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PREPARATION AND PROPERTIES OF YTTRIUM COMPLEXES WITH ALKANODICARBOXYLIC ACIDS

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Malonate, succinate and glutarate of yttrium were obtained by dissolving $Y(OH)_3$ in a solution of the corresponding acid and crystallization, whereas adipate, pimelate, suberate, azelate and sebacate in the reaction of YCl_3 with the ammonium salt of the acid. Yttrium alkanodicarboxylates were prepared as crystalline solids with general formula $Y_2O_3.nH_2O$, where $n = 3, 4, 6, 7$. On the basis of IR spectra the way of coordination $COO^- - Y^{3+}$ was established. Yttrium malonate, succinate, glutarate, azelate and sebacate heated lose crystallization water and next anhydrous complexes are transformed to Y_2O_3, whereas yttrium adipate, pimelate and suberate on heating lose some water molecules and, the mono- or dihydrates formed are decomposed to Y_2O_3. The properties of the studied complexes change discretely according to odd or even number of carbon atoms in the chain.

In the literature there are many papers describing the thermal decomposition of the complexes of rare earth element, with organic acids. In most papers Sc, Y, La and other lanthanide oxalates are dealt with [1-5]. The thermal decomposition of cerium(III), neodymium and europium malonate, succinate, glutarate, adipate, pimelate, suberate, azelainate and sebacate was also studied [7-11]. Brzyska [12] has studied solubilities of anhydrous alkanodicarboxylates of Y, La and light lanthanides in water and separated lanthanides by homogeneous precipitation of individual salts. Rare earth malonates and succinates [13-15] as well as dysprosium and holmium fumarates and tartarates [16] have been prepared and their thermal decomposition have been studied. Huraiski *et al.* [17] have prepared malonates from Ce to Eu as hexahydrates and from Gd to Lu as octahydrates. The authors found that the hexahydrates were dehydrated in one step, whereas the octahydrates in three steps. Nabov and Jukov [18-19] prepared the

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double malonates with general formula $Na_5LnL_4.7H_2O$ and K_5LnL_4 (where Ln = Gd, Ho, Y and L - malonate ion) and studied their thermal stabilities. Vdovina and Koblova [20] studied the preparation conditions of yttrium oxalate, succinate, fumarate, maleate and tartrates, and their thermal stabilities. The dicarboxylates of Cr(III) [21], Zr, Hf [23], Zn [24], Cu(II) [25] and Tl(III) [26] have been prepared and studied, too.

The aim of our work has been to obtain the malonate, succinate, glutarate, adipate, pimelate, suberate, azelate and sebacate of yttrium and to examine their composition, way of metal - ligand coordination and thermal decomposition in air.

Experimental

Malonate, succinate and glutarate of yttrium were prepared by dissolving freshly precipitated $Y(OH)_3$ in 0.3M solution of the corresponding acid at 333K and subsequent crystallization. Adipate, pimelate, suberate, azelate and sebacate of yttrium were prepared by adding the ammonium salt of the acid to a hot solution of YCl_3. The precipitates formed (pH 5.5-6.0) were heated in the mother liquor for 0.5 h at 333-343K, washed with water to remove NH_4^+ ions. All the complexes thus prepared were dried at 303K to constant weight.

The content of carbon and hydrogen in the prepared complexes was determined by elemental analysis with V_2O_5 as oxidizing agent. The yttrium content was the determined by igniting the complexes to Y_2O_3 at 1073K and from the TG curve. The water of crystallization was determined from the TG curve and by heating the prepared alkanodicarboxylates at given temperature.

The IR spectra of alkanodicarboxylic acids and their compounds with yttrium and sodium were recorded by a Zeiss UR-20 spectrophotometer over the range 4000-400 cm^{-1}. The samples were prepared as KBr pellets. X-ray diffraction patterns were taken on a DRON-2 diffractometer using Ni filtered CuK_α radiation. The measurements were made by means of the powder Debye-Scherrer method, within the range $2\theta = 5\text{-}60^\circ$.

