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Spectroscopic and Thermal Studies of Y(III) and Lanthanide(III) Complexes with 3,4-Dichlorobenzoic Acid

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Summary. The *tris*(3,4-dichlorobenzoate) complexes of Y(III) and (La-Lu)(III) were prepared. Their solubilities in water at 293 K were determined (6.57×10^{-4}–3.04×10^{-4} mol·dm^{-3}). The IR spectra suggest that the carboxylate ligand is bidentate. The dihydrated complexes (Y, Ce–Lu) are dehydrated in one step, the tetrahydrated La complex in two steps. The anhydrous compounds decompose to oxides Ln_2O_3, Pr_6O_{11}, and Tb_4O_7 (Y, La, Pr–Lu) with intermediate formation of *Ln*OCl or directly to the oxide in the case of Ce (CeO_2)

Keywords. 3,4-Dichlorobenzoic acid; Complexes; IR spectra; Rare earths; Thermal analysis.

Spektroskopische und thermische Untersuchungen der Komplexe von dreiwertigen Lanthaniden und Y(III) mit 3,4-Dichlorbenzoesäure

Zusammenfassung. Die *Tris*(3,4-dichlorbenzoat)-Komplexe der dreiwertigen Lanthaniden La–Lu sowie von Y(III) wurden hergestellt; ihre Löslichkeit in Wasser bei 293 K wurde bestimmt (6.57×10^{-4}–3.04×10^{-4} mol·dm^{-3}). Die IR-Spektren legen eine bidentate Funktion der Carboxylatliganden nahe. Die zweifach hydratisierten Komplexe (Y, Ce–Lu) werden in einem Schritt dehydratisiert, der vierfach hydratisierte La-Komplex in zwei Schritten. Die wasserfreien Verbindungen zersetzen sich zu den Oxiden Ln_2O_3, Pr_6O_{11} und Tb_4O_7 (Y, La, Pr–Lu) unter intermediärer Bildung von *Ln*OCl. Der Cer-Komplex reagiert direkt zu CeO_2.

Introduction

A survey of the literature shows that the complexes of 3,4-dichlorobenzoic acid are not well described. The 3,4-dichlorobenzoates of Ca(II) and Ba(II) were prepared as tri- and tetrahydrates, respectively, and are soluble in water and ethanol [1]. The complexes of Ni(II) and Co(II) were prepared as water soluble tetrahydrates, whereas the complexes of Cu(II) and Zn(II) form sparingly water soluble dihydrates [2]. The carboxylate groups in the complexes of Co(II), Ni(II), and Zn(II) act as monodentate ligands; these complexes decompose to oxides of the form *M*O when heated in air, whereas that of Cu(II) yields a gaseous product.

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This work is a continuation of our study on the structure and physicochemical properties of rare earth(III) complexes with dichlorobenzoate ligands [3–10] and their thermal decomposition in air.

Results and Discussion

The *tris*(3,4-dichlorobenzoates) of Y(III) and lanthanides(III) of La to Lu were prepared as crystalline solid dihydrates with colors characteristic for *Ln*(III) ions; only that of La(III) gave a tetrahydrate. They are sparingly soluble in water. The solubilities of the prepared complexes change irregularly in the lanthanide series from $6.57\times10^{-4}\ \mathrm{mol\cdot dm^{-3}}$ for La to $3.04\times10^{-4}\ \mathrm{mol\cdot dm^{-3}}$ for Yb. Generally, the solubilities of compounds of the early lanthanides are higher than those of the heavy ones.

