V=O) and ν(U=O) modes respectively [20,21].

From the above data, the structure shown in Form 1 has been proposed for the polychelates.



Thermal studies

The use of thermogravimetric data to evaluate kinetic parameters of solid state reactions involving mass loss has been investigated by a number of workers [22–24]. We have followed the method of Broido [25]. This is a simple sensitive graphical method of treating TGA data. The decomposition equation of a first order reaction of the type A(s) → B(s) + C(g) will be $K = A\ \exp(-E/RT)$. For a first order reaction, i.e. $n = 1$, this equation takes the form

$$\ln[\ln(1/Y)] = -(E/R)(1/T) + \text{constant}$$

where the fraction not yet decomposed, i.e. the residual mass fraction, is

$$Y = (W_t - W_\alpha)/(W_0 - W_\alpha)$$

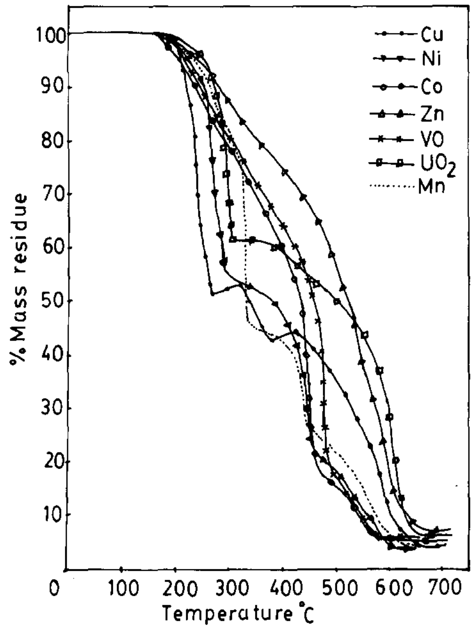


Fig. 1. TG curves for polychelates.

where W_t is the mass of the substance at temperature t, W_0 is the mass of the substance at initial stage and W_α is the mass of the residue at the end of the decomposition.

Thermal degradation curves for selected polychelates are shown in Fig. 1. TG curves show three decomposition stages in all polychelates. The plots of $\ln[\ln(1/Y)]$ against $(1/T)$ result in a straight lines of slope E/R (Fig. 2). The order of reaction was assumed to be unity in all cases. The plots made according to the Broido method were found to be linear over the entire range of decomposition and this strengthens the assumption regarding the overall order of the thermal decomposition reaction. The apparent activation energy was calculated for all three decomposition stages and values are reported in Table 2.

The degradation of copper(II), nickel(II) oxovanadium(IV) and dioxouranium(VI) chelates may be due to degradation of carbonyl group, methyl group and thiourea moeities in the first stage, methylene bridges in the second stage and the aromatic ring in the third stage. The degradation of manganese(II), cobalt(II) and zinc(II) chelates may be due to degradation of carbonyl group in the first stage, thiourea, methyl group and methylene bridges in the second stage and aromatic ring in the third stage. The greater mass loss in the first stage of copper(II), nickel(II), oxovanadium(IV) and dioxouranium(VI) chelates than manganese(II), cobalt(II) and zinc(II) chelates may be due to catalytic oxidative effect of copper(II), nickel(II), oxovanadium(IV) and dioxouranium(VI) ions [26].

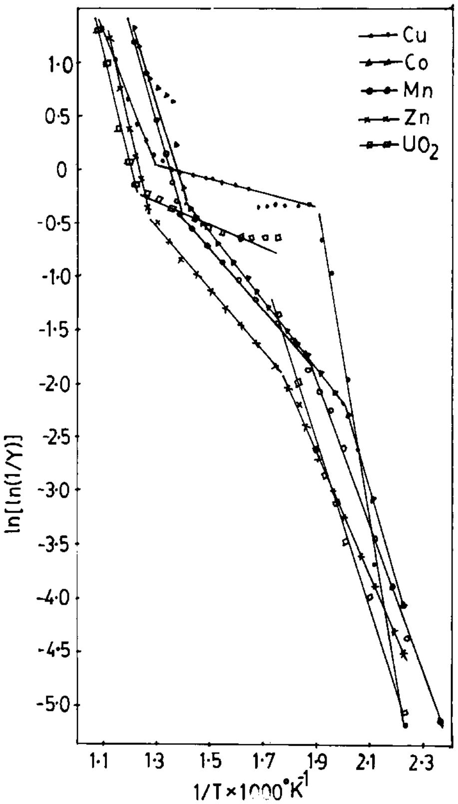


Fig. 2. Plot of ln[ln(1/*Y*)] versus 1/*T* for polychelates.

