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SPECTRAL AND THERMAL STUDIES OF RARE EARTH COMPLEXES WITH 2,4,6-TRIMETHYLBENZOIC ACID

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Abstract

The rare earth element 2,4,6-trimethylbenzoates were prepared as solids with the general formula $Ln(C_{10}H_{11}O_2)_3{\cdot}nH_2O$, where n=2 for Ln=Y, La–Nd, and n=1 for Ln=Sm–Lu. The IR spectra of the complexes prepared were recorded and their solubilities in water and thermal decomposition in the air were investigated. During heating the hydrated complexes lose all the crystallization water molecules in one (Y, Ce–Lu) or two steps (La) and then the anhydrous complexes decompose either directly to oxides (Y, Ce, Pr, Sm–Lu) or with intermediate formation oxocarbonates $Ln_2O_2CO_3$ (La, Nd). The carboxylate groups in the complexes prepared act probably as mono- and bidentate.

Keywords: DTA, IR, rare earth complexes, 2,4,6-trimethylbenzoates

Introduction

2,4,6-Trimethylbenzoic acid $C_6H_2(CH_3)_3COOH$, known as mesitic acid, is a crystalline solid, sparingly soluble in water, and soluble in ethanol, ether and acetone [1]. Its compounds with metal ions are little known. There are some data [1] on the preparation and properties of 2,4,6-trimethylbenzoates of Ca(II) and Ba(II), which are prepared as dihydrates soluble in water. The complexes of Zn(II), Cd(II) and Hg(II) were prepared as solids with the molar ratio of metal to organic ligand of 1:2 [2]. On the basis of the IR spectra the carboxylate groups in Zn(II) and Cd(II) complexes were found as bidentate bridging, whereas in Hg(II) one as monodentate. The complexes prepared are non electrolytes. Odunola *et al*. [3] prepared 2,4,6-trimethylbenzoates of Mn(II), Ni(II) and Co(II) as solid clusters, in which the carboxylate groups are bidentate. Deacon *et al*. [4] prepared a mixed complex of Yb(III) with formula $Yb(Cp)_2L$ (where Cp – cyclopentadienyl, L – $C_6H_2(CH_3)_3COO^-$) as monomer, in which the carboxylate groups are bidentate. The structure of this complex could not be determined, because it was decomposed by X-rays. The complexes of rare earth with 2,4,6-trimethylbenzoic acid acid were unknown before the present work.

The aim of this work was to prepare rare earth complexes with 2,4,6-trimethylbenzoic acid in solid state and to examine their physico-chemical properties and thermal decomposition in the air.

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Table 1 Analytical data

Complex	C/%		H/%		M/%		Solubility/
	calc.	found	calc.	found	calc.	found	mol dm^{-3} 10^{-3}
$LaL_3 \cdot 2H_2O$	54.22	54.2	5.61	5.6	20.90	20.9	1.20
$CeL_3 \cdot 2H_2O$	54.12	54.1	5.60	5.6	21.05	21.0	11.70
$PrL_3 \cdot 2H_2O$	54.06	54.0	5.60	5.6	21.14	21.0	7.27
$NdL_3 \cdot 2H_2O$	53.79	53.8	5.57	5.5	21.53	21.5	5.98
$SmL_3 \cdot H_2O$	53.30	53.2	5.52	5.5	22.24	22.2	6.08
$EuL_3 \cdot H_2O$	54.63	54.6	5.35	5.3	23.04	23.0	5.90
$GdL_3 \cdot H_2O$	54.19	54.0	5.30	5.3	23.65	23.6	6.50
$TbL_3 \cdot H_2O$	54.06	54.0	5.29	5.3	23.84	23.8	5.80
$DyL_3 \cdot H_2O$	53.68	53.7	5.26	5.2	24.25	24.5	5.60
$HoL_3 \cdot H_2O$	53.58	53.7	5.25	5.2	24.52	24.4	4.54
$ErL_3 \cdot H_2O$	53.39	53.5	5.23	5.1	24.78	24.7	4.78
$TmL_3 \cdot H_2O$	53.26	53.0	5.21	5.1	24.97	25.0	3.40
$YbL_3 \cdot H_2O$	52.94	53.0	5.18	5.2	25.42	25.4	1.73
$LuL_3 \cdot H_2O$	52.79	53.0	5.17	5.1	25.63	25.5	3.30
$YL_3 \cdot H_2O$	58.64	58.8	6.07	6.0	14.47	14.6	6.80

L^* – $C_6H_2(CH_3)_3COO^-$ (2, 4, 6)