Infrared spectra

All rare earth element 3,4-dichlorobenzoates show similar solid state IR spectra. They change insignificantly for light and heavy lanthanide complexes. In the IR spectrum of free 3,4-dichlorobenzoic acid, there is a single strong absorption band of the COOH group at $1680\,\mathrm{cm^{-1}}$. In the IR spectra of the rare earth complexes, the bands of asymmetrical $\mathrm{OCO^-}$ vibrations (ν_{as}) appear at 1588–$1576\,\mathrm{cm^{-1}}$ and 1528–$1520\,\mathrm{cm^{-1}}$, bands of symmetrical vibrations (ν_{s}) at 1416–$1408\,\mathrm{cm^{-1}}$. The corresponding values of the sodium salt of 3,4-dichlorobenzoic acid are 1592 and $1404\,\mathrm{cm^{-1}}$, respectively. The broad ν(OH) bands at 3420–$3400\,\mathrm{cm^{-1}}$ confirm the presence of crystal water. The bands of ν(C–Cl) in the IR spectra of Y(III) and heavy lanthanide(III) complexes appear at 760 and $780\,\mathrm{cm^{-1}}$. Those of the light lanthanide complexes are found at 776–$784\,\mathrm{cm^{-1}}$ and are insignificantly displaced compared to ν(C–Cl) of free acid (780 and $760\,\mathrm{cm^{-1}}$), suggesting that Cl atoms do not participate in metal ligand bonding. The bands of asymmetrical vibrations $\nu_{\mathrm{as}}(\mathrm{OCO^-})$ are shifted to lower frequencies compared to the bands of the sodium salt, whereas the absorption bands of symmetrical vibrations $\nu_{\mathrm{s}}(\mathrm{OCO^-})$ are shifted to higher frequencies. The value of $\Delta\nu = \nu_{\mathrm{as}-\nu_{\mathrm{s}}}$ is smaller for the lanthanide complexes ($\Delta\nu = 136$–$144\,\mathrm{cm^{-1}}$) than for the sodium salt ($\Delta\nu = 164\,\mathrm{cm^{-1}}$). The $\mathrm{OCO^-}$ groups therefore obviously coordinate the lanthanide ions as bidentate ligands, and the ionic character of the metal-ligand bond in the prepared complexes is smaller than in the sodium salt [11, 12]. With increasing the atomic number Z in the lanthanide series, the ionic radius of the metal decreases, and the polarization and deformation of the organic ligand and the participation of ionic bonding increases. This tendency is very often observed for complexes in the lanthanide series. The yttrium(III) complex behaves similar to those of the heavy lanthanides, presumably connected with the similarity of the ionic radii. A more precise interpretation of the coordination mode is possible after determination of the molecular and crystallographic structures of single crystals.

Thermal analysis

The results presented in Tables 1 and 2 indicate that rare earth element 3,4-dichlorobenzoates (except those of La(III) and Ce(III)) decompose in a similar way

Table 1. Data for dehydration of Y(III) and lanthanide(III) 3,4-dichlorobenzoates; ΔT_1: temperature range of dehydration, ΔT_2: temperature range of compound stability

	ΔT_1 (K)	Loss of mass (%)		Moles of H_2O lost	T_{endo} (K)	ΔT_2 (K)	Compounds formed
		Calcd.	Found				
$\mathrm{Y}L_3 \cdot 2H_2O$	344–462	5.18	5.36	2	389, 519	462–622	$\mathrm{Y}L_3$
$\mathrm{La}L_3 \cdot 4H_2O$	341–423	6.92	6.95	3	405	556–623	LaL_3
	423–556	9.23	9.20	1	556		
$\mathrm{Ce}L_3 \cdot 2H_2O$	369–410	4.10	4.83	2	395, 541	410–541	$\mathrm{Ce}L_3$
$\mathrm{Pr}L_3 \cdot 2H_2O$	372–474	4.82	4.59	2	393, 553	474–591	$\mathrm{Pr}L_3$
$\mathrm{Nd}L_3 \cdot 2H_2O$	356–421	4.80	5.10	2	397, 555	421–633	$\mathrm{Nd}L_3$
$\mathrm{Sm}L_3 \cdot 2H_2O$	367–425	4.76	4.51	2	390, 541	425–633	$\mathrm{Sm}L_3$
$\mathrm{Eu}L_3 \cdot 2H_2O$	357–424	4.75	5.00	2	396, 537	424–619	$\mathrm{Eu}L_3$
$\mathrm{Gd}L_3 \cdot 2H_2O$	359–418	4.72	4.75	2	396, 532	418–613	$\mathrm{Gd}L_3$
$\mathrm{Tb}L_3 \cdot 2H_2O$	341–462	4.73	4.63	2	400, 520	462–631	$\mathrm{Tb}L_3$
$\mathrm{Dy}L_3 \cdot 2H_2O$	341–475	4.69	4.63	2	375, 531	475–628	$\mathrm{Dy}L_3$
$\mathrm{Ho}L_3 \cdot 2H_2O$	344–456	4.67	5.00	2	481, 530	456–641	$\mathrm{Ho}L_3$
$\mathrm{Er}L_3 \cdot 2H_2O$	353–453	4.66	5.00	2	394, 530	453–629	$\mathrm{Er}L_3$
$\mathrm{Tm}L_3 \cdot 2H_2O$	338–479	4.65	5.00	2	389, 530	479–635	$\mathrm{Tm}L_3$
$\mathrm{Yb}L_3 \cdot 2H_2O$	345–436	4.62	5.00	2	383, 541	436–680	$\mathrm{Yb}L_3$
$\mathrm{Lu}L_3 \cdot 2H_2O$	342–430	4.61	4.70	2	378, 546	430, 673	$\mathrm{Lu}L_3$