The thermal stability of the prepared yttrium alkanodicarboxylates was studied by means of TG, DTG and DTA technique. The measurements were made with an OD-102 derivatograph. The samples were heated at a rate of 12 $deg.min^{-1}$ to 1473K in ceramic crucibles in air. The thermal curves of yttrium adipate, pimelate and suberate heated previously at 473K, were also recorded.

Results

Alkanodicarboxylates of yttrium were prepared as crystalline white solids. On the basis of elemental analysis and thermal curves (Table 1) the prepared alkanodicarboxylates were found to be complexes with a 2:3 metal to ligand molar ratio. Yttrium malonate, succinate, glutarate and adipate were obtained as heptahydrates, pimelate and suberate as hexahydrates while azelate and sebacate as tetrahydrates.

Table 1 Analytical data

Complex	% Y		% C		%H		Solubility
	calcd.	found	calcd.	found	calcd.	found	mol.dm^{-3}
$Y_2(C_3H_2O_4)_3.7H_2O$	29.18	29.02	17.17	17.94	3.27	3.52	$2.5.10^{-3}$
$Y_2(C_4H_4O_4)_3.7H_2O$	27.30	27.92	22.08	22.20	3.98	4.09	$1.2.10^{-3}$
$Y_2(C_5H_6O_4)_3.7H_2O$	25.64	25.50	25.93	26.05	4.61	4.61	$2.0.10^{-4}$
$Y_2(C_6H_8O_4)_3.7H_2O$	24.18	23.80	29.34	29.95	5.16	5.04	$1.2.10^{-4}$
$Y_2(C_7H_{10}O_4)_3.6H_2O$	23.42	23.80	33.15	33.64	5.52	5.75	$1.9.10^{-4}$
$Y_2(C_8H_{12}O_4)_3.6H_2O$	22.19	22.28	35.91	35.64	5.98	6.25	$3.0.10^{-5}$
$Y_2(C_9H_{14}O_4)_3.4H_2O$	22.02	22.00	40.09	39.23	6.18	6.38	$2.0.10^{-5}$
$Y_2(C_{10}H_{16}O_4)_3.4H_2O$	20.94	20.85	42.35	42.62	6.58	6.28	$2.8.10^{-5}$

In order to confirm the results obtained, to study the type of bonding between ligand and metal ion, and to elucidate the structure of the complexes their IR spectra, the spectra of alkanodicarboxylic acids, $(HOOC(CH_2)_nCOOH$ where $n = 1\text{-}8)$ and their sodium salts were recorded (Tables 2-3). In the IR spectra of acids, for which $n = 1\text{-}4$, two adsorption bands of the COOH group at 1745-1680 cm^{-1} were observed while for acids having $n > 5$ only one adsorption band appeared at ca 1690 cm^{-1}. In the IR spectra of the complexes the bands of the COOH group disappear, which indicates that the hydrogen atoms in the two carboxylic groups are replaced by yttrium. In the IR spectra of yttrium alkanodicarboxylates the absorption bands of asymmetrical and symmetrical bonds of COO^- group appear at 1590-1530 cm^{-1} and 1465-1400 cm^{-1} (for $n = 1\text{-}3$ double bonds), respectively; the broad absorption band of ν OH with maximum at 3600 and 3300 cm^{-1} characteristic of hydrated compounds, bands of δ CH_2 at 1430-730 cm^{-1},

Table 2a Frequencies of absorption bands in the IR spectra of alkanodicarboxylic acids and their complexes with yttrium (cm^{-1})