Experimental

2,4,6-Trimethylbenzoates of Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by adding stoichiometric quantities of hot (~333 K) 0.1 M solution of ammonium 2,4,6-trimethylbenzoate (pH 4.5–5.0) to a hot solution of Y(III) and separated lanthanide(III) chlorides (Ce(III) was used as its nitrate). The precipitate formed was heated in mother solution for 0.5 h and then was filtered off, washed with hot water to remove of NH_4^+ ions and dried at 303 K to a constant mass. The carbon and hydrogen contents in the complexes prepared were determined by elemental analysis. The metal contents were determined from the TG curve and by ignition the complexes to the oxides at 1273 K. The content of crystallization water was determined from the TG curve and by heating the samples at a set temperature to a constant mass. The results are concording to theoretical data (Table 1). The IR spectra of 2,4,6-trimethylbenzoic acid and the separated rare earth complexes, and sodium salt were recorded over the range of 4000–400 cm^{-1} using M-80 Carl Zeiss Jena spectrophotometer. The samples were prepared as KBr discs.

The thermal stability and solid products of decomposition of the prepared complexes were determined using a Paulik-Paulik-Erdey Q 1500 D derivatograph with Derill converter. TG, DTG and DTA curves were recorded. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples (100 mg) were heated in platinum crucibles in static air to 1273 K with a sensitivity of TG=100 mg. DTG and DTA sensitivities were regulated by computer Derill program. The products of decomposition were calculated from the TG curves and were verified by IR spectra or diffraction pattern registration.

Results and discussion

2,4,6-Trimethylbenzoates of Y(III) and lanthanides(III) from La to Lu were prepared as crystalline solids with colour characteristic for Ln(III) ions and with molar ratio of metal to organic ligand of 1:3. The complexes of Y and La–Nd were prepared as dihydrates, whereas those of Sm–Lu as monohydrates (Table 1). The degree of hydration for the light lanthanide complexes has higher values than those determined for the heavy lanthanide 2,4,6-trimethylbenzoates are sparingly soluble in water. Their solubilities are in order of 10^{-3} mol dm^{-3} and decrease in light lanthanide series from Ce to Eu, and in heavy lanthanide series from Gd to Yb. The Y(III) complex is the most soluble and that of La(III) – the least in the lanthanide group.

In order to confirm the composition of the complexes and to determine the metal-ligand coordination, the IR spectra of 2,4,6-trimethylbenzoic acid, its complexes with rare earth elements and sodium salt were recorded. The IR spectra of the prepared complexes are similar to each other and have many absorption bands. In the IR spectrum of free 2,4,6-trimethylbenzoic acid there are very strong absorption bands of the COOH group at 1680 cm^{-1}, the bands of asymmetrical vibrations of the CH_3 group at 2920 and 1432 cm^{-1}, the symmetrical vibrations of the CH_3 group at 2850 and 1376 cm^{-1}. In the IR spectra of the 2,4,6-trimethylbenzoates prepared, the absorption band of the COOH group disappears and the bands of the asymmetrical (ν_{as}) and symmetrical (ν_s) vibrations of the (OCO^-) group appear at 1540–1535 and 1512 cm^{-1}, and 1408–1400 cm^{-1}, respectively. The broad absorption band of ν(OH) with maximum at 3600–3200 cm^{-1} confirms the presence of crystallization water molecules. The split bands of asymmetrical vibrations $\nu(OCO^-)$ suggest that the carboxylate groups coordinate the metal ions in different way. The separation values ($\Delta\nu$) of $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ in the IR spectra of the complexes studied are greater ($\Delta\nu$=135–132 cm^{-1}) and smaller ($\Delta\nu$=112–104 cm^{-1}) compared to the respective bans for the sodium salt. The split bands of $\nu_{as}(OCO^-)$ are shifted to higher and to lower frequencies and the $\nu_s(OCO^-)$ are shifted to higher frequencies for the complexes of heavy lanthanides and do not change their position for the complexes of light lanthanides comparing to the corresponding bands of the sodium salt. From spectroscopic criteria [5–7] and our previous work [8, 9], the carboxylate groups in the complexes prepared are probably bidentate bridging and monodentate similarly as in the rare earth benzoates [10]. The nature of the metal–ligand bonding can be explained in detail after the determination of the crystal and molecular structure monocrystals.