when heated. Two typical examples are shown in Figs. 1 and 2. The dihydrated complexes (Y, Ce–Lu) dehydrate at 338–479 K, losing two molecules of crystal water and forming the anhydrous compounds (Table 1). The tetrahydrated La(III) complex dehydrates in two steps, losing three water molecules in the first step at 341–423 K and one water molecule in the second step at 423–556 K. This

Table 2. Data for the decomposition of Y(III) and lanthanide(III) 3,4-dichlorobenzoates; ΔT_3: temperature range of decomposition to *Ln*OCl, ΔT_4: temperature range of decomposition to oxides

	ΔT_3 (K)	Loss of mass (%)		ΔT_4 (K)	Loss of mass (%)		TBD (K)	T_{exo} (K)	T_{k} (K)
		Calcd.	Found		Calcd.	Found			
$\mathrm{Y}L_3$	622–999	79.74	80.0	999–1200	83.80	84.01	622	863	1200
$\mathrm{La}L_3$	623–850	75.63	76.0	850–1592	79.14	80.0	624	804	1592
$\mathrm{Ce}L_3$	–	–	–	541–853	76.93	76.7	523	770	853
$\mathrm{Pr}L_3$	591–863	74.25	74.1	863–1491	77.21	78.0	591	810	1431
$\mathrm{Nd}L_3$	633–853	73.92	74.0	853–1444	77.58	77.0	633	811	1444
$\mathrm{Sm}L_3$	633–855	73.32	73.0	856–1380	76.95	77.0	633	814	1386
$\mathrm{Eu}L_3$	618–899	73.16	73.0	899–1366	76.95	77.0	619	820	1367
$\mathrm{Gd}L_3$	613–880	72.66	72.8	881–1361	76.25	76.6	613	816	1361
$\mathrm{Tb}L_3$	631–964	72.50	72.7	964–1238	75.56	75.7	631	831	1238
$\mathrm{Dy}L_3$	628–962	72.16	72.5	962–1223	75.73	76.0	628	822	1223
$\mathrm{Ho}L_3$	641–979	71.93	72.0	979–1219	75.49	75.7	641	873	1219
$\mathrm{Er}L_3$	629–957	71.72	72.0	957–1182	75.24	75.8	629	866	1182
$\mathrm{Tm}L_3$	635–980	71.58	72.3	980–1159	75.10	75.0	635	884	1160
$\mathrm{Yb}L_3$	680–992	71.19	71.0	992–1159	74.71	74.4	680	882	1159
$\mathrm{Lu}L_3$	673–996	71.01	71.0	996–1156	74.52	75.0	673	891	1155

