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SPECTRAL AND THERMAL STUDIES OF LIGHT LANTHANIDE 4-CHLOROPHTHALATES

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Conditions for the preparation of light lanthanide 4-chlorophthalates were investigated and their composition, solubility in water at 295 K, IR spectra and thermal decomposition were determined. 4-Chlorophthalates of La–Nd(III) were prepared as complexes with general formula $NaLn[ClC_6H_3(CO_2)_2]_2$, whereas compounds of Sm and Eu have general formula $Ln_2[ClC_6H_3(CO_2)_2]_3\cdot 6H_2O$. During heating all complexes decompose to oxides with intermediate formation of oxochlorides. The carboxylate groups in the complexes studied are bidentate bridging (Sm, Eu) or bidentate chelating and bridging (La–Nd).

Keywords: *4-chlorophthalic acid-monosodium salt, IR spectra, lanthanide complexes, thermal analysis*

Introduction

4-Chlorobenzene-1,2-dicarboxylic acid, $ClC_6H_3(COOH)_2$, known as 4-chlorophthalic acid was prepared by different methods with different yields (maximum 90%) [1–5]. This acid is a white solid soluble in water and ethanol. The salts of 4-chlorophthalic acid are little known. 4-Chlorophthalates of Na, K and Ba were obtained as acid salts sparingly soluble in water [1, 2, 6]. Monopotassium salt is less soluble than the monosodium salt [2]. The complexes of Y(III) and heavy lanthanides from Gd to Lu(III) with 4-chlorophthalate ion have been prepared as solids with general formula $Ln_2[ClC_6H_3(CO_2)_2]_3\cdot nH_2O$; n=2, 3, 4, 6 [7]. The COO^- groups in these complexes act as bidentate chelating. During heating the hydrated complexes are dehydrated in one or two steps and next decompose to the oxides Ln_2O_3 and Tb_4O_7, with intermediate formation oxochlorides. The complexes of 4-chlorophthalate ion with light lanthanides have not been studied so far.

This work is a continuation of our study on the physicochemical properties and thermal decomposition during heating in static air prepared by us solid Y(III) and lanthanide(III) complexes with benzenecarboxylic acids [8–16].

The aim of the present work was to prepare 4-chlorophthalates of light lanthanide (La–Eu, without Pm) as solids under the same conditions and to examine some of their physical and chemical properties.

Experimental

4-Chlorophthalates of light lanthanides from La(III) to Eu(III) were prepared by adding a double excess of 0.2 mol dm^{-3} ammonium sodium 4-chlorophthalate (pH 4.7) to a hot solution of lanthanide chlorides (Ce(III) was used as its nitrate). Precipitates formed were heated in mother liquor for 10 h, then were filtered off, washed with hot water to remove NH_4^+ and Na^+ ions and dried at 303 K to a constant mass.

The quantitative composition of the prepared complexes was determined by the elemental analysis on a Perkin Elmer CHN 2400 analyser (C, H), by AAS on a SPECTRAA 880 (Varian) (Na) and spectrophotometrically with arsenazo III (lanthanide(III) ions) using Specord M-40 spectrophotometer. The content of lanthanides were also determined by ignition of the complexes to the oxides at 1673 K and from TG curve. The content of crystallization water was determined from TG curve and by isothermal heating the complexes at a special temperature. The analytical data of the complexes were in a good agreement with theoretical values.

IR spectra of the prepared complexes, spectra of 4-chlorophthalic acid – monosodium salt and disodium salt were recorded as KBr discs on a Specord M-80 spectrophotometer (4000–400 cm^{-1} range).

The solubility in water at 295 K was determined using saturated solutions prepared under isothermal conditions and measuring spectrophotometrically the concentration of Ln(III) ions with arsenazo III on a Specord M-40 spectrophotometer.

The powder diffraction patterns are registered on a HZG (Carl–Zeiss, Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within 5–60° 2θ range by the Debye–Scherrer method.

The thermal stability of the prepared 4-chlorophthalates was investigated by TG and DTA curves, using Setsys 16/18 (Setaram) derivatograph with a

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heating rate of 10 K min^{-1}. Samples were heated in air in platinum crucibles up to 1673 K using α-Al_2O_3 as a standard. The products of decomposition were confirmed by registering their powder diffraction patterns.

Results and discussion

4-Chlorophthalates of lanthanides were prepared as crystalline solids with colour characteristic for lanthanide(III) ions. 4-Chlorophthalates of La–Nd(III) were obtained as complexes with a 1:1:2 molar ratio of sodium to lanthanide and to organic ligand, and general formula $NaLn[ClC_6H_3(COO)_2]_2$. The compounds of Sm and Eu(III) were prepared as solid complexes with a 2:3 molar ratio of metal to organic ligand, and general formula $Ln_2[ClC_6H_3(COO)_2]_3\cdot 6H_2O$. Such complexes of La–Nd(III) with 4-chlorophthalate ion, despite of many tests, were not obtained.

