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Coordination Polymers

5. Chelate Polymers of 2,4-Dihydroxybenzaldehyde

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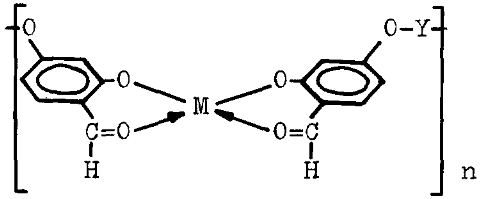
SUMMARY:

Chelate polymers obtained from bis(2,4-dihydroxybenzaldehyde)M^{2+} ($M = Fe^{2+}$, Co^{2+}, Ni^{2+}, Zn^{2+}) with organic acid chlorides were synthesized and characterized by elemental analysis, magnetic and electric measurements, spectral and thermogravimetric studies.

INTRODUCTION

In earlier papers (Spiratos et al.1979, Spiratos et al. 1980, Singurel et al.1980, Spiratos et al.1981) some chelate polymers of bisphenol complexes and aromatic acid clorides have been described. The present paper deals with the preparation and physico-chemical properties of some chelate polymers obtained from bis(2,4-dihydroxybenzaldehyde)M^{2+} ($M = Fe^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+}) with organic acid chlorides. These polymers obey the following general formula:



Where: $M = Fe^{2+}$ (I)
$M = Co^{2+}$ (II)
$M = Ni^{2+}$ (III) for the chelates
$M = Zn^{2+}$ (IV)

and: I_a, II_a, III_a, IV_a ; $Y = p\text{-}COC_6H_4CO\text{-}$ for the polymers.
I_b, II_b, III_b, IV_b ; $Y = m\text{-}COC_6H_4CO\text{-}$

All the polymers are obtained by interfacial polycondensation.

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EXPERIMENTAL

Bis (2,4-dihydroxybenzaldehyde)Fe^{2+} (I) and Zn^{2+}(IV) were prepared according to the literature (Locquette and Marechal, 1975).

Bis(2,4-dihydroxybenzaldehyde)Co^{2+} (II) and Ni^{2+} (III) were obtained by the reaction between 2 moles of resorcylic aldehyde and 1 mole of cobalt or nickel acetate in water, in the presence of sodium acetate, on water bath for two hours.

The chelate polymers were synthesized starting from the chelates (I - IV) and the diacid chloride by interfacial polycondensation (Eareckson, 1959). Thus, $8.33\cdot10^{-3}$ moles of complex salt in aqueous alkali ($1.67\cdot10^{-2}$ moles in 100 ml of water) reacted with $8.33\cdot10^{-3}$ moles diacid chloride (terephtaloyl and isophtaloyl chlorides) in dichlormethane, in the presence of sodium lauryl sulfate, as dispersion agent. The mixture was strongly stirred for 5 - 8 minutes and the polychelates were isolated by precipitation in acetone. They were than purified by repeated extractions with methanol and ethanol.

The polychelates in form of coloured powders were insoluble in common organic solvents. They showed some solubility in dimethylformamide.

The infrared absorption spectra were recorded on a Perkin-Elmer Spectrophotometer Model 577, in KBr pellets, the electronic reflexion spectra on an Unicam SP-800 Spectrophotometer.

The magnetic susceptibilities were measured at room temperature by Gouy's method using $HgCo(SCN)_4$ as a calibrant. The magnetic moments were calculated using the relation:

$$\mu_{eff} = 2.83\sqrt{\chi_M\cdot T}$$

were χ_M is the molar susceptibility after the application of a diamagnetic correction. The results are shown in Table 1.

The thermal behaviour in air was studied by means of a Derivatograph MOM-Budapest, type Paulik-Paulik-Erdey using a heating rate of 9°/min..

The electrical conductivity of the polychelates was measured in pellets of 1 cm in diameter. The pellets were obtained by pressing finely powdered polymers at 10 t/cm^2, in vacuum. The electrical resistivity of the polymers over a range of temperature was determined with an arrangement previously described (Singurel et al. 1980, Rusu 1971, Rusu 1969).

The corresponding Cu^{2+} polymers were synthesized and described previously (Spiratos et al. 1979).

RESULTS AND DISCUSSION

Since the chelate polymers were insoluble in common organic solvents it was not possible to use conventional characterisation methods as viscometry, osmometry, etc.

The analytical data (table 1) are in good agreement with a metal to ligand ratio 1:2 for the chelate polymers.

All polychelates were paramagnetic, excepting the Zn^{2+} polymers (IV_a, IV_b). The paramagnetism of these polymers is the result of an octahedral configuration achieved by the metal atoms by coordination of two water molecules. The binding of water molecules is evidenced by thermogravimetric analysis. The magnetic data and electronic reflexion spectra, indicate a strongly distorted octahedral configuration for Fe^{2+} polymers confirmed by the small values of magnetic moment and the absorption band at 500 nm. The smaller value of the magnetic moments may be due to the contamination of the sample with Fe^{3+}. This fact did not affect the elemental analysis and therefore it could not be evidenced (de Vries et al. 1974, Earnshow et al. 1968a).

The Co^{2+} polymers have generally a planar structure. By coordination of two water molecules, the tetragonal distorsion is reduced and the magnetic properties will correspond to those of an octahedral structure. In the case of polychelates (II_a, II_b) the higher value of the magnetic moment and the absorption band at 450 nm suggest the simultaneous existence of two configurations (Earnshow et al. 1968b, Figgis and Nyholm 1959, Busetto et al. 1973, Calligaris et al. 1973, Ochiai 1973).