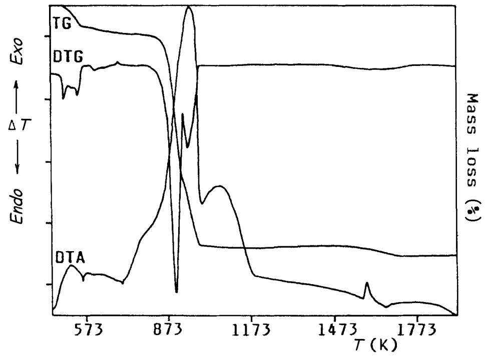

Fig. 1. TG, DTG, and DTA curves for $La(C_7H_3O_2Cl_2) \cdot 4H_2O$

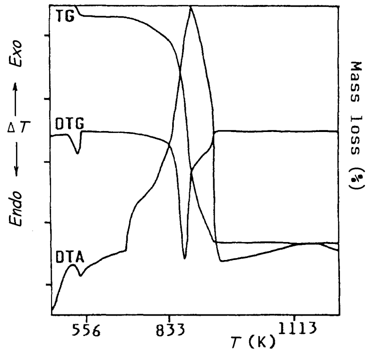

Fig. 2. TG, DTG, and DTA curves for $Ce(C_7H_3O_2Cl_2)_3 \cdot 2H_2O$

result suggests that the water molecules in the crystals of this complex are bonded in different modes, and also in a different mode than in the complexes of the remaining lanthanides. For a full interpretation of the nature of the bonding of water molecules, it is necessary to establish the coordination and molecular structure of the complexes on the basis of an X-ray crystallographic study of single crystals. The dehydration process is connected with a strong endothermic effect at 375–481 K and 556 K for the second step of dehydration for the La(III) complex.

The anhydrous crystalline complexes undergo a transition to amorphous compounds at 519–556 K (DTA) connected with endothermic effect. The anhydrous complexes are stable up to 410–680 K and then decompose to oxides with intermediate formation of the very stable *Ln*OCl (Table 2, Fig. 1). Only the anhydrous complex of Ce(III) (Fig. 2) decomposes directly to CeO_2 when heated to 541–853 K. The complexes of Ce(III) with other organic acids [3–7] also decompose directly to CeO_2. The process of organic ligand decomposition and combustion is accompanied by a strong exothermic effect (DTA) with a maximum at 770–891 K (Table 2). The final products of decomposition of rare earth 3,4-

dichlorobenzoates are the oxides Ln_2O_3, CeO_2, Pr_6O_{11}, and Tb_4O_7 which are formed at 853–1592 K. The temperatures of oxide formation (T_k) change regularly with increasing atomic number (Z) of the metal from 1512 K for La_2O_3 to 1156 K for Lu_2O_3 except of CeO_2. The temperature of CeO_2 formation is the lowest (853 K, Table 2) as has been observed for the thermal decomposition of many series of lanthanide complexes [3–7]. The decrease of the temperature of oxide formation in the lanthanide series is connected with increasing ionic potential of Ln^{3+} ions and deformation of the ligand with increasing atomic number of the metal and the contraction effect. The yttrium(III) 3,4-dichlorobenzoate has thermal properties similar to those of heavy lanthanide complexes. The temperature of Y_2O_3 formation (1200 K) is similar to that of Dy_2O_3 (1219 K) due to the similarity of the ionic radii of these elements.

The results indicate that the thermal decomposition of rare earth element 3,4-dichlorobenzoates proceeds as follows:

$$LnL_3 \cdot 2H_2O \rightarrow LnL_3 \rightarrow LnOCl \rightarrow Ln_2O_3, Pr_6O_{11}, Tb_4O_7 \quad Ln = Y, Pr-Lu$$

$$LaL_3 \cdot 4H_2O \rightarrow LaL_3 \cdot H_2O \rightarrow LaL_3 \rightarrow LaOCl \rightarrow La_2O_3$$

$$CeL_3 \cdot 2H_2O \rightarrow CeL_3 \rightarrow CeO_2$$

Comparing the dehydration process of 2,4-, 2,5-, 2,6- [3–6], and 3,4-dichlorobenzoates of rare earth elements, it is found that the dehydration of 2,4- and 2,5-dichlorobenzoates proceeds in two steps, whereas the dehydration of 2,6- and 3,4-dichlorobenzoates proceeds in one step (except for the La(III) complex).

Comparing the temperatures of oxide formation, it is possible to suggest for 2,4-, 2,5-, and 2,6- as well as for 3,4-dichlorobenzoates that they decrease regularly with increasing atomic number of the metal and have similar values. In all discussed complexes, the temperatures of CeO_2 formation (T_k) are the lowest in the series [3–6].

