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COORDINATION POLYMERS. 9. CHELATE POLYMERS DERIVED FROM BISPHENOLIC COMPLEXES AND PROPYLENEDIAMINE

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ABSTRACT

Chelate polymers derived from bis(2,4-dihydroxybenzaldehyde)propylenediimine M and bis(2,4-dihydroxyacetophenone)propylenediimine M ($M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$) with aromatic acid chlorides were prepared by interfacial polycondensation. Also, chelate polysiloxanes were obtained from the same monomers and α,ω-dichloropolydimethylsiloxane. The spectral, thermal, magnetic, and electrical properties of the polychelates were studied.

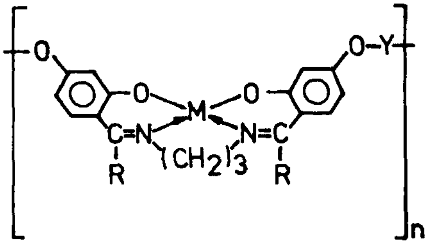
INTRODUCTION

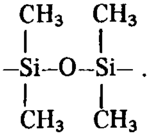
Coordination polymers having one-dimensional metal atom chain are of great interest as potential materials with high thermal resistance and semiconductor properties [1, 2].

This paper reports the preparation and characteristics of some new chelate polyesters and polysiloxanes based on bis(2,4-dihyhydroxybenzaldehyde)-propylenediimine M and bis(2,4-dihydroxyacetophenone)propylenediimine M ($M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$).

EXPERIMENTAL

The polymers have the following general formula:



For the chelates I_a-IX_a, $Y = p\text{-}COC_6H_4CO-$, with 1) R = –H, and M = Fe^{2+} (I), Co^{2+} (II), Ni^{2+} (III), Cu^{2+} (IV), Zn^{2+} (V); and with 2) R = $-CH_3$, and M = Fe^{2+} (VI), Ni^{2+} (VII), Cu^{2+} (VIII), Zn^{2+} (IX). For the polymers III_b, IV_b, VII_b, and $VIII_b$, Y =  $-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-$.

Synthesis

Bis(2,4-dihydroxybenzaldehyde)propylenediimine Fe^{2+} (I), Co^{2+} (II), Ni^{2+} (III), Cu^{2+} (IV), and Zn^{2+} (V) were obtained by literature methods [3].

Bis(2,4-dihydroxyacetophenone)propylenediimine Fe^{2+} (VI), Ni^{2+} (VII), Cu^{2+} (VIII), and Zn^{2+} (IX) were prepated by an original method: First, bis(2,4-dihydroxyacetophenone)propylenediimine was prepared by heating an ethanolic solution of 0.1 mol 2,4-dihydroxyacetophenone and 0.05 mol propylenediamine for 2 h on a water bath. Then the complexes were obtained by reaction between 1 mol bis(2,4-dihydroxyacetophenone)propylenediimine in ethanol and 1 mol iron sulfate, or nickel, copper, and zinc acetate in water, respectively, and refluxing several hours.

α,ω-Dichloropolydimethylsiloxane was synthesized as described elsewhere [4].

The chelate polyesters were obtained from the chelates (I-IX) and terephthaloyl chloride by interfacial polycondensation [5, 6].

The chelate polysiloxanes were prepared by polycondensation in a heterogeneous system [7, 8]. First, the sodium salt of the chelate monomers was obtained by dissolving them in aqueous alkali and then precipitating with acetone. After that, 1 mol sodium salt in the form of a benzene suspension was reacted with 1 mol α,ω-dichloropolydimethylsiloxane with stirring at room temperature for 40 h. The synthesis of these polychelates is very difficult and requires numerous precautions because of the sensitivity to hydrolysis of α,ω-dichloropolydimethylsiloxane.

The polymers were purified by repeated extractions with methanol and ethanol.

Physicochemical measurements were made as described earlier [9, 10].