Table 2 Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) of rare earth(III) 2,4,6-trimethylbenzoates

Complex	ν_{as}(OCO)	ν_s(OCO)	$\Delta\nu$	$\nu_{as}(CH_3)$	$\nu_s(CH_3)$	$\delta(H_2O)$
$LaL_3\cdot 2H_2O$	1535/1512	1400	135/112	2920, 1436	2870, 1380	1610
$CeL_3\cdot 2H_2O$	1540/1512	1400	140/112	2920, 1440	2870, 1380	1610
$PrL_3\cdot 2H_2O$	1540/1512	1400	140/112	2920, 1440	2870, 1380	1610
$NdL_3\cdot 2H_2O$	1540/1512	1400	140/112	2920, 1440	2870, 1380	1610
$SmL_3\cdot H_2O$	1540/1512	1400	140/112	2920, 1440	2870, 1380	1610
$EuL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2879, 1376	1610
$GdL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2870, 1380	1610
$TbL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2870, 1380	1610
$DyL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2870, 1380	1610
$HoL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2880, 1380	1595
$ErL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2880, 1385	1595
$TmL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2880, 1385	1595
$YbL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1448	2880, 1385	1595
$LuL_3\cdot H_2O$	1540/1512	1408	132/104	2920, 1444	2870, 1380	1605
$YL_3\cdot 2H_2O$	1540/1512	1408	132/144	2970, 1444	2870, 1380	1665
$NaL\cdot nH_2O$	1530	1400	130	2960, 1432	2870, 1380	1590

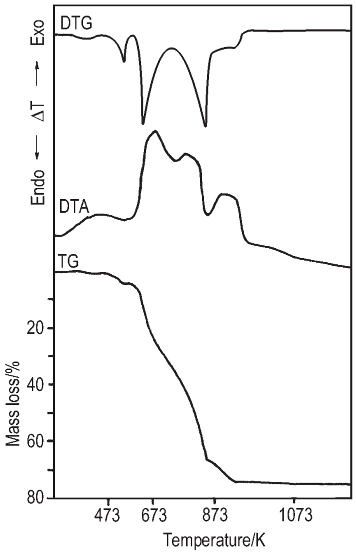

Fig. 1 TG, DTG and DTA curves of $CeL_3\cdot 2H_2O$

Table 3 Thermal data of dehydration and decomposition of rare earth(III) 2,4,6-trimethylbenzoates

Complex	ΔT_1/K	Mass loss/%		n_{H_2O}	ΔT_2/K	Mass loss/%		ΔT_3/K	Mass residue/%		T_K/K
		calc.	found			calc.	found		calc.	found	
$LaL_3 \cdot 2H_2O$	333–373	2.71	2.0	1	593–963	72.17	72.0	823–1173	24.51	24.5	1173
	473–573	5.46	5.5	1							
$CeL_3 \cdot 2H_2O$	473–533	5.41	5.5	2	–	–	–	613–923	25.85	26.0	923
$PrL_3 \cdot 2H_2O$	473–533	5.40	5.5	2	–	–	–	633–973	25.54	25.5	973
$NdL_3 \cdot 2H_2O$	473–533	5.38	5.5	2	613–933	71.60	72.0	973–1073	25.11	25.0	1073
$SmL_3 \cdot H_2O$	473–533	2.74	3.0	1	–	–	–	613–1073	26.50	26.0	1073
$EuL_3 \cdot H_2O$	473–533	2.75	3.0	1	–	–	–	613–1073	26.88	27.0	1073
$GdL_3 \cdot H_2O$	473–523	2.71	3.0	1	–	–	–	603–1093	27.26	27.5	1093
$TbL_3 \cdot H_2O$	473–533	2.70	2.5	1	–	–	–	593–933	28.04	28.0	933
$DyL_3 \cdot H_2O$	473–553	2.69	2.5	1	–	–	–	593–933	27.85	28.0	933
$HoL_3 \cdot H_2O$	473–553	2.68	3.0	1	–	–	–	573–933	28.09	28.0	933
$ErL_3 \cdot H_2O$	473–553	2.67	2.5	1	–	–	–	573–933	28.34	28.0	933
$TmL_3 \cdot H_2O$	473–533	2.66	2.5	1	–			573–933	28.52	28.5	933
$YbL_3 \cdot H_2O$	473–553	2.65	2.5	1	–			573–913	28.95	29.0	913
$LuL_3 \cdot H_2O$	493–643	2.64	2.5	1	–			613–983	29.15	29.0	983
$YL_3 \cdot 2H_2O$	493–573	5.86	6.0	2	–			613–833	18.37	18.5	833

ΔT_1 – temperature range of dehydration
ΔT_2 – temperature range of decomposition to oxocarbonate
ΔT_3 – temperature range of decomposition to oxides Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7
T_K – temperature of oxide formation

