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Coordination polymers

V. Polycondensation of Cu, Ni, Co and Mn rezorcylaldehyde-o-phenylendiamine with terephthalic and isophthalic dichloride

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SUMMARY

By interfacial polycondensation of Cu,Ni,Co and Mn rezorcylaldehyde-ophenylenediamine sodium salt with terephthalic and isophthalic dichloride respectively, coordination polymers, particularly chelate plyesters, as coloured powders, insoluble in organic solvents, were obtained. The identification of coordination polymers has been carried out by the elementary analysis and IR spectroscopy.

INTRODUCTION

The synthesis of the coordination polymers may be performed by several procedures. One of these is the polycondensation of sodium salt of chelates with acid dichlorides, using the interfacial techniques.

In the previous papers synthesis of coordination polymers (chelate polyesters) of Ni-bis(2,4-dioxyacetophenoneimine)(1) and Cu-bis(rezorcylaldehyde) with terephthalic and isophthalic dichloride (2)respectively, has been presented.

The present work deals with synthesis of the chelate polymers of Cu,Ni,Co and Mn rezorcylaldehyde-o-phenylenediamine with terephthalic and isophthalic dichlorides by interfacial polycondensation reactions. The insolubility of the coordination polymers in common organic solvents left the elementary analysis and IR spectroscopy (3),(4),(5), as the means for their identification.

EXPERIMENTAL

The Schiff base, Cu,Ni,Co and Mn rezorcylaldehyde-o-phenylenediamine and terephthalic and isophthalic dichloride were synthesized according to the methods described in the literature (6,7).

Synthesis of Coordination Polymers

10^{-3}mol. of Cu(I) rezorcylaldehyde-o-phenylenediamine was dissolved with magnetic stirring in a stoechiometric quantity of 0,1 n NaOH. The sodium salt of the chelate solution was added to a solution of 10^{-3}mol. terephthalic (A) or isophthalic (B) dichloride in 25 ml methylene chloride. The reaction mixture was vigorously stirred for 10 min., and the mixture was poured into 100 ml acetone. In a similar way were synthesized coordination

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polymers with Ni(II), Co(III) and Mn(IV). The coordination polymers (I_A-IV_A) and (I_B-IV_B) were filtered, washed with EtOH and then dried at 110°C.

Table I

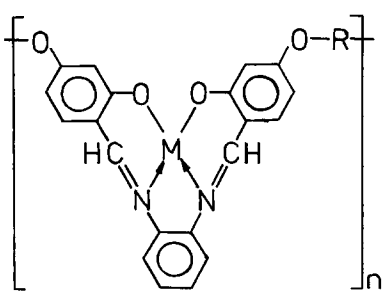
The Elementary Analysis of Chelates I-IV of the Coordination Polymers I_A-IV_A and I_B-IV_B

	C %		H %		N %		M %	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found
I	58.60	58.05	3.41	4.25	6.83	6.55	15.51	14.89
I_A	62.27	61.30	2.96	3.61	5.18	5.88	11.77	10.85
I_B	62.27	61.99	2.96	2.85	5.18	5.10	11.77	11.75
II	59.30	59.01	3.45	3.88	6.63	6.70	14.50	13.97
II_A	62.84	61.71	2.99	3.27	5.23	4.83	10.97	10.00
II_B	62.84	61.70	2.99	3.10	5.23	5.00	10.97	12.77
III	59.26	58.96	3.45	3.43	6.91	7.01	14.55	14.13
III_A	62.81	61.48	2.99	3.00	5.23	5.45	11.01	11.00
III_B	62.81	61.99	2.99	2.89	5.23	5.10	11.01	11.00
IV	59.86	5946	3.49	3.93	6.98	6.44	13.17	13.10
IV_A	63.28	61.75	3.01	3.33	5.27	5.43	10.34	10.75
IV_B	63.28	62.18	3.01	2.99	5.27	5.18	10.34	10.27

The IR spectra were recorded on a Perkin Elmer 577 spectrophoto-meter, in the range of 300-4000 cm^{-1}. The samples were ground on a Perkin Elmer vibratory mill for 5 min., and the powder was pelleted with KBr and CsI.

RESULTS AND DISCUSSION

The reaction between Cu(I), Ni(II), Co(III) and Mn(IV) rezercylaldehyde-o-phenylendiamine and stoechiometric quantity of NaOH yields sodium salts. By the interfacial polycondensation, using alkaline aqueous solution and terephthalic or isophthalic dichloride dissolved in methylene chloride, chelate polyesters are formed as coloured powders, which have the following structure of the macromolecular chain unit



where:

I	M-Cu	I_A	: R = p-CO-C_6H_4-CO
		I_B	: R = m-CO-C_6H_4-CO
II	M-Ni	II_A	: R = p-CO-C_6H_4-CO
		II_B	: R = m-CO-C_6H_4-CO
III	M-Co	III_A	: R = p-CO-C_6H_4-CO
		III_B	: R = m-CO-C_6H_4-CO
IV	M-Mn	IV_A	: R = p-CO-C_6H_4-CO
		IV_B	: R = m-CO-C_6H_4-CO

The chelate polyesters are insoluble in the common organic solvents and have following colours: I_A and I_B olive, II_A and II_B red-brown, III_A and III_B dark-brown, IV_A and IV_B black.

In order to estimate from the spectral point of view the synthesized products, the vibration interval of 300-1800 cm^{-1} was chosen.