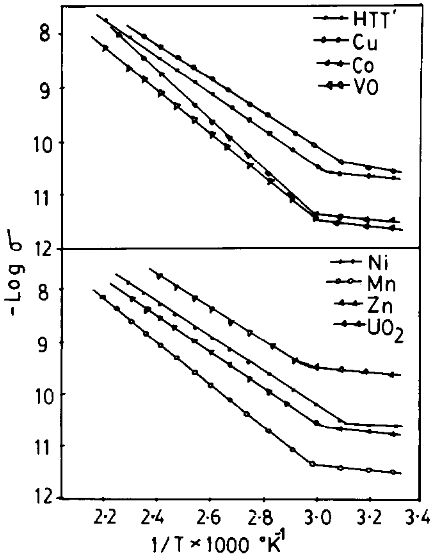


Fig. 3. Plot of log σ versus 1/*T* for resin and its polychelates.

TABLE 2

Kinetic parameters of polychelates

Polychelate [a]	Stage	Temperature range (°C)	Stage analysis	
			Mass loss (%)	Activation energy (kJ mol^{-1})
[Cu(HTT$'$)$_2$]	I	155–255	45.78	126.1
	II	255–495	17.79	5.3
	III	495–625	31.72	52.0
[Ni(HTT$'$)$_2$]	I	145–335	45.63	50.2
	II	335–415	13.81	7.9
	III	415–600	36.35	37.9
[Co(HTT$'$)$_2$]	I	160–230	10.32	67.6
	II	230–435	42.63	25.6
	III	435–570	41.59	71.8
[Mn(HTT$'$)$_2$]	I	150–260	13.08	59.6
	II	260–440	30.47	23.3
	III	440–575	50.67	63.7
[Zn(HTT$'$)$_2$]	I	160–295	12.44	46.8
	II	295–515	34.31	24.1
	III	515–640	45.44	89.4
[VO(HTT$'$)$_2$]	I	155–295	44.52	84.3
	II	295–410	10.22	6.3
	III	410–600	39.31	37.1
[UO$_2$(HTT$'$)$_2$]	I	170–300	38.32	64.5
	II	300–545	15.32	9.2
	III	545–645	39.98	87.3

[a] See Table 1 for key

The polychelates are less stable than the parent polymeric ligand [7] as expected [27]. The thermogram of copper(II) polychelate shown in Fig. 1 indicates that there is a small increase in the mass residue at 325 and 375°C. This increase in the mass may be due to the formation of copper sulphide and copper sulphate [28,29].

Electrical conductivity study

Semiconducting behaviour was systematically developed by Brattain et al. [30]. Pekaln and Kotosonov have studied the electrical conductivity of phenol–formaldehyde resin [31]. Dewar and Talati [32] have reported an industrially useful semiconducting material.

The electrical conductivity of ligand and its polychelates was studied over a wide range of temperature. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relationship

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

TABLE 3

Electrical data of polymeric ligand and its polychelates

Compound [a]	Electrical conductivity σ (ohm^{-1} cm^{-1})	T (K)	T_c [b] (K)	Activation energy (kJ mol^{-1})	σ_0 (ohm^{-1} cm^{-1})
HTT′	2.53×10^{-11}	303	325	64.5	5.31×10^{-1}
	8.74×10^{-9}	433			
[Cu(HTT′)$_2$]	2.74×10^{-11}	303	323	61.3	4.71×10^{-1}
	9.13×10^{-9}	423			
[Ni(HTT′)$_2$]	2.13×10^{-11}	303	323	63.8	2.06×10^{-1}
	1.55×10^{-8}	433			
[Co(HTT′)$_2$]	2.56×10^{-12}	303	333	88.4	2.98×10^{2}
	1.74×10^{-8}	453			
[Mn(HTT′)$_2$]	3.19×10^{-12}	303	333	79.3	1.12×10^{1}
	8.01×10^{-9}	453			
[Zn(HTT′)$_2$]	2.02×10^{-11}	303	333	65.0	5.03×10^{-1}
	1.20×10^{-8}	453			
[VO(HTT′)$_2$]	2.44×10^{-12}	303	333	77.1	5.18×10^{0}
	6.32×10^{-9}	453			
[UO$_2$(HTT′)$_2$]	2.39×10^{-10}	303	338	60.9	8.97×10^{-1}
	1.74×10^{-8}	413			

[a] See Table 1 for key.

[b] T_c is the temperature at which the polymers have intrinsic conduction.

where σ_0 is a constant, E_a is the activation energy and k is the Boltzmann constant. The plots of log σ versus $1/T$ are shown in Fig. 3. In general, the two steps observed have lower activation energies in the lower temperature region. This agrees well with the observations of Spiratos et al. [33] that the activation energy approaches higher values at high temperatures suggesting intrinsic conduction, while that at lower temperature has much lower values and is due to extrinsic conduction. The values of σ at temperature T, the temperature at which the polymers have intrinsic conduction T_c, activation energy and σ_0 values for the higher temperature region are given in Table 3.

The electrical conductivity at room temperature in decreasing order is, UO_2 > Cu > HTT′ > Ni > Zn > Mn > Co > VO. The activation energy decreases in the order Co > Mn > VO > Zn > HTT′ > Ni > Cu > UO_2, which is in partial agreement with the order reported earlier [34].

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