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Studies on Polymeric Chelates

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ABSTRACT

Chelates of Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), and dioxouranium(VI) have been prepared from p-hydroxybenzoic acid (P)-urea (U)-formaldehyde (F) copolymer (PUF). The metal-ligand ratios in the chelates were established by elemental analysis. The probable structures were elucidated on the basis of reflectance and IR spectra in conjunction with magnetic moments. These indicated a distorted octahedral structure for all the chelates except for dioxouranium(VI) chelate. Thermogravimetric analysis has been carried out to ascertain the relative thermal stability of ligand and chelates.

INTRODUCTION

A survey of the literature reveals that metal chelates of salicylic acid-formaldehyde polymer are reported to find use in photographic development [1] and rececpter layer for pressure-sensitive copy paper [2]. However, no work seems to have been reported on the synthesis and characterization of the chelates derived from a polymer containing p-hydroxybenzoic acid moiety. Hence it was thought interesting to prepare the chelates from p-hydroxybenzoic acid-urea-

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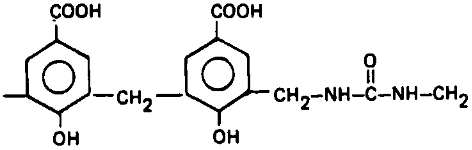
formaldehyde copolymer and characterize them, with a view that they may find some useful applications as mentioned above. We have prepared and characterized p-hydroxybenzoic acid-urea-formaldehyde copolymers (PUF) earlier [3]. The ligand (PUF) was prepared by the condensation of p-hydroxybenzoic acid, urea, and formaldehyde in the molar ratio 2:1:3, respectively. Almost the same mole composition as in the feed was estimated by elemental analysis in the copolymer [3]. Hence, on the basis of molar ratio of p-hydroxybenzoic acid unit to urea unit (2:1), for convenience, the probable chelating unit available in the polymeric chain for the divalent metal ion will be represented as 2L (MW = 372) as shown in (I):



(I)

In the present investigation we report the preparation and properties of Cu(II), Ni(II), Co(II), Mn(II), Fe(III), Zn(II), and dioxouranium(VI) chelates with PUF copolymer. The probable structures of these chelates have been determined on the basis of their characterization by elemental analysis, magnetic moments, and electronic and infrared spectral studies. Thermal (TG) properties were studied with a view to compare the thermal stability.

EXPERIMENTAL

Materials

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

Preparation of Chelates

Ligand (1.86 g, 0.01 mol) was dissolved in DMF (100 mL) and filtered through a G_2 grade sintered funnel. Copper nitrate (1.206 g, 0.005 mol) was also dissolved in DMF (100 mL) containing a slight amount of water. The metal solution was then added slowly to the ligand solution with stirring. A green solid was precipitated out at 5.5 pH when the saturated solution of sodium acetate in water was added in an adequate quantity. The product was digested for some time on a water bath. It was filtered and washed with DMF, a large amount of hot water, and acetone. The air-dried chelate was finely powdered and kept in a vacuum desiccator over silica gel. The yield was quantitative. The remaining chelates were prepared following a similar procedure. Metal nitrates were used for the Ni(II), Co(II), Fe(III), Zn(II), and dioxouranium(VI) chelates while a chloride salt was used for the Mn(II) chelate.

Measurements

The metal contents in the chelates were estimated by volumetric (EDTA) and gravimetric analysis. Carbon, hydrogen, and nitrogen were determined by a university C–H–N analyzer. Water contents in chelates were indicated by IR spectra and TG thermograms. The diffuse reflectance spectra were measured on a Beckman-DU 10 spectrophotometer using MgO as a reference. The magnetic measurements were made on a Sartosious Semimicro Gouy balance at room temperature.

RESULTS AND DISCUSSION

All the chelates described in the present study are insoluble in common organic solvents. They are soluble in alkali and concentrated H_2SO_4. The metal contents in each chelate were determined by titrating against the standard EDTA and gravimetric oxide method after decomposing the corresponding chelate. The elemental analysis indicated 1:2 and 1:3 (metal:ligand) stoichiometry for divalent metal ions and Fe(III), respectively (Table 1).

The diffuse reflectance spectrum of Cu(II) chelate exhibits a medium band at 10,204 cm^{-1}, a broad band centered at 13,071 cm^{-1} and an intense broad band at 24,096 cm^{-1}. The first two bands may be due to d-d transitions and the last might be due to a charge transfer [4]. The band positions are in accordance with distorted octahedral geometry [5]. The broad band remains unresolved in the spectrum, indicating that negligible distortion is present in the chelate. The observed transitions may be assigned as $^2A_{1g} \leftarrow {}^2B_{1g}$ (10,204 cm^{-1}), $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ ($\sim$13,071 cm^{-1}). The absorption bands in an electronic spectrum of Ni(II) chelate are obtained at 8,510, 13,986 and 25,316 cm^{-1} which may be assigned in an octahedral geometry as ν_1: $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ (8,510 cm^{-1}), ν_2: $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (13,986 cm^{-1}), and ν_3: $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ (25,316 cm^{-1}). The ν_2/ν_1 ratio (1.643) lies in the range required for octahedral chelates [6]. The diffuse reflectance spectrum of Co(II) chelate shows a medium band at 8,438 cm^{-1} and a broad band around 18,018