The Schiff base is characterised by a 1,2,4 trisubstituted ring (TS) with substituents: 1 "heavy", 2,4 di- "light", 2 adjacent free H and 1 free H. An orto substituted ring (OS) with substituents: 1,2 di - "heavy" and 4 adjacent free H.

Table II
The Specific Bands of the Schiff Base

1612^s cm^{-1}	$\nu(C = N)$
1365	def OH — $\delta'(OH) + \nu(\phi - O)^{OH}$
1217	$\nu(\phi - O)^{OH}$
845	TS, 1 free H, γ (= CH)
792	TS, 2 adjacent free H, γ (= CH)
752	OS, 4 adjacent free H, γ (= CH)

s = shoulder

The chelates (I - IV) are caracterized by 1,2,4 trisubstituted ring (TS) with substituents: 1,2 di - "heavy", 4 "light", 2 adjacent free H and 1 free H. An orto substituted ring (OS) with substituents: 1,2 di - "heavy" and 4 adjacent free H.

The coordination polymers of terephthalic dichloride (I_A - IV_A) have a 1,2,4 trisubstituted ring (TS), with substituents: 1,2, 4 tri-"heavy", 2 adjacent free H and 1 free H. The orto substitution (OS) has 1,2 di-"heavy" substituents and 4 adjacent free H, the para substituted ring (PS) has the substituents 1,4 di-"heavy" and 2 adjacent free H.

The coordination polymers of isophthalic dichloride (I_B - IV_B) have the same TS and OS as polymers (I_A - IV_A). The meta substituted ring MS has substituents: 1,3 di- "heavy", 3 adjacent free H and 1 free H.

Table III

The Specific Bands of the Chelates I-IV

I	II	III	IV	
1614^{s}	1615^{s}	1610^{s}	1610^{s} cm^{-1}	ν(C = N)
1365	1368	1365	1350	def OH—δ'(OH)+ ν(ϕ-O)^{OH}
1235	1248	1235^{s}	1225	ν(ϕ-O)^{chelate}
1198	1200	1200	1200	ν(ϕ-O)^{OH}
840	840	840	840	TS,1 free H, γ(=CH)
800	787	790	805	TS,2 adjacent free H,γ(=CH)
750	743	742	755	OS,4 adjacent free H, γ(=CH)
640	650	650	650	ν(M - O)
532	542	542	527	ν(M - N)
380	430	430	403	ν(M - N)

Table IV

The Specific Bands of the Coordination Polymers I_A-IV_A

I_A	II_A	III_A	IV_A	
1732	1725	1720	1730 cm^{-1}	ν(C = O)
1612^{s}	1610^{s}	1610^{s}	1612^{s}	ν(C = N)
1235	1234	1235	1230	ν(ϕ - O)^{chelate}
1190	1192	1200	1198	ν(ϕ - O)^{carboxyl}
1065	1060	1065	1060	ν(C(=O) - O)
870	870	872	870	PS,2 adjacent free H, γ(=CH)
846	840	840	840	TS,1 free H,γ(=CH)
785	785	788	802	TS,2 adjacent free H, γ(=CH)
752	743	742	758	OS,4 adjacent free H, γ(=CH)
640	630	655	652	ν(M - O)
548	540	550	522	ν(M - N)
385	430	430	403	ν(M - N)

Table V

The Specific Bands of the Coordination Polymers I_B-IV_B

I_B	II_B	III_B	IV_B		
1730	1732	1730	1730	cm^{-1}	ν(C = O)
1612^s	1612^s	1613^s	1610^s		ν(C = N)
1230^s	1235^s	1235	1230		ν(Φ - O) chelate
1190	1195	1195	1195		ν(Φ - O) carboxyl
1058	1055	1055	1051		ν(C(O) - O)
865^s	870^s	865^s	865^s		TS,2 adjacent free H, δ(=CH)
855	855	850	843		TS,1 free H, δ(=CH) MS,1 free H, δ(=CH)
790	785	790	803		TS,2 adjacent free H, δ(=CH)
750	745	750	755		MS, 3 adjacent free H, δ(=CH) OS,4 adjacent free H, δ(=CH)
717	715	725	716		MS,3 adjacent free H, δ(=CH) δ'(ring)
640	660	655	650		ν(M - O)
546	540	540	525		ν(M - N)
380	436	458	403		ν(M - N)

The Fig.1 shows the spectral differences between the Schiff Base (SB), Cu chelate (I) and the coordination polymers with terephthalic (I_A) and isophthalic dichloride (I_B)

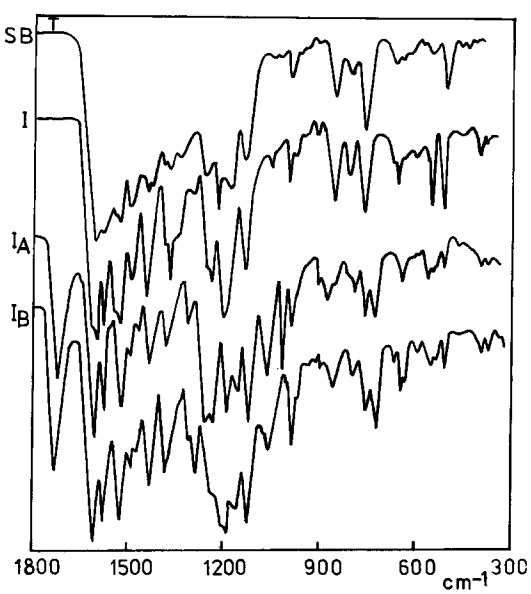


Fig. 1.

CONCLUSION

The elementary analysis and the IR spectra are in agreement with the proposed structures.

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