Compound	ν_{OH}	ν_{C-H}	$\nu_{C=O}$	ν_{as}	ν_{s}	ν_{C-C}	δ_{CH_2}			δ_{Y-O}
				COO^-	COO^-		scissoring	wagging	rocking	
$HOOC(CH_2)COOH$	-	3000	1745	-	-	935	1435	1305	775	-
		2600	1700			920		1220		
$Y_2(C_3H_2O_4)_3.7H_2O$	3600, 3430	2985	-	1570	1400	960	1420	1305	760	575
	3300	2920		1530	1430	925		1220		430
$HOOC(CH_2)_2COOH$	-	3000	1720	-	-	920	1420	1305	805	-
		2650	1700			895		1180		
$Y_2(C_4H_4O_4)_3.7H_2O$	3340	2930	-	1590	1460	985	1410	1285	800	565
				1570	1450	950		1190		420
$HOOC(CH_2)_3COOH$	-	3000	1690	-	-	1070	1410	1300	765	-
		2710	1680			920		1205		
$Y_2(C_5H_6O_4)_3.7H_2O$	3400	2970	-	1590	1460	1060	1430	1315	760	565
				1535	1450	860		1200		420
$HOOC(CH_2)_4COOH$	-	2960	1705	-		1050	1420	1310	740	-
		2670	1695		-	930		1190		
$Y_2(C_6H_8O_4)_3.7H_2O$	3340, 3250	2950	-	1545	1460	1145	1410	1315	780	520
		2910				955		1195		430

Table 2b Frequencies of absorption bands in the IR spectra of alkanodicarboxylic acids and their complexes with yttrium (cm^{-1})

Compound	ν_{OH}	ν_{C-H}	$\nu_{C=O}$	ν_{as}	ν_s	ν_{C-C}	δ_{CH_2}			
				COO^-	COO		scissoring	wagging	rocking	δ_{Y-O}
$HOOC(CH_2)_5COOH$	-	2940	1690	-	-	1030	1410	1290	730	-
		2875				920		1220		
$Y_2(C_7H_{10}O_4)_3.6H_2O$	3370	2940	-	1550	1445	1080	1370	1310	795	580
		2865				955		1135		425
$HOOC(CH_2)_5COOH$	-	2950	1690	-	-	1015	1410	1275	800	-
		2875				930		1190		
$Y_2(C_8H_{12}O_4)_3.6H_2O$	3350	2935	-	1550	1465	1090	1425	1290	795	550
		2865				970		1220		430
$HOOC(CH_2)_7COOH$	-	2935	1690	-	-	1010	1400	1280	780	-
		2850				930		1195		
$Y_2(C_9H_{14}O_4)_3.4H_2O$	3350	2935	-	1550	1450	1010	1320	1240	790	580
		2850				945		1190		420
$HOOC(CH_2)_8COOH$	-	2930	1685	-	-	1005	1350	1240	760	-
		2855				930		1190		
$Y_2(C_{10}H_{16}O_4)_3.4H_2O$	3360	2935	-	1550	1365	1110	1350	1240	760	580
		2850				940		1190		420

and absorption bands of the yttrium - oxygen bond at 580-520 cm^{-1} and 430-420 cm^{-1}.

Table 3 The shifts of absorption bands of ν_{as} COO^- and ν_s COO^- of yttrium alkanodicarboxylates in comparison with sodium salts

Complex	ν_{as} COO^-	$\Delta\nu_{as}$ COO^-	ν_s COO^-	$\Delta\nu_s$ COO^-	$\nu_{as}-\nu_s$ COO^-
$Na_2C_3H_2O_4.nH_2O$	1580		1400		180
$Y_2(C_3H_2O_4)_3.7H_2O$	1570	–30	1400	15	135
	1530		1430		
$Na_2C_4H_4O_4.nH_2O$	1570		1430		140
$Y_2(C_4H_4O_4)_3.7H_2O$	1590	10	1460	25	125
	1570		1450		
$Na_2C_5H_6O_4.nH_2O$	1575		1420		155
$Y_2(C_5H_6O_4)_3.7H_2O$	1550	–30	1460	35	90
	1540		1450		
$Na_2C_6H_8O_4.nH_2O$	1565		1410		155
$Y_2(C_6H_8O_4)_3.7H_2O$	1545	–20	1460	50	85
$Na_2C_7H_{10}O_4.nH_2O$	1580		1420		160
$Y_2(C_7H_{10}O_4)_3.6H_2O$	1550	–30	1445	25	105
$Na_2C_8H_{12}O_4.nH_2O$	1565		1410		155
$Y_2(C_8H_{12}O_4)_3.6H_2O$	1550	–15	1465	55	85
$Na_2C_9H_{14}O_4.nH_2O$	1570		1430		140
$Y_2(C_9H_{14}O_4)_3.4H_2O$	1550	–20	1450	20	100
$Na_2C_{10}H_{16}O_4.nH_2O$	1560		1410		150
$Y_2(C_{10}H_{16}O_4)_3.4H_2O$	1550	–10	1465	55	85