Experimental

The 3,4-dichlorobenzoates of Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by adding equivalent amounts of 0.1 M ammonium 3,4-dichlorobenzoate ($pH = 4.5$–5.0) to a hot solution of lanthanide(III) chloride (Ce(III) was used as its nitrate). The precipitates formed were heated in their mother liquor for 1 h, filtered off, washed with hot water to remove NH_4^+ and Cl^- ions, and dried at 303 K to constant mass. The composition of the prepared complexes was determined by elemental analysis by ignition of the complexes to form oxides, and from TG curves by the method described in Ref. [3]. The experimental results are concordant with the calculated data (Table 3). The solubilities of the prepared 3,4-dichlorobenzoates were determined in water at 293 K. Saturated solutions were prepared under isothermal conditions. After equilibrium had been established, samples of 50 cm^3 were withdrawn, and the concentrations of Ln(III) ions were determined gravimetrically using the oxalate method. The IR spectra were recorded as KBr discs on a Specord M 80 spectrophotometer (Carl Zeiss-Jena) in the range of 4000–400 cm^{-1}. The thermal stabilities of the complexes and the products of their decomposition were studied in air using a Paulik-Paulik-Erdey Q 1500 Derivatograph with a Derill converter; TG, DTG, and DTA curves were recorded. The samples (100 mg) of the complexes of light lanthanides (La(III)-Gd(III)) were heated to 1773 K, whereas those of Y(III) and heavy the lanthanides (Tb(III)-Lu(III)) were heated to

Table 3. Analytical data and water solubility at 293 K of 3,4-dichlorobenzoates of Y(III) and lanthanides(III)

	(%) Ln		% C		% H		% Cl		Solubility
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	(10^{-4} mol · dm^{-3})
$YL_3 \cdot 2H_2O$	13.74	13.8	38.99	39.0	2.03	2.0	32.88	33.0	5.22
$LaL_3 \cdot 4H_2O$	18.95	19.0	34.31	34.5	2.34	2.5	29.02	29.0	6.57
$CeL_3 \cdot 2H_2O$	20.07	20.0	36.13	36.2	1.88	1.9	30.46	30.5	6.27
$PrL_3 \cdot 2H_2O$	20.16	20.0	36.12	36.2	1.87	1.9	30.43	30.5	5.23
$NdL_3 \cdot 2H_2O$	20.54	20.8	35.92	36.0	1.87	2.0	30.23	30.3	5.23
$SmL_3 \cdot 2H_2O$	21.23	21.0	35.61	35.6	1.85	2.0	30.03	30.0	3.90
$EuL_3 \cdot 2H_2O$	21.40	21.5	35.53	35.5	1.85	1.9	29.96	30.0	4.38
$GdL_3 \cdot 2H_2O$	21.98	21.9	35.26	35.2	1.83	1.9	29.74	29.9	4.86
$TbL_3 \cdot 2H_2O$	22.17	22.1	35.18	35.2	1.83	1.8	29.67	29.8	4.71
$DyL_3 \cdot 2H_2O$	22.55	22.7	35.01	35.0	1.82	1.7	29.52	29.5	4.71
$HoL_3 \cdot 2H_2O$	22.81	22.8	34.40	34.5	1.81	1.8	29.42	29.5	4.76
$ErL_3 \cdot 2H_2O$	23.06	23.0	34.78	34.8	1.81	1.7	29.33	29.3	3.82
$TmL_3 \cdot 2H_2O$	23.24	23.4	34.70	34.7	1.80	1.7	29.26	29.3	3.73
$YbL_3 \cdot 2H_2O$	23.67	23.6	34.50	34.5	1.79	1.8	29.09	29.0	3.04
$LuL_3 \cdot 2H_2O$	23.87	23.9	34.41	34.3	1.79	1.7	29.01	29.0	4.07

1273 K. Measurements were made at a sensitivity of 100 mg (TG). The sensitivities of DTG and DTA were regulated by the Derill computer programme. Al_2O_3 was used as a standard. The products of decomposition were calculated from the TG curves and were confirmed by recording the IR spectra and X-ray diffraction patterns.

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