Metal Complexes of Polyesters

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Abstract

Polyesters obtained from 2,5-dihydroxyterephthalic acid and 1,*n*-alkanediols were used to complexate the metal ions Mg^{2+}, Ca^{2+}, Sn^{2+}, Pb^{2+}, Ga^{3+}, In^{3+}, Bi^{3+}, Si^{4+}, Ce^{3+}, $UO_2{}^{2+}$, Mn^{2+}, Mn^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}. The metal ions are always six-coordinated with additional ligands (mostly H_2O) besides the four from the polyester system. The H_2O-ligands can be removed by heating in vacuum, as was proven for the complexes of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, and are added again in moist air. For the waterfree Ni^{2+}-complex a tetrahedral surrounding is suggested by magnetic measurements. Polymerization degrees of the polyesters were found to be 30–70 by the membrane osmometric method. Thermal stabilities of the metal complexes (200–300 °C) are less than those of the polyesters themselves (300–350 °C).

Introduction

In a series of previous papers, we reported the special complexing abilities of polymeric Schiff bases obtained from methylene-bridged bis-salicylaldehydes and diamines [1–4] and the unusual adsorption qualities of these compounds [5–8]. Later on we also synthesized similar complexes with 4N ligands better suited to stabilize metal ions of the second and third row of the periodic table [9]. It seemed also worthwhile, to modify the ligand system in the other direction, *i.e.* to replace the N of the aldimine group by an O base to get four O ligands for metal ions, which prefer coordination to harder bases. Unfortunately, esters of 5,5′-methylene-bis-salicylic acid with alkanediols are not easily obtainable. However, polyesters using 2,5-dihydroxyterephthalic acid instead of salicylic acid are known [10–13]. They may prove equally suitable for complexation reactions.

Experimental

Poly-1,n-alkanediol-2,5-dihydroxyterephtalates (n = 2–5)

100 mmol of 2,5-dihydroxyterephthalic acid diethylester are reacted with 200 mmol of alkanediol in an inert solvent (250 ml l-methyl-naphthalene) by stirring for 24 h under a N_2 atmosphere, using 0.1% $Zn_3(BO_3)_2$ as catalyst and choosing the correct temperature (dependent on the boiling point of the alkanediol). Hydroxyalkylesters are formed first, which polymerize, when the excess alkanediol is removed as an azeotrope with 1-methyl-naphthalene by distillation [13].

Poly-1,6-hexanediol-2,5-dihydroxyterephthalate

This compound can be most easily obtained by melting a mixture of 2,5-dihydroxyterephtalic acid (100 mmol) or its diethylester with the double to triple molar amount of 1,6-hexandiol at 180 °C for 3 h and removing the volatile component (H_2O or C_2H_5OH) together with the excess 1,6-hexanediol by distillation. The reaction is continued by adding 2% *p*-toluene-sulfonic acid as catalyst at 280 °C in vacuum until completion (6 h) [10–12].

Poly-1,6-hexanediol-2,5-dihydroxydihydroterephthalate

The mixture of 100 mmol of 1,4-cyclohexanedione-2,5-dicarboxylic acid diethylester and 100 mmol 1,6-hexanediol together with 1% *p*-toluenesulfonic acid as catalyst is molten at 150 °C. After solidification, the alcohol was removed in vacuum. The reaction was then continued for 40 h in chlorobenzene as solvent. The product was precipitated by adding methanol.

Synthesis of the Metal Complexes

Depending on its solubility, the polyester is dissolved either in pure dimethylformamide or in an 1:1 mixture of dimethylformamide and 1,2,4-trichlorobenzene by heating. Then, an equimolar amount of the metal salt (water containing acetates or nitrates) in the same solvent is added dropwise. Adding a Brönsted base like triethylamine, pyridine, or sodium acetate, the mixture is heated to 150 °C for another 3 h until precipitation of the complex is complete. If educts or products are sensitive to oxygen, the reaction may be run in an inert N_2 atmosphere. The precipitate is sucked off and treated with absolute ethanol and chloroform in a Soxhlet apparatus, then dried at 95 °C in vacuum. The coordi-

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nated water molecules can be removed by heating for 12 h at 160 ℃ in vacuum.

Measurements

Molecular weights of the polyester ligands were determined by a membrane osmometer (Knauer 01.00) using regenerated cellulose as membrane material and *m*-cresol as solvent.

The thermal stability was evaluated with a Netzsch TG 409 E apparatus; magnetic moments were determined at room temperature using Gouy's method and $CoHg(SCN)_4$ as standard.

Infrared spectra were recorded as a Nujol mull with a Perkin-Elmer model 577 instrument.

Results and Discussion

The hitherto known polyesters from 2,5-dihydroxyterephtalic acid and alkanediols [10–13] were supplemented by poly-1,5-pentanediol-2,5-dihydroxyterephtalate to give a continuous series from 1,2-ethanediol up to 1,6-hexanediol; in addition, poly-1,6-hexanediol-2,5-dihydroxydihydroterephtalate was synthesized as a non-aromatic ligand system. The evaluation of mean molecular weights by the osmometric method showed the mean degree of polymerization to be 30–70 for these polyesters. Analytical data for the polyesters is given in Table I.