The shift of the absorption bands of assymetric (ν_{as} COO^-) and symmetric (ν_s COO^-) vibrations of the carboxylate group ($\Delta\nu_{as}$ and $\Delta\nu_s$) of yttrium alkanodicarboxylates compared to the absorption bands of sodium complexes are given in Table 3.The values of $\Delta\nu_{as}$ COO^- and $\Delta\nu_s$ COO^- for yttrium alkanodicarboxylates change discretely having higher values for alkanodicarboxylates with odd number of C atoms in the chain than for neighbouring alkanodicarboxylates with even number of C atoms. The values of splitting for absorption bands of COO^- group ($\Delta\nu=\nu_{as}-\nu_s$) for sodium salts are between 180-140 cm^{-1}, whereas for yttrium complexes between 135-85 cm^{-1}, which is due to the higher degree of covalency of the $COO...Y^{3+}$ bond than of the $COO...Na^+$ bond. The values of splitting $\Delta\nu$ for yttrium alkanodicarboxylates have variable values with increasing number of CH_2 groups in the chain. On the basis of the shift, of asymmetric and symmetric bands of the COO^- group for yttrium alkanodicarboxylates com-

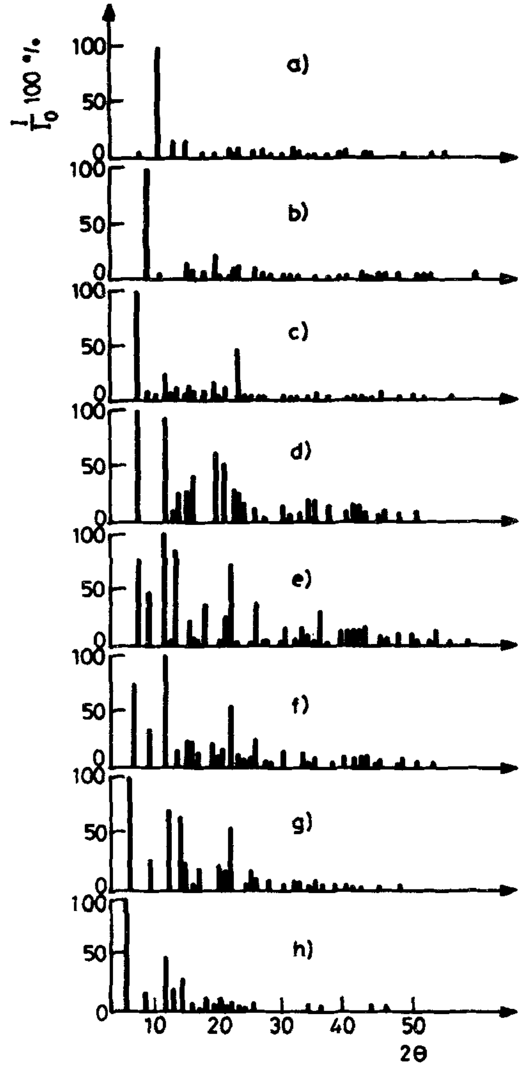

Fig. 1 X-ray spectrum of yttrium a) malonate, b) succinate, c) glutarate, d) adipate, e) pimelate, f) suberate, g) azelate, h) sebacate

pared to those of the sodium salt it is possible to suggest that the COO^- group behaves as a bidentate ligand.