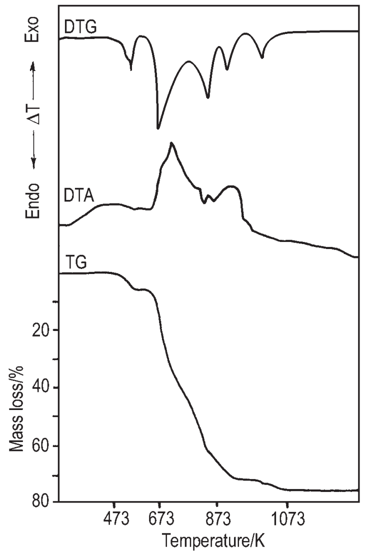

Fig. 2 TG, DTG and DTA curves of $NdL_3 \cdot 2H_2O$

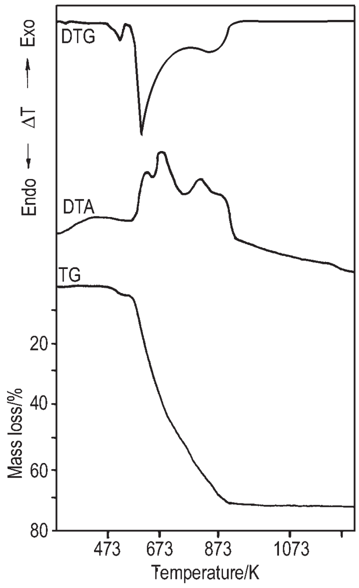

Fig. 3 TG, DTG and DTA curves of $ErL_3 \cdot H_2O$

The rare earth hydrated 2,4,6-trimethylbenzoates are stable up to 473–493 K (except of lanthanum(III) complex which is stable up to 333 K) and when heated in air decompose in some steps in various ways (Table 3, Figs 1–4). During heating the hydrated

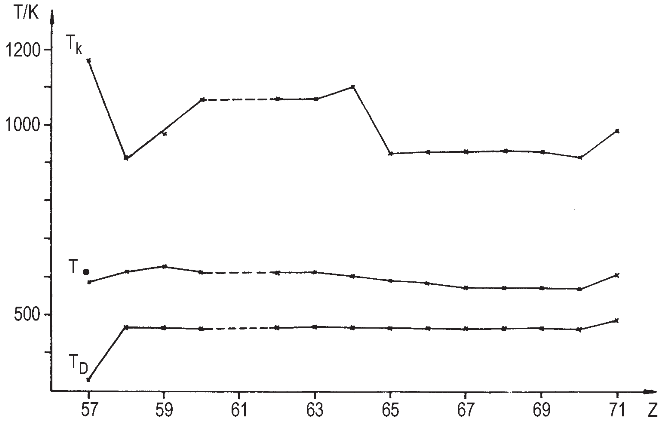

Fig. 4 Relationship between T_D, T_o, T_K and Z of Ln

complexes of Y, Ce–Lu are dehydrated in one step and then decompose directly to oxides (Y, Ce–Pr, Sm–Lu) or with intermediate formation of the oxocarbonates (Nd). The hydrated complex of La(III) is dehydrated in two steps and then decomposes to oxide La_2O_3 with intermediate formation of $La_2O_2CO_3$. The results indicate that the thermal decomposition of the hydrated rare earth 2,4,6-trimethylbenzoates can be presented as:

$$LaL_3{\cdot}2H_2O \rightarrow LaL_3{\cdot}H_2O \rightarrow LaL_3 \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$$

$$NdL_3{\cdot}2H_2O \rightarrow NdL_3 \rightarrow Nd_2O_2CO_3 \rightarrow Nd_2O_3$$

$$LnL_3{\cdot}nH_2O \rightarrow LnL_3 \rightarrow Ln_2O_3,\ Pr_6O_{11},\ Tb_4O_7;\ n{=}1,\ 2;\ Ln{=}\mathrm{Y, Ce, Pr, Sm–Lu}$$

The dehydration and decomposition of the complexes prepared are connected with an endothermic effect at 493–533 and 613–633 K, respectively, whereas the combustion of the organic ligand and the products of decomposition show an exothermic effect. On the basis of the results obtained it is possible to suggest that the water molecules present in Y and the rare earth complexes of Ce to Lu are bonded in similar way, except of the La complex. The relationship of the temperature of the beginning of dehydration (T_D), the beginning of decomposition (T_o) for the complexes and temperature of oxide formation (T_k) are presented on Fig. 4. The temperatures of dehydration are similar for all lanthanide complexes, except of La one. The temperatures of decomposition generally decrease insignificantly with increasing the atomic number Z of the metal and polarization effect. The temperature of oxide formation is the highest for La_2O_3 (1173 K) and the lowest for CeO_2 (923 K). Generally, it is possible to state that the temperatures of the heavy lanthanide oxide formation are lower than those for the light lanthanides.

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