RESULTS AND DISCUSSION

All the polychelates listed in Table 1 are stable, colored, amorphous powders, insoluble in water and common organic solvents. The chelate polysiloxanes showed some solubility in dimethylformamide and dimethylsulfoxide. The results of the elemental analyses (Table 1) suggest a metal: ligand/stoichiometry of 1:2 in all polymers with two water molecules associated with the formula $(-ML \cdot 2H_2O-)_n$. The presence of water molecules is supported by thermogravimetric analysis and infrared absorption spectra. α,ω-Dichloropolydimethylsiloxane contains 8-9 Si–O units on the average. The polycondensation between bisphenolic complexes and siloxane derivative results in a dimer or trimer mixture containing only two Si–O units. Increasing the polymerization time from 40 to 70 h and the temperature from 25 to 40-50°C does not achieve an increase in the siloxane chain length.

All the polymers are paramagnetic except the Zn^{2+} polymers, which are diamagnetic. The magnetic moments (μ_{eff}) of some of the polychelates are given in Table 1.

The values of the magnetic moment and the electronic reflection spectra indicate high-spin, slowly distorted octahedral configurations for the Fe^{2+} polychelates [11].

The Co^{2+} hexacoordinated bis(azooxo) polychelates exhibit distortions due to the Jahn-Teller effect, passing from an octahedral configuration to a square planar one. The greater the distortion, the higher is the magnetic moment of the spin-paired compounds [12].

Generally, the Ni^{2+} bis(azooxo) complexes with two water molecules coordinated in an axial arrangement have diamagnetic planar structures [13]. For our polychelates the intensity of the ligand field decreases because of the increase in the number of carbon atoms between the two nitrogen atoms. This causes the distortion of the planar configuration to a pseudotetrahedral one and thus the appearance of paramagnetism [14]. The lower magnetic

TABLE 1. Analytical Data and Physical Properties of Polychelates

Sample	MW of repeat unit,[a] g/mol	C	H	N	M	μ_{eff}, BM	Decomposition temperature, °C
		Found (calculated), %					
I	403.84	50.49 (50.51)	4.53 (4.95)	6.72 (6.93)	13.07 (13.82)	4.35	
I_a	533.84	55.01 (56.19)	3.60 (4.12)	4.95 (5.24)	9.13 (10.46)	4.45	195
II	406.93	49.97 (50.13)	4.27 (4.91)	6.59 (6.88)	13.63 (14.48)	2.19	
II_a	536.93	54.27 (55.87)	3.35 (4.09)	4.96 (5.21)	9.58 (10.97)	2.23	220
III	406.71	49.76 (50.15)	4.45 (4.91)	6.15 (6.88)	13.20 (14.43)		
III_a	536.71	54.46 (55.89)	3.32 (4.09)	4.63 (5.21)	10.09 (10.93)	2.18	235
III_b	536.71	47.23 (46.95)	3.27 (4.09)	4.73 (5.21)	10.26 (10.93)		
IV	411.54	48.93 (49.56)	4.50 (4.85)	6.25 (6.80)	14.13 (15.43)	1.83	

IV_a	541.54	54.35 (55.39)	3.27 (4.06)	4.72 (5.17)	12.50 (11.73)	2.22	250
IV_b	541.54	47.13 (46.53)	3.35 (4.06)	4.66 (5.17)	10.96 (11.73)		205
V	413.37	48.93 (49.35)	4.52 (4.83)	6.90 (6.77)	15.02 (15.81)	diamagnetic	
V_a	543.37	54.05 (55.21)	3.54 (4.04)	5.30 (5.15)	11.60 (12.03)	diamagnetic	230
VI	431.84	52.30 (52.79)	5.15 (5.55)	6.63 (6.48)	12.01 (12.93)	4.44	
VI_a	561.84	56.34 (57.66)	4.23 (4.62)	5.15 (4.98)	8.75 (9.93)	4.50	
VII	434.71	52.11 (52.74)	5.01 (5.52)	5.87 (6.44)	12.74 (13.50)	2.57	
VII_a	564.71	56.63 (57.37)	4.23 (4.60)	4.12 (4.95)	10.76 (10.39)	2.77	230
VII_b	564.71	47.63 (48.87)	4.21 (4.60)	4.72 (4.95)	11.26 (10.39)		210

(continued)

TABLE 1 (continued)