From the recorded X-ray diffractograms (Fig. 1) the alkanodicarboxylates of yttrium were found to be crystalline. They are characterized by low symmetry, since the interference reflections disappear when the angles are

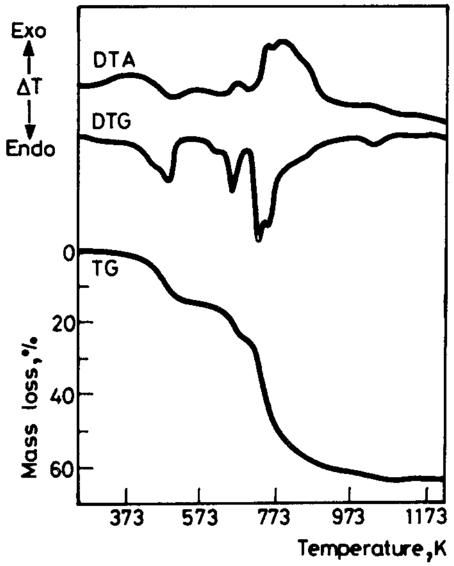

Fig. 2 TG, DTG and DTA curves of $Y_2(C_3H_2O_4)_3.7H_2O$

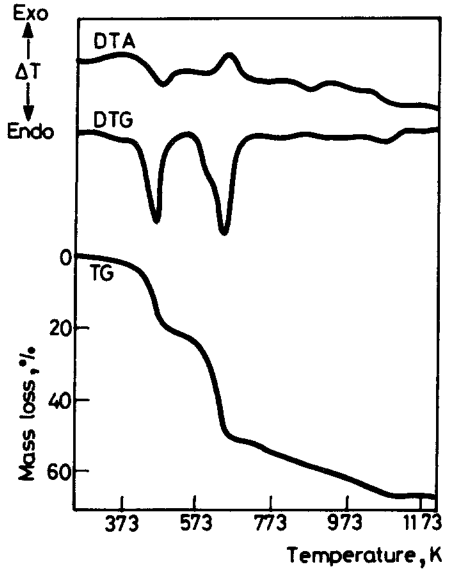

Fig. 3 TG, DTG and DTA curves of $Y_2(C_4H_4O_4)_3.7H_2O$

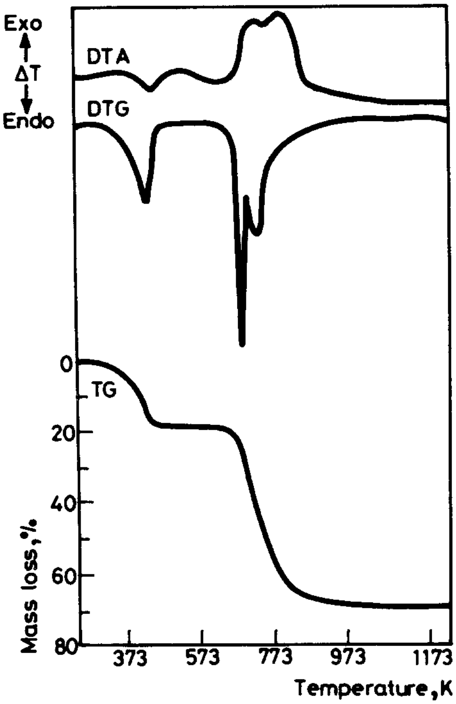

Fig. 4 TG, DTG and DTA curves of $Y_2(C_5H_6O_4)_3.7H_2O$

small. The appearance of the first interference reflections, corresponding to small angles, indicates large sizes of the unit cells. The degrees of crystallinity of the complexes heated at 473K are smaller than that of the hydrated complexes.