The Ni^{2+} polymers have a slightly distorted octahedral configuration noticed by the absorption bands at 380 and 500 - 750 nm (Drago, 1965) and the smaller magnetic moments.

TABLE 1

Elemental analysis, magnetic properties and decomposition temperatures of chelate polymers

Sample	C	H	M	μ_{eff} (MB)	T_d^+ (°C)
	Found (Calcd.), %				
I	47.02 (45.92)	3.25 (3.82)	14.88 (15.26)	2.36	
I_a	53.01 (53.24)	3.38 (3.22)	11.76 (11.26)	2.36	245
I_b	52.44 (53.24)	3.82 (3.22)	12.84 (11.26)	2.36	240
II	44.97 (45.53)	3.56 (3.79)	13.79 (15.79)	2.15	
II_a	52.21 (52.91)	3.62 (3.20)	10.53 (11.81)	2.15	221
II_b	53.85 (52.91)	3.47 (3.20)	10.21 (11.81)	2.15	300
III	47.02 (45.56)	3.25 (3.79)	14.88 (15.92)	2.64	
III_a	51.45 (52.93)	3.85 (3.20)	12.65 (11.77)	2.64	267
III_b	51.07 (52.93)	3.92 (3.20)	13.01 (11.77)	2.64	242
IV	45.25 (44.75)	3.53 (3.72)	15.07 (17.41)	diamagnetic	
IV_a	54.15 (52.23)	3.25 (3.16)	10.14 (12.93)	diamagnetic	
IV_b	54.36 (52.23)	3.37 (3.16)	9.87 (12.93)	diamagnetic	

+ Decomposition temperature taken as point of deviation from the base line.

The coordination polymers of Zn^{2+} (IV_a, IV_b) were hexa-coordinated and diamagnetic as expected (Batley and Gaddon 1967, Furuhashi and Yokota, 1979).

The thermograms show the presence of water molecules in all polychelates. This observation is in agreement with IR absorption spectra. The loss of water at higher temperatures suggest its presence in coordination sphere (Das et al. 1978). The decomposition temperature for the polychelates have been given in Table 1. From this data the following thermal stability order can be assumed for the polychelates.

$$Ni^{2+} > Fe^{2+} > Cu^{2+} > Co^{2+}$$

The decomposition temperature of the chelates is smaller than of the respective polychelates, suggesting herewith the polymeric nature of these compounds.

The initially weight loss of the polychelates is 6-7% and corresponds to two moles of water per mole of polymer.

The ulterior rapid weight loss indicates the decomposition of the ligand. The residues calculated according to the TG curves do not correspond always to the calculated metal oxydes, suggesting an incomplete decomposition of the polychelates at 600°C.

Polychelates with $Y = m\text{-}COC_6H_4CO\text{-}$ were less stable than those with $Y = p\text{-}COC_6H_4CO\text{-}$. This behaviour can be explained by the fact that the free rotation of the $-COC_6H_4CO-$ group is hindered in meta substitution, the breaking of the bond requiring suplementary thermal energy.

TABLE 2

Electrical properties of polychelates

Sample	T (°C)	ΔE (eV)	σ_{298K} $(\Omega^{-1}.cm^{-1})$	σ_o $(\Omega^{-1}.cm^{-1})$
I_a	300-475	1.65	$6.66 \cdot 10^{-8}$	$1.67 \cdot 10^{3}$
I_b	300-465	1.60	$6.95 \cdot 10^{-8}$	$8.77 \cdot 10^{2}$
II	300-465	1.50	$2.45 \cdot 10^{-7}$	$6.97 \cdot 10^{2}$
II_a	300-480	1.80	$4.50 \cdot 10^{-8}$	$9.94 \cdot 10^{3}$
II_b	300-460	1.45	$4.10 \cdot 10^{-7}$	$5.64 \cdot 10^{2}$
III	300-475	1.45	$1.75 \cdot 10^{-10}$	$8.01 \cdot 10^{1}$
III_a	300-460	1.95	$6.86 \cdot 10^{-10}$	$1.34 \cdot 10^{3}$
III_b	300-480	1.85	$5.56 \cdot 10^{-9}$	$2.54 \cdot 10^{3}$

The IR absorption spectra of the polychelates were similar, but completely different from those of the ligands.

IR absorption spectra of the polychelates exhibit strong absorption bands at aproximately 1725 cm^{-1}, assigned to stretching frequencies of the carbonyl resulted from the polycondensation reaction between -OH groups and diacid chloride. A weak band at aproxymately 3400 cm^{-1} indicates the presence of water molecules.

The dependence on temperature of the conductivity obeys the well known relation:

$$\sigma = \sigma_0 . \exp(-\Delta E/2KT)$$

where: σ_0 is the electrical conductivity at infinite temperature and ΔE the activation energy.

The plots of ln σ versus reciprocal temperature are linear. The results are given in Table 2. Over the range temperature studied the electrical conductivity varies between $10^{-12} - 10^{-7} \Omega^{-1}.cm^{-1}$. However, despite of metal content, the conductivity of the chelate polymers is rather low.

The values of the obtained activation energy increase in the following order:

$$Cu^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$$

The sign of the Seebeck coefficient is positive suggesting the predominance of holes as majority charge carriers and that the polychelates are p-type semiconductors.

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