The excellent complexing properties of these polyesters were proven by the preparation of a lot of metal complexes, containing ions of various main group as well as first row transition metals as central atoms (see Table II). The length of the alkane chain of the diol seems to have no influence on the complex formation.

The analytical results are only consistent with an octahedral surrounding of the central ion, assuming two additional water molecules as ligands for the divalent metal ions, one water and one anion (in the case of NO_3^- giving also the proper amount of N in elemental analysis) for the trivalent ones. The Si^{4+} complex has two acetate anions; in the UO_2^{2+} complex, the oxygens of the uranyl group are in the fifth and sixth coordination position, additional ligands are thus unnecessary. The magnetic moments of the Mn^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+} complexes are consistent with an octahedral high spin configuration too, the Co^{2+} complexes having an appreciable orbital contribution as usual [14, 15].

More structural information, especially if a third chelate ring is formed by the alkane bridge of the diol resulting in a chain like polymer metal complex for which a degree of polymerization analogous to the polyester ligand itself might by assumed, or if the metal ion is forming highly polymer coordination compounds, linking different polyester chains, which seems more probable, cannot be deduced from the present experimental data.

The thermal stability of the complexes is remarkably less than that of the polyester itself, with the complexes of Mg^{2+}, Ca^{2+}, Ga^{3+}, Sn^{2+}, UO_2^{2+} and Ni^{2+} the most stable Pb^{2+} and Cu^{2+} the least stable ones. There was no appreciable change of the decomposition temperature by heating the complexes in a N_2 atmosphere instead of air, thus indicating that there is no initial attack of oxygen.

By heating for 12 h at 160 ℃ in vacuum, the two water ligands could be removed from the complexes Mn^{2+}-1,5T, Co^{2+}-1,2T, Ni^{2+}-1,3T, Ni^{2+}-1,6H, Cu^{2+}-1,4T and Zn^{2+}-1,6T. This was proven by infrared spectroscopy, as the broad band at 3500 cm^{-1}, otherwise always present, disappeared completely. For the Ni^{2+} complexes, magnetic moments of 3.9 and 4.0 BM were obtained indicating a tetrahedral surrounding of the Ni^{2+} ion. All these water-free complexes are extremely hygroscopic, which prevented the evaluation of exact analytical data. On the other hand unusual adsorption qualities might be expected as for the polymer Schiff base complexes [5–8], but have still be be proven more extensively.

TABLE I. Analytical Data for Polyesters[a]

Polyester from		Abbreviation	Found(calc.)		Thermal stability (℃ (in air))	Mean molecular weight
Terephthalic acid or ethylester	Diol		C	H		
2,5-dihydroxy-	1,2-ethane-	1,2-T	56.42(53.58)	4.08(3.60)	345	
2,5-dihydroxy-	1,3-propane-	1,3-T	56.68(55.47)	4.82(4.23)	330	9485
2,5-dihydroxy-	1,4-butane-	1,4-T	57.38(57.15)	4.88(4.80)	320	
2,5-dihydroxy-	1,5-pentane-	1,5-T	58.89(58.65)	5.42(5.30)	340	18782
2,5-dihydroxy-	1,6-hexane-	1,6-T	61.69(60.00)	6.40(5.75)	325	18636[b]
2,5-dihydroxy-dihydro	1,6-hexane-	1,6-H	59.13(59.57)	6.70(6.43)	300	7865

[a] Colour of all polyesters of terephthalic acid are brown–green, that of the dihydro-compound is yellow. [b] From terephtalic acid: 13 644.

TABLE II. Data for Polyester Metal Complexes[a]