TABLE 1. Analytical Data and Magnetic Moment for the Chelates

Chelate[a]	Analysis[b] (%) Metal	C	H	N	Magnetic moment μ_{eff} (BM)	Color	pH for precipitation of chelates
$[Cu(L)_2(H_2O)_2]$	13.92 (13.53)	44.8 (46.00)	3.52 (3.83)	7.46 (5.96)	2.01	Green	5.8
$[Ni(L)_2(H_2O)_2]$	12.74 (12.63)	44.62 (46.48)	3.63 (3.87)	6.48 (6.02)	3.45	Greenish-yellow	6.3
$[Co(L)_2(H_2O)_2]$	11.58 (12.67)	47.13 (46.45)	3.68 (3.87)	6.60 (6.02)	4.78	Pink	6.0
$[Fe(L)_3]$	12.52 (11.17)	49.37 (51.05)	3.82 (3.36)	6.37 (6.72)	4.5	Dark violet	2.5
$[Mn(L)_2(H_2O)_2]$	10.55 (11.91)	47.67 (46.46)	4.50 (3.90)	6.35 (6.07)	5.24	Grey	6.5
$[Zn(L)_2(H_2O)_2]$	12.77 (13.87)	46.17 (45.82)	6.21 (5.99)	6.21 (5.94)	Dimagnetic	Grey white	5.5
$[UO_2(L)_2(H_2O)_2]$	33.53 (35.20)	33.41 (31.95)	4.07 (4.14)	4.07 (4.14)	Dimagnetic	Orange	3.5

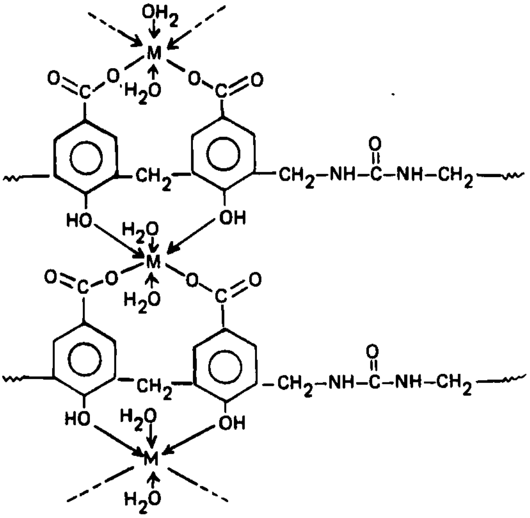
[a] $2L = C_{18}H_{16}O_7N_2$ (MW = 372).

[b] Theoretical values are given in parentheses.

cm^{-1} attributed to ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ transitions, respectively, for octahedral structure. ${}^4A_{2g} \leftarrow {}^4T_{1g}$ (ν_2) is not observed. The shoulder on a charge transfer band on the high energy side at 26,666 cm^{-1} may be due to appreciable tetragonal distortion [7]. The reflectance spectrum of Mn(II) chelate shows three weak bands in the normally expected regions for octahedral steriochemistry [8]. They may be assigned to the following transitions: ${}^4T_{1g} \leftarrow {}^6A_{1g}$ (17,391 cm^{-1}), ${}^4T_{2g} \leftarrow {}^6A_{1g}$ (21,052 cm^{-1}), and ${}^4A_{1g}, {}^4E_g \leftarrow {}^6A_{1g}$ (25,641 cm^{-1}). The diffuse reflectance spectrum of Fe(III) chelate shows bands at 14,300-17,500, 22,820, and 28,200 cm^{-1} which may be assigned to ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}$, ${}^4A_{1g}(G)$ and ${}^4T_{1g} \leftarrow {}^6A_{1g}$ transitions, respectively, for octahedral chelate [9].

The magnetic moments (Table 1) of Cu(II), Ni(II), Co(II), and Mn(II) chelates lie almost in the range required for octahedral geometry. The magnetic moment of Fe(III) (4.5 BM), is lower than required for octahedral Fe(III) chelates. The low value may be attributed to distortion from regular symmetry [10] or positive spin-orbit coupling and small magnetic antisotropy [11, 12]. Zn(II) and dioxouranium(VI) chelates are dimagnetic in nature.

