Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 381–385

THERMAL ANALYSIS OF LANTHANIDE(III) AND Y(III) COMPLEXES WITH 4-HYDROXY-3-METHOXYBENZOIC ACID

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The complexes of lanthanides(III) and Y(III) with 4-hydroxy-3-methoxybenzoic acid (vanillic acid) of the formula $Ln(C_8H_7O_4)_3 \cdot nH_2O$ where n=2 for La(III), Pr(III); n=3 for Nd(III); n=4 for Sm(III); n=5 for Ce(III) and n=6 for Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) were prepared and IR spectra and X-ray diffraction patterns and their thermal decomposition were investigated. The carboxylate group in the studied complexes is a bidentate chelating or a bidentate chelating and bridging ligand. They are crystalline compounds. When heated, the complexes lose their crystallisation water and decompose to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7. The intermediate decomposition products of complexes of La(III) to Lu(III) (except Ce(III)) are oxocarbonates $Ln_2O_2CO_3$.

Keywords: *complexes, 4-hydroxy-3-methoxybenzoates, IR spectra, lanthanide(III), synthesis, thermal analysis, vanillates*

Introduction

4-Hydroxy-3-methoxybenzoic acid (vanillic acid) is a natural agent. It is an intermediate product in the two-step bioconversion of ferulic acid to vanillin or slow oxidation of vanillin [1, 2]. Copper complexes with vanillic acid were investigated and conditional stability constants were calculated from the fluorescence and UV spectra [3]. The crystal structure of the dimeric copper complex of vanillic acid $[CuL_2H_2O]_2$ was determined [4]; Cu...Cu distance is short, associated with the hydrogen bond link of the apically coordinated water molecules with the nearest neighbour vanillic hydroxyl group. The structure parameters of uranium(VI) complex indicate that the carboxylic group coordinated the uranyl cation in a bidentate mode in the equatorial plane [5]. The complexes of lanthanide(III) and Y(III) with vanillic acid have not been studied so far.

The aim of this work was the preparation and study of thermal and spectral properties of the complexes of lanthanide(III) and Y(III) with 4-hydroxy-3-methoxybenzoic acid as solids as well as the examination of influence of the –OH and $–OCH_3$ group in benzene ring on the properties of the complexes.

Experimental

4-Hydroxy-3-methoxybenzoates of lanthanide(III) from La(III) to Lu(III) and Y(III) were obtained by dissolving the freshly precipitated lanthanide(III) carbonates in a solution of 4-hydroxy-3-methoxybenzoic acid (0.06M). The precipitate formed was filtered off, washed with water and dried at 303 K to a constant mass.

The quantitative composition of the prepared complexes was determined by elemental analysis, by ignition of the complexes to the oxides and from TG curve. The content of crystallisation water was determined from TG curve and by isothermal heating of the complexes at a specified temperature. The analytical data of the complexes were in agreement with the theoretical calculations. The X-ray diffraction patterns of the complexes obtained were taken on a HZG 4 A2 diffractometer, using Ni – filtered radiation. The measurements were made in the range of 2θ=5–60° by the Debye–Scherrer method.

The IR spectra of 4-hydroxy-3-methoxybenzoic acid, the lanthanide complexes and the sodium salt were recorded in the range of 4000–400 cm^{-1}, using M-80 Carl-Zeiss Jena spectrophotometer. The samples were prepared as KBr discs.

The thermal stability of the complexes obtained, the processes of their dehydration and decomposition as well as the solid product of decomposition were studied in air, using Setsys 16/18 (Setaram) derivatograph; samples were heated to 1273 K at a heating rate of 10 K min^{-1}. Netzsch TG apparatus coupled with a Brucker FTIR IR 556 spectrophotometer identified the gas – phase products of decomposition. The sample (23 mg) were heated to 1273 K in Al_2O_3 crucibles in Ar atmosphere, at a heating rate of 10 K min^{-1}.