Metal ion	Ligands (see Table I)	Additional ligands	Found(calc.)			Thermal stability (°C) (in air)	Magnetic moment (BM)
			C	H	Metal		
Mg^{2+}	1,2-T	$2H_2O$	45.26(42.51)	4.74(3.56)	6.51(8.60)	290	
Mg^{2+}	1,3-T	$2H_2O$	41.79(44.52)	3.88(4.08)	8.12(8.19)	270	
Mg^{2+}	1,5-T	$2H_2O$	47.01(48.07)	4.31(4.96)	7.80(7.48)	280	
Mg^{2+}	1.6-T	$2H_2O$	48.36(49.63)	5.33(5.35)	7.67(7.17)	275	
Ca^{2+}	1,6-T	$2H_2O$	47.83(47.42)	5.53(5.12)		275	
Ga^{3+}	1,6-T	H_2O, NO_3^-	43.78(39.29)	4.99(3.77)	13.30(16.29)	280	
In^{3+}	1,6-T	H_2O, NO_3^-	32.99(35.53)	3.40(3.41)	23.27(24.26)	225	
Si^{4+}	1,6-T	$2Ac^-$	45.03(50.94)	4.82(4.75)		245	
Sn^{2+}	1,6-T	$2H_2O$	37.97(38.84)	3.14(3.72)	26.70(27.41)	305	
Pb^{2+}	1,2-T	$2H_2O$	25.97(25.80)	1.73(2.16)	43.70(44.52)	205	
Pb^{2+}	1,3-T	$2H_2O$	26.14(27.56)	1.52(2.52)	44.55(43.22)	205	
Pb^{2+}	1,4-T	$2H_2O$	23.47(29.21)	1.24(2.86)	46.54(41.99)	220	
Pb^{2+}	1,6-T	$2H_2O$	28.72(35.25)	2.60(3.48)	35.20(39.73)	205	
Bi^{3+}	1,6-T	H_2O, NO_3^-	26.21(29.64)	2.58(2.84)	45.89(36.84)	245	
Ce^{3+}	1,3-T	H_2O, NO_3^-	25.36(28.95)	2.34(2.21)	30.48(30.71)	250	
Ce^{3+}	1,6-T	H_2O, NO_3^-	33.38(33.74)	2.98(3.24)	24.80(28.11)	230	
Ce^{3+}	1,6-H	H_2O, NO_3^-	28.19(33.60)	2.73(3.63)	28.56(28.00)	220	
UO_2^{2+}	1,6-T		29.77(29.77)	3.21(2.57)	39.10(43.41)	275	
Mn^{2+}	1,2-T	$2H_2O$	38.26(38.35)	3.36(3.21)	12.20(17.54)	240	5.9
Mn^{2+}	1,5-T	$2H_2O$	42.29(46.31)	3.81(4.78)	16.60(16.29)	250	5.8
Mn^{2+}	1,6-T	$2H_2O$	47.64(47.88)	4.32(5.17)	13.70(15.64)	250	5.9
Mn^{2+}	1,6-H	$2H_2O$	40.13(45.30)	3.86(5.43)	14.80(14.80)	210	
Mn^{3+}	1,3-T	H_2O, Ac^-	41.08(42.41)	3.51(3.56)		245	
Mn^{3+}	1,6-T	H_2O, Ac^-	44.40(46.84)	3.88(5.65)		250	
Co^{2+}	1.2-T	$2H_2O$	37.10(37.87)	3.62(3.17)	17.50(18.58)	255	
Co^{2+}	1,3-T	$2H_2O$	40.06(39.90)	3.50(3.65)	15.95(17.80)	235	4.7
Co^{2+}	1,4-T	$2H_2O$	39.84(41.76)	3.38(4.08)	14.86(17.07)	250	4.9
Co^{2+}	1,6-T	$2H_2O$	45.11(45.06)	4.47(4.86)	15.81(15.79)	240	5.2
Co^{2+}	1,6-H	$2H_2O$	39.29(44.81)	4.59(5.37)	20.31(15.71)	230	5.0
Ni^{2+}	1,3-T	$2H_2O$	38.32(39.92)	3.72(3.65)	15.72(17.74)	270	3.0
Ni^{2+}	1,4-T	$2H_2O$	36.25(41.79)	3.97(4.09)	18.25(17.02)	280	3.2
Ni^{2+}	1,5-T	$2H_2O$	41.97(43.50)	4.07(4.49)	17.70(16.36)	255	3.2
Ni^{2+}	1,6-T	$2H_2O$	45.95(45.11)	5.13(4.86)	15.67(15.75)	285	3.2
Ni^{2+}	1,6-H	$2H_2O$	43.74(44.84)	4.78(5.38)	11.80(15.65)	250	3.1
Cu^{2+}	1,2-T	$2H_2O$	36.11(37.33)	2.69(3.13)	24.00(19.75)	230	
Cu^{2+}	1,3-T	$2H_2O$	34.96(39.35)	2.58(3.92)	25.30(18.93)	205	
Cu^{2+}	1,4-T	$2H_2O$	41.20(41.21)	2.65(4.03)	18.60(18.17)	205	2.1
Cu^{2+}	1,5-T	$2H_2O$	42.97(42.92)	3.58(4.43)	16.93(17.47)	190	2.2
Cu^{2+}	1,6-T	$2H_2O$	44.97(44.53)	4.22(4.80)	16.11(16.82)	230	2.2
Zn^{2+}	1,2-T	$2H_2O$	35.60(37.12)	2.89(3.11)	21.20(20.20)	230	
Zn^{2+}	1,2-T	$2H_2O$	35.60(37.12)	2.89(3.11)	21.20(20.20)	230	
Zn^{2+}	1,6-T	$2H_2O$	46.08(44.26)	4.73(4.78)	13.44(17.21)	240	
Cd^{2+}	1,6-T	$2H_2O$	39.76(39.41)	3.71(4.25)	21.51(26.34)	265	

[a] Colours of all complexes are yellow to brown, with those of Mn^{2+} having the brightest colour (yellow), those of Ce^{3+} the darkest (almost black).

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