Comparison of the IR spectra of the chelates and ligand (Table 2) 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. A broad absorption band obtained in the range 2800-3400 cm^{-1} in the spectrum of polymeric chelates is much less broad in the ligand, indicating the absence of hydrogen bonding in the chelates and the participation of phenolic –OH in the coordination. Considerable broadening around 3400 cm^{-1} in the chelates may be due to water molecules. Bending frequency of the –OH is shifted to a higher frequency in all the chelates supporting the –OH involvement in the coordination (Table 1). A band at 1675 cm^{-1} due to $\nu_{C=O}$ in the ligand is shifted to lower frequency at about 1655 cm^{-1} in all the chelates, which indicates the ionization of the –COOH group [13]. δ_{NH} is found unaltered in the chelates, suggesting the absence of coordination through the nitrogen of the urea unit. ν_{NH} and ν_{CH} of $-CH_2-$ are not clearly visualized from the spectra because this region is rendered complex due to ν_{NH}, ν_{CH} of $-CH_2-$, aromatic ring, and ν_{OH} of phenolic hydroxyl group and of coordinated water molecules. Only a weak broad band is obtained in this region. However, a small but sharp band at 845 cm^{-1} in the chelates may be attributed to $-CH_2-$ linkage [14]. In dioxouranium(VI) chelate a band at 920 cm^{-1} may be assigned to $\nu_{U=O}$. From what has been stated above and considering the random nature of the polymeric ligand [3], the following structure may be proposed for the chelates.



(II)

The analysis of TG data (Table 3) indicates that the polymeric chelates decompose in two stages. In all the chelates the rate of decomposition in the first stage is slow as compared to the second stage. Decomposition is complete at about 600°C in all the chelates. The possibility of coordinated water molecules as suggested from IR spectra is confirmed by TG data. Weight loss in Cu(II), Ni(II), Co(II), Mn(II), Zn(II), and dioxouranium(VI) chelates in the range 150-250°C may involve the loss due to the two water molecules (8%). The observed weight loss is a little higher than required in this region and this may be due to some other chain degradation reactions involved in pyrolysis of the chelates. The Fe(III) chelate in the above temperature range seems to be stable. Since the loss of water molecule is observed at higher temperature, it may be attributed to coordinated water molecules and not the water of crystallization.

The stability order of the chelates and ligand found is Fe(III) > Co(II) > Cu(II) > Ni(II) > dioxouranium(VI) > [Zn(II) ≈ Mn(II)] > ligand. The broido method [15] was applied to the thermal data obtained to determine the energy of activation and the order of the reaction.

TABLE 2. Infrared Data in cm^{-1}[a]

	Chelates							
Ligand	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(III)	Zn(II)	UO_2(II)	Assignment
1675 m	1655 m	1655 m	1650 w	1660 m	1655 m	1650 m	1660 m	$\nu_{C=O}$
3200-3400 b	3090-3425 b	3000-3400 b	3000-3400 b	2590-3400 b	3300-3400 b	2850-3400 b	3060-3400 b	Chelated –OH
1208 m	1215 m	1210 w	1210 w 1245 w	1220 w	1225 w	1225 w	1215 w	–OH bending (in-plane)
900-1000 wb	930 w	935 w	928 w	950 w	940 w	930 w	920 w	–OH deformation (out-of-plane)
1526 w 1545 w	1530 w 1550 w	1535 w	1535 w	1530 w	1530 w 1550 w	1525 w 1550 w	1530 w 1550 w	δ_{NH}
2825 w 2845 w	-	2950 w	-	2860 m	-	2850 w	-	ν_{CH} of $-CH_2-$
1445 w 1480 w	1485 w	1445 w 1475 w	1485 w	-	1445 w 1480 w	1430 m 1480 w	1445 w	δ_{CH} of $-CH_2-$
940 w 1135 m	930 m	940 w 1100 w	935 w 1130 w	950 w 1100 w	930 w 1090 w	935 w 1145 w	940 w 1145 m	1,3,4,5 substitution (in plane bending)
851 m	860 msh	865 w	860 m	860 msh	865 w	865 w	865 w	1,3,4,5 substitution (out of plane bending)

[a] m = medium, msh = medium sharp, b = broad, w = weak.

TABLE 3. Thermogravimetric Analysis Data

Chelate	Weight loss at temperature T(°C), %							Decomposition temperature (°C)		Energy of activation (E^x kcal/mol)		Order of reaction (n)	
	100	200	300	400	500	600	700	First stage	Second stage	First stage	Second stage	First stage	Second stage
Ligand	10.10	42.42	60.60	78.70	80.80	80.80	-	60-280	280-480	6.64	4.92	1	1
$[Cu(L)_2(H_2O)_2]$	2.38	11.90	41.27	51.58	64.28	82.54	83.33	60-240	240-640	4.83	3.14	1	1
$[Ni(L)_2(H_2O)_2]$	5.26	17.54	29.82	59.65	82.45	84.21	-	60-280	280-520	6.04	5.67	1	1
$[Co(L)_2(H_2O)_2]$	2.5	12.50	23.75	42.50	70.00	85.00	-	60-300	300-580	7.19	5.57	1	1
$[Fe(L)_3]$	1.57	10.52	22.63	44.21	55.79	63.15	72.10	60-280	280-640	6.68	4.04	1	1
$[Mn(L)_2(H_2O)_2]$	5.26	19.29	31.57	59.65	82.45	85.96	-	60-280	280-540	6.82	4.75	1	1
$[Zn(L)_2(H_2O)_2]$	4.13	16.7	28.38	62.61	75.1	82.73	-	60-275	275-530	5.35	4.82	1	1
$[UO_2(L)_2(H_2O)_2]$	2.73	15.36	32.74	53.6	73.0	83.21	-	60-275	275-545	7.23	6.37	1	1

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