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1388–6150/$20.00

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Results and discussion

4-Hydroxy-3-methoxybenzoates of lanthanide(III) from La(III) to Lu(III) and Y(III) were obtained as solids, with a molar ratio of metal to organic ligand 1:3 and general formula $LnL_3 \cdot nH_2O$; where *L* is $[C_6H_3(OH)(OCH_3)COO]^-$, *n*=2 for La(III), Pr(III); *n*=3 for Nd(III); *n*=4 for Sm(III); *n*=5 for Ce(III) and *n*=6 for Eu(III) to Lu(III) and Y(III). All complexes obtained are crystalline compounds. The complexes of La(III)–Sm(III) have different structure, whereas hexahydrated complexes of Eu(III)–Lu(III) are isostructural (Fig. 1). The $Tb(C_8H_7O_4)_3 \cdot 6H_2O$ crystallizes in the triclinic system: cell parameters: a=13.90 Å, b=17.23 Å, c=18.83 Å, α=75.09°, β=46.85°, γ=43.36°, V=1995 Å^3.

IR spectra of 4-hydroxy-3-methoxybenzoic acid, its sodium salt and lanthanide(III) complexes obtained were recorded. The data is presented in Table 1. In the IR spectrum of the free 4-hydroxy-3-methoxybenzoic acid there is a sharp absorption band of carboxylic group –COOH at 1676 cm^{-1}, absorption bands of δOH at 1456 cm^{-1} and at 900 cm^{-1} as well as νCOH at 1280 cm^{-1}. The characteristic bands of $\nu_{as}CH_3$, ν_sCH_3 and C–O–C appear at 1432, 1380, 1300 and 1112 cm^{-1}, respectively [6–8].

In the IR spectra of the complexes obtained asymmetric absorption bands of $\nu_{as}(OCO^-)$ at 1552–1544 cm^{-1} and the symmetric absorption bands at 1408–1396 cm^{-1} can be observed (Table 1). In the IR spectra of the lanthanide(III) complexes the asymmetric bands of $\nu_{as}(OCO^-)$ are shifted to lower frequencies, while the symmetric bands of $\nu_s(OCO^-)$ do not change their position or then are slightly shifted to higher frequencies (4–12 cm^{-1}), when compared to the sodium salt. The band shifts of $\nu_{as}(OCO^-)$ of light lanthanide complexes are greater than of the other complexes. The asymmetric absorption bands of $\nu_{as}(OCO^-)$ are split, forming a double band at 1552 and 1512 cm^{-1}. The separation value, $\Delta\nu=\nu_{as}-\nu_s$ are lower than for sodium salt ($\Delta\nu$=160 cm^{-1}). The deformation vibration bands of phenolic group δ(OH) at 1456 cm^{-1} in free acid are insignificantly shifted to higher frequencies, the bands at 900 cm^{-1} and the bands νOH at 1280 cm^{-1} are insignificantly shifted to

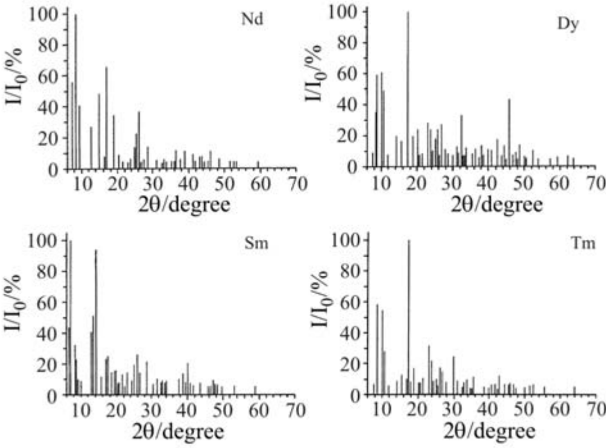

Fig. 1 Diffractograms of some $LnL_3 \cdot nH_2O$

Table 1 Frequencies of absorption bands of OCO^- and OH groups of 4-hydroxy-3-methoxybenzoic acid and its compounds (cm^{-1})