On the basis of the thermal curves recorded for the studied complexes heated in air, the temperatures and mass losses of decomposition were established and given in Figs 2-6 and in Table 4. Alkanodicarboxylates of yttrium heated in static air decompose in various ways. Heptahydrated yttrium malonate is stable up to 373K, then the water of crystallization is released in two steps with accompanying two endothermic effects. In the first step it loses 4 water molecules and at 573K three ones giving anhydrous complex which decomposes directly to Y_2O_3. Heptahydrated yttrium succinate and glutarate stable up to 333K on further heating are dehydrated in one step and the anhydrous complexes are transformed into Y_2O_3. Yttrium adipate heptahydrate loses six water molecules at 333K resulting the monohydrate which is stable up to 593K then decomposing to give Y_2O_3. Yttrium pimelate

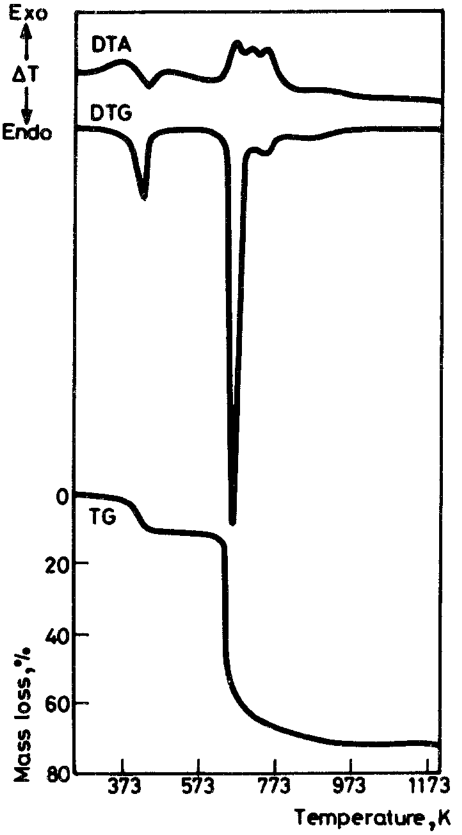

Fig. 5 TG, DTG and DTA curves of $Y_2(C_7H_{10}O_4)_3.6H_2O$

on heating loses at 353K five water molecules, and the monohydrate stable up to 633K, on further heating decomposes to Y_2O_3, whereas yttrium pimelate loses four water molecules at 373K and the dihydrate formed loses the residual water molecules during decomposition. From these results it is possible to confirm that one water molecule in yttrium adipate and pimelate, and two water molecules of yttrium suberate are inner sphere water whereas water molecules lost during dehydration are outer sphere water molecules. Additionally, the thermal curves of yttrium adipate, pimelate and suberate heated at 473K were recorded. The results obtained confirm the presence of inner sphere water in the complexes studied. Tetrahydrated yttrium azelate and suberate heated in air at 353-433K are dehydrated endothermically and the anhydrous complexes decompose at 573K to give Y_2O_3. The activation

Table 4 Thermoanalytical data of yttrium alkanodicarboxylates heated in air atmosphere

Complex	Temperature range of dehydration K	Loss of H_2O molecules	Activation energy kJ.mol^{-1}	Mass loss, % calcd.	Mass loss, % found	Temperature range of decomp. K	Mass loss, % calcd.	Mass loss, % found	Temperature of Y_2O_3 formation K
$Y_2(C_3H_2O_4)_3.7H_2O$	373-513	4	29.74	11.8	12.0	673-1073	52.0	52.6	1073
	573-673	3	10.63	10.0	10.0				
$Y_2(C_4H_4O_4)_3.7H_2O$	333-513	7	12.79	19.3	20.0	573-1073	57.0	56.3	1073
$Y_2(C_5H_6O_4)_3.7H_2O$	323-433	7	20.65	18.1	18.0	633-1053	60.9	60.2	1053
$Y_2(C_6H_8O_4)_3.7H_2O$	333-433	6	14.46	14.0	14.0	593-973	64.0	63.8	973
$Y_2(C_7H_{10}O_4)_3.6H_2O$	353-423	5	29.74	11.8	11.5	633-973	66.0	66.0	973
$Y_2(C_8H_{12}O_4)_3.6H_2O$	373-443	4	36.24	8.9	9.0	613-1013	69.8	69.2	1013
$Y_2(C_9H_{14}O_4)_3.4H_2O$	353-433	4	16.52	8.9	9.0	573-1013	69.2	69.3	1013
$Y_2(C_{10}H_{16}O_4)_3.4H_2O$	353-453	4	18.95	8.5	9.0	573-1013	70.8	71.0	1013