Sample	MW of repeat unit,[a] g/mol	C	H	N	M	μ_{eff}, BM	Decomposition temperature, °C
		Found (calculated), %					
VIII	439.54	51.32 (51.87)	5.17 (5.46)	5.96 (6.37)	15.28 (14.45)		
$VIII_a$	569.54	55.76 (56.88)	4.23 (4.56)	4.26 (4.91)	11.94 (11.15)	1.83	200
$VIII_b$	569.54	48.53 (48.46)	4.39 (4.56)	4.26 (4.91)	11.93 (11.15)		210
IX	441.37	51.20 (51.65)	5.12 (5.43)	6.73 (6.34)	13.95 (14.81)	diamagnetic	
IX_a	571.37	55.27 (56.70)	4.05 (4.55)	5.17 (4.90)	10.11 (11.44)	diamagnetic	

[a] Molecular weights of repeat unit estimated from elemental analysis.

moments (Table 1) and the absorption bands at 380, 600, and 720 nm support the simultaneous presence of both configurations.

The presence of six ligands suggests octahedral structures for the Cu^{2+} polychelates, but the electronic reflection spectra show a square planar environment around the metal ion, supported by the broad absorption band at about 590 nm.

The infrared absorption spectra of the chelate polymers resemble each other in general shape. The broad absorption band observed in the 3500-3300 cm^{-1} region, with a maximum around 3420 cm^{-1}, is attributed to OH-stretching vibrations of coordinated water molecules [15]. The presence of water molecules is also supported by the thermogravimetric data. The strong IR absorption band at 1720 cm^{-1} is assigned to C=O stretching as a result of the esterification reaction between the OH phenolic groups and the diacid chloride. There is also a strong absorption band at about 1600 cm^{-1} due to the C=N stretching. The chelate polysiloxanes show an absorption band in the 1000-1100 cm^{-1} region due to asymmetric Si–O–Si stretching [16].

The polymers start to decompose at 200-250°C (Table 1). The order of their thermal stabilities was found to be Cu > Ni > Zn > Co > Fe, which is comparable to the reported order [2, 17]. The experimental weight loss due to water in the polymers corresponds to the amount calculated for dihydrates. The abrupt change in weight shows decomposition of the ligand. Among the polymers obtained, Cu^{2+} polychelate is the most stable.

The electrical measurements were carried out over a range of temperatures (Table 2). It was found that the negative logarithm of conductivity of the polychelates is a linear function of the reciprocal temperature in this range. The activation energy (E_a) and the specific conductivity (σ_0) were calculated by the expression $\sigma = \sigma_0 \exp(-E_a/2kT)$, where σ is the electrical conductivity at T K, σ_0 is a constant, and k is the Boltzmann constant. These values and the room-temperature electrical conductivity are summarized in Table 2. The activation energy decreases in the order Ni > Cu > Co > Zn for the polyesters derived from bis(2,4-dihydroxybenzaldehyde)propylenediimine, which is in partial agreement with the order observed previously [18].

CONCLUSIONS

Coordination polymers have been obtained from bisphenolic complexes and terephthaloyl chloride by interfacial polycondensation. Chelate poly-

TABLE 2. Electrical Data of Some Polychelates

Sample	ΔT, K	E_a, eV	$\sigma_{298\text{ K}}$, $\Omega^{-1}\text{cm}^{-1}$	σ_0, $\Omega^{-1}\text{cm}^{-1}$
II_a	298-425	1.35	7.15×10^{-10}	2.80×10^{1}
III_a	300-450	1.60	1.20×10^{-10}	3.24×10^{4}
III_b	300-475	1.35	7.20×10^{-9}	1.51×10^{3}
IV_a	300-490	1.45	6.85×10^{-9}	1.05×10^{4}
V_a	300-420	1.25	8.33×10^{-10}	3.10×10^{1}
VI	300-430	1.70	7.51×10^{-11}	1.76×10^{4}
VII_a	300-470	1.40	6.52×10^{-9}	3.64×10^{3}
$VIII_a$	300-440	1.45	2.35×10^{-11}	4.20×10^{1}
$VIII_b$	300-480	1.20	2.40×10^{-8}	2.85×10^{2}

siloxanes have been synthesized from the same monomers and α,ω-dichloropolydimethylsiloxane by polycondensation in heterogeneous systems.

The configurations of the chelate ring (stereochemistry) of these polychelates have been derived by using elemental analysis, electronic and infrared spectral data, and magnetic measurements.

The decomposition temperature of the polychelates is in the order Cu> Ni > Zn > Co > Fe, while the thermal activation energy of the electrical conduction follow the order Ni > Cu > Co > Zn.

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