Compound	$\nu_{as}OCO^-$	ν_sOCO^-	$\nu_{as}–\nu_s$	δOH	νCOH	δOH	νM–O
$LaL_3 \cdot 2H_2O$	1516	1396	120	1460	1272	886	454
$CeL_3 \cdot 5H_2O$	1508	1400	108	1464	1270	880	458
$PrL_3 \cdot 2H_2O$	1512	1404	108	1460	1270	882	452
$NdL_3 \cdot 3H_2O$	1508	1396	112	1460	1270	886	452
$SmL_3 \cdot 4H_2O$	1548, 1512	1400	148, 112	1462	1272	886	452
$EuL_3 \cdot 6H_2O$	1544, 1512	1400	144, 112	1462	1272	888	456
$GdL_3 \cdot 6H_2O$	1544, 1512	1400	144, 112	1460	1270	886	456
$TbL_3 \cdot 6H_2O$	1552, 1512	1404	144, 108	1462	1272	886	456
$DyL_3 \cdot 6H_2O$	1552, 1512	1408	144, 104	1460	1270	886	456
$HoL_3 \cdot 6H_2O$	1552, 1512	1408	144, 104	1460	1272	884	456
$ErL_3 \cdot 6H_2O$	1548, 1512	1408	144, 104	1462	1270	880	450
$TmL_3 \cdot 6H_2O$	1552, 1512	1408	144, 104	1462	1272	882	450
$YbL_3 \cdot 6H_2O$	1544, 1512	1404	140, 108	1460	1272	884	450
$LuL_3 \cdot 6H_2O$	1544, 1512	1406	138, 106	1462	1272	880	452
$YL_3 \cdot 6H_2O$	1552, 1512	1408	144, 104	1460	1272	884	456
NaL	1556	1396	160	1468	1270	880	468
HL				1456	1280	900	

$L=[C_6H_3(OH)(OCH_3)COO]^-$

Table 2 Data of decomposition of yttrium(III) and lanthanide(III) 4-hydroxy-3-methoxybenzoates in air

Complex	ΔT_1/K	Mass loss/%			ΔT_2/K	Mass loss/%		ΔT_3/K	Mass loss/%		T_0/K
		calc.	found	nH$_2$O		calc.	found		calc.	found	
$LaL_3\cdot2H_2O$	398–473	5.3	6.5	2	508–773	72.5	72.0	953–1018	75.8	76.0	1018
$CeL_3\cdot5H_2O$	351–418	12.3	13.1	5	–	–	–	443–931	77.0	76.5	931
$PrL_3\cdot2H_2O$	340–443	5.3	5.6	2	465–783	72.5	72.1	798–844	75.5	74.3	844
$NdL_3\cdot3H_2O$	340–403	2.5	2.1	1	485–853	72.8	73.5	878–929	75.3	75.5	929
	403–446	5.3	5.2	2							
$SmL_3\cdot4H_2O$	333–408	9.9	10.4	6	450–798	72.9	71.6	830–938	75.9	75.9	938
$EuL_3\cdot6H_2O$	340–429	14.1	13.4	6	458–821	74.0	73.7	855–933	76.8	76.2	933
$GdL_3\cdot6H_2O$	338–423	14.0	13.8	6	459–808	73.5	72.6	845–963	76.3	76.0	963
$TbL_3\cdot6H_2O$	338–418	14.0	13.4	6	463–803	73.3	74.7	843–908	76.1	74.7	908
$DyL_3\cdot6H_2O$	345–428	13.9	13.4	6	460–778	73.0	72.9	815–933	75.8	75.4	933
$HoL_3\cdot6H_2O$	351–418	13.9	13.3	6	450–803	72.8	71.9	864–988	75.6	75.4	988
$ErL_3\cdot6H_2O$	353–418	13.9	13.0	6	488–796	72.6	72.1	865–993	75.3	74.6	993
$TmL_3\cdot6H_2O$	353–405	13.8	13.1	6	488–808	72.4	72.0	903–998	75.1	74.9	998
$YbL_3\cdot6H_2O$	348–398	13.7	13.1	6	498–805	72.0	72.1	908–996	74.8	73.8	996
$LuL_3\cdot6H_2O$	340–396	13.7	13.2	6	498–808	71.8	72.2	918–919	74.6	72.2	819
$YL_3\cdot6H_2O$	340–418	15.4	14.5	6	498–803	80.6	80.6	843–985	83.8	82.8	985

$L=C_8H_7O_4^-$; ΔT_1 – range of dehydration temperature; ΔT_2 – range of decomposition temperature from LnL_3 to $Ln_2O_2CO_3$;
ΔT_3 – range of decomposition temperature $Ln_2O_2CO_3$ to oxides; T_0 – temperature over which oxides exist (Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7)

lower frequencies in the lanthanide complexes. In the IR spectra of hydrated complexes a broad valency absorption band of the OH groups from H_2O at 3464–3424 cm^{-1} can be observed. In all complexes an absorption band at 460–450 cm^{-1} due to metal-oxygen bond appears. Spectroscopic data suggest that in coordination of metal ligand only carboxylate groups take part [9, 10]. The splitting of the asymmetric bands indicates that the carboxylate groups in the complex coordinate the metal ion in a different way. The separation value, Δν, of the (OCO^-) group, splitting and the direction of the shift of these bands, may suggest that carboxylate groups act as bidentate chelating in light lanthanide complexes and as bidentate chelating and bridging in the other ones. The way of coordination of carboxylate groups is different in mono- and dihydroxybenzoates [11–15] and dimethoxybenzoates [16–22] of lanthanide(III). The carboxylate groups act as mono-, bi- and tridentate chelating or chelating and bridging ligand.