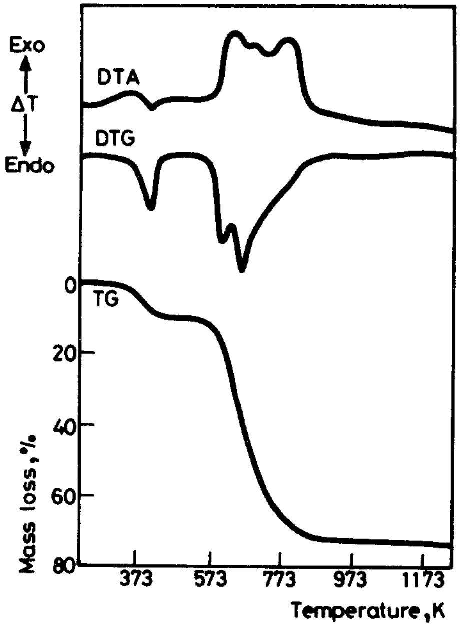

Fig. 6 TG, DTG and DTA curves of $Y_2(C_9H_{14}O_4)_3 \cdot 4H_2O$

energies of dehydration calculated by Chuchas and Jezierskaya's method [27] are between 12.79-36.29 kJ (Table 4) and change discretely in the alkanodicarboxylate series, as well as the temperatures of decomposition and Y_2O_3 formation.

The solubilities of yttrium alkanodicarboxylates in water at 291K (Table 1) decrease from 10^{-3} mol.dm^{-3} for yttrium malonate to 10^{-5} mol.dm^{-3} for sebacate with increasing number of CH_2 groups in the chain and molecular weight of the compound.

The properties of yttrium alkanodicarboxylates change discretely according to odd or even number of carbon atoms in the chain, which is connected with the structure and properties of alkanodicarboxylic acids, distance and position of the two carboxylic groups.

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Zusammenfassung — Durch Auflösen von $Y(OH)_3$ in einer Lösung der entsprechenden Säure und anschliessendem Kristallisieren wurden Yttriummalonat,-succinat und -glutarat dargestellt, das Yttriumadipat, -pimelat-, -suberat und -azelainat und sebacate hingegen in der Reaktion von YCl_3 mit dem Ammoniumsalz der Säure. In Form kristalliner Feststoffe wurden Yttriumalkanodicarboxylate der allgemeinen Formel $Y_2L_3.nH_2O$ mit n = 3, 4, 6 bzw. 7 hergestellt. Ausgehend von den IR-Spektren konnte die Art der Koordinierung als $COO^- - Y^{3+}$ festgestellt werden. Beim Erhitzen geben Ytrriummalonat, -succinat, -glutarat, -azelainat und -sebazat ihr Kristallwasser ab, aus den anhydratierten Komplexen bildet sich anschliessend Y_2O_3, während Yttriumadipet, pimelat und -suberat einige Wassermoleküle verlieren und die mono- oder dihydratierten Formen sich dann zu Y_2O_3 zersetzen. Die Eigenschaften der untersuchten Komplexe variieren eindeutig in Abhängigkeit davon, ob sich in der Kette eine gerade oder ungerade Anzahl von Kohlenstoffatomen befindet.