The thermal stability of the complexes obtained was studied in air and the data is presented in Table 2. 4-Hydroxy-3-methoxybenzoates of lanthanide(III) from La(III) to Lu(III) and Y(III) are stable in air below the temperature range from 333 K (for Sm) to 398 K (for La). When heated in air hydrated complexes lose their crystallization water in one step (except for Nd(III) complex), forming anhydrous compounds. Trihydrated complex of Nd(III) loses water in two steps, firstly one molecule then two molecules of H_2O (Fig. 2). The dehydration process is accompanied by endoeffect on DTA curve. The dehydration temperature decreases with the increase of the atomic number Z of the metal from 445 K for La(III) to 378 K for Lu(III). On the DTA curves of the anhydrous complexes of Ce(III) and Nd(III) to Er(III) the exothermic peak is observed at 437–446 K due to the change in crystal structure or solid–solid interaction. After dehydration anhydrous complexes are stable below the temperature range from 443 K (for Ce) to 508 K (for La); when heated they decompose to oxides: Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 (Fig. 3). The intermediate decompo-

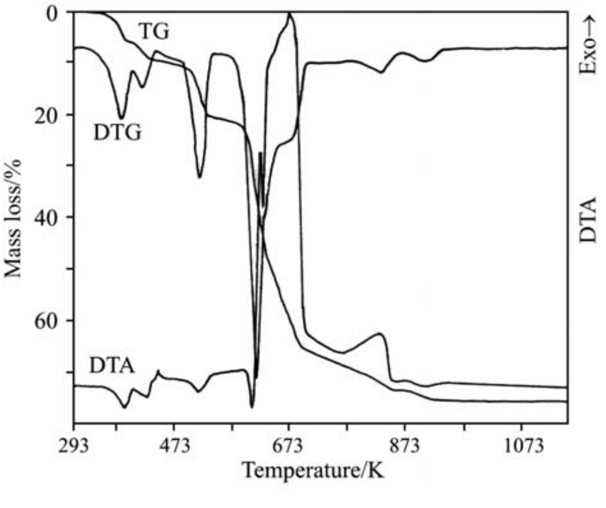

Fig. 2 TG, DTG and DTA curves of $Nd(C_8H_7O_4)_3\cdot3H_2O$

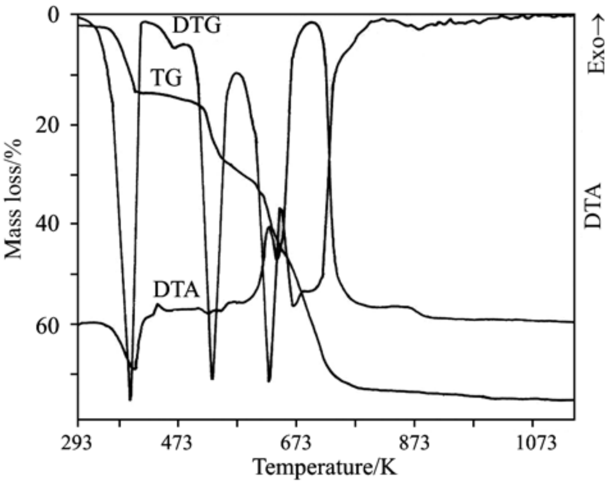

Fig. 3 TG, DTG and DTA curves of $Ho(C_8H_7O_4)_3 \cdot 6H_2O$

sition products of complexes of La(III) to Lu(III) (except Ce(III)) are oxocarbonates $Ln_2O_2CO_3$; they are stable in the temperature range from 773 to 953 K. The combustion of the organic ligand is connected with exothermic effect on DTA curve – 615–637 and 673–708 K. The temperature over which oxides exist changes in the lanthanide series from 819 K (for Lu) to 1018 K (for La). The double-double effect characteristic of lanthanides is observed.

The FTIR spectra of the gaseous products of thermal decomposition of the obtained complexes were recorded. As an example FTIR spectrum of the complex Nd(III) is shown (Fig. 4). The valence and the deformation vibration bands, characteristic of water molecules in the ranges 4000–3400 and 2100–1250 cm^{-1} appear at the temperature 390 K. They are connected with the dehydration process in which first one, then two water molecules are removed from the hydrated complex. At the temperature 522 K the weak bands in the range 2350–2250 cm^{-1} begin to appear, which is characteristic of CO_2. At the temperature 539 K these bands increase and then a band of CO_2 in the range 750–600 cm^{-1} appears. It means that the decomposition of organic ligand began. At the temperature 548 K the bands appear in the ranges 3750–3500, 1100–950 and 3100–2750 cm^{-1} . These ranges are characteristic of vibrations which come from νC–(OH) and νC–H respectively. The first of these bands are characteristic of alcohols, the next ones are connected with the occurrence of gaseous hydrocarbons. At the temperature 719 K these bands disappear. At 799 K, the band characteristic of carbon oxide at 2100 cm^{-1} appears; carbon oxide is formed during decomposition of $Ln_2O_2CO_3$.

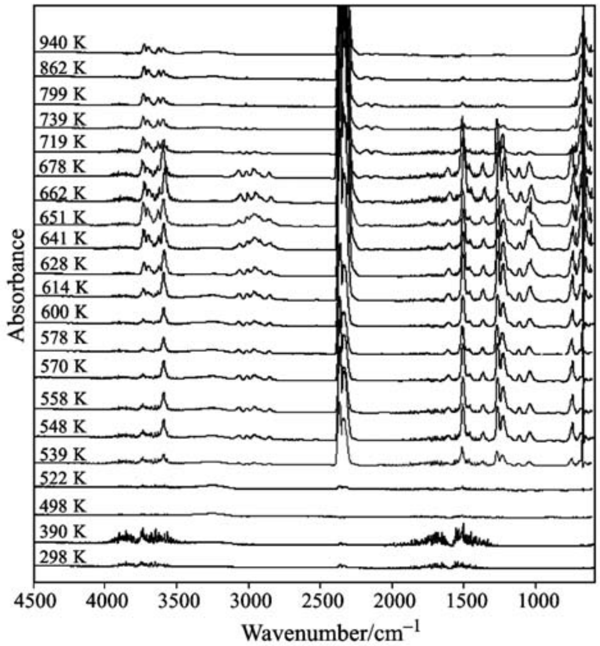

Fig. 4 FTIR spectra of gaseous product of thermal decomposition of $NdL_3 \cdot 3H_2O$

Thermal decomposition of obtained lanthanide(III) and Y(III) complexes with 4-hydroxy-3-methoxybenzoic acid can be presented as follows:

$$LnL_3 \cdot nH_2O \rightarrow LnL_3 \rightarrow Ln_2O_2CO_3 \rightarrow$$
$$\rightarrow Ln_2O_3(Pr_6O_{11},\ Tb_4O_7);\ (Ln\text{=La, Pr, Sm–Lu, Y})$$

$$NdL_3 \cdot 3H_2O \rightarrow NdL_3 \cdot 2H_2O \rightarrow NdL_3 \rightarrow$$
$$\rightarrow Nd_2O_2CO_3 \rightarrow Nd_2O_3$$

$$CeL_3 \cdot 5H_2O \rightarrow CeL_3 \rightarrow CeO_2$$

Conclusions

4-Hydroxy-3-methoxybenzoates (vanillates) of lanthanides and yttrium were synthesized as hydrated complexes. The complexes are crystalline compounds which are characterized by various symmetry. Hexahydrated complexes of Eu(III) to Lu(III) are isostructural. The carboxylate group in these complexes acts as bidentate chelating in light lanthanide complexes and as bidentate chelating and bridging in the other ones. The obtained complexes are stable at room temperature. When heated in air to 1173 K, the complexes decompose in various ways. In the first step they dehydrate to anhydrous compounds, then they decompose to the oxocarbonates $Ln_2O_2CO_3$. After that they decompose to oxides of the respective metals. The temperature over which oxides exist changes with the increase of the atomic number of the metal from 819 K (for Lu) to 1018 K (for La).

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Received: December 13, 2004
In revised form: March 30, 2005

DOI: 10.1007/s10973-005-6513-2