In order to confirm the composition of the prepared complexes and to determine the coordination mode of COO groups, the IR spectra of 4-chlorophthalic acid – monosodium salt and prepared lanthanide and sodium 4-chlorophthalates were recorded (Table 1).

The monosodium salt of 4-chlorophthalic acid exhibit the following absorption bands: the broad absorption band of the OH group with the maximum at 3400 cm^{-1}, the week band of C=O in the COOH group at 1685 cm^{-1}, the strong band of the stretching vibration of C–O in COOH group at 1276 cm^{-1}, the absorption bands of the asymmetrical $\nu_{as(COO)}$ and symmetrical $\nu_{s(COO)}$ vibrations at 1568 and 1400 cm^{-1}, respectively, the bands of the stretching vibrations of C–C at 1456 cm^{-1}, the bands of the C–H group in the benzene ring trisubstituted in the 1,2,4-position at 1144, 1112 and 880 cm^{-1} and the bands of C–Cl bond at 712–580 cm^{-1}.

The IR spectra of the anhydrous 4-chlorophthalates of La–Nd(III) are different from the IR spectra of the hydrated Sm and Eu(III) complexes. The IR spectra of $NaLn[ClC_6H_3(COO)_2]_2$, where *Ln*=La–Nd, do not show absorption bands characteristic for COOH group, but exhibit strong double bands of asymmetrical valency vibrations of the COO^- group at 1552 and 1524 cm^{-1} , the band of symmetrical valency vibrations of the COO^- group at 1428 cm^{-1} and the absorption bands of the M–O bond at 544 cm^{-1}. In the IR spectra of hydrated 4-chlorophthalates of Sm and Eu(III) exists a broad valency absorption band of the OH group from H_2O at 3440–3400 cm^{-1}, which points to the presence of crystallization water molecules, the asymmetrical absorption bands of $\nu_{as(COO)}$ at 1552 cm^{-1}, symmetrical absorption bands of $\nu_{s(COO)}$ at 1420–1416 cm^{-1} and the absorption bands of the metal–oxygen at 536 cm^{-1} (Table 1).

The $\nu_{M–O}$ values for La–Nd 4-chlorophthalates are only slightly different from the $\nu_{M–O}$ values of the complexes of Sm and Eu, that may suggest a similar bond energy. The vibrations of M–O are not pure ones, they are conjugate with the C–O and C–C bonds. The slight shift (5 cm^{-1}) or their lack of the absorption bands of valency vibrations of the C–Cl bond in comparison with the spectra of 4-chlorophthalic acid – monosodium salt suggests that the Cl atoms do not take part in coordination with the metal ion [17, 18].

The splitting of the absorption bands arising from the vibrations $\nu_{as(COO)}$ and $\nu_{s(COO)}$ ($\Delta\nu=\nu_{as}-\nu_s$) for complexes of Sm and Eu(III) 4-chlorophthalates (136 and 132 cm^{-1}) are smaller than for the sodium salt (152 cm^{-1}) suggesting a smaller degree of ionic bond character in these complexes compared to the sodium salt.

The bands of $\nu_{as(COO)}$ in the IR spectra of the prepared complexes Sm and Eu are shifted to lower frequencies and the bands of $\nu_{s(COO)}$ are only slightly shifted to higher frequencies (4–8 cm^{-1}) compared to corresponding bands for the sodium salt. Due to the spectroscopic criteria [19–21], the carboxylate groups in the studied complexes are probably bidentate bridging. Taking into account the structure of ligand it is possible to suggest that the complexes exist as polymers. In the complexes of La–Nd the carboxylate groups act probably as bidentate chelating and bridging and the negative charge of $[LnL_2]^-$ anion is neutralized by positive charge of Na^+ ion.

4-Chlorophthalates of light lanthanides are sparingly soluble in water. Their solubilities at 295 K are of the order 10^{-3}–10^{-2} mol dm^{-3} and change irregularly in the lanthanide series (Table 1). The complexes of La–Nd are less soluble than the complexes of Sm(III) and Eu(III). 4-Chlorophthalates of Sm(III) and Eu(III) are less soluble in water than corresponding 4-methylphthalates (10^{-2} mol dm^{-3}) [22] and more soluble than 4-nitrophthalates (10^{-4} mol dm^{-3}) [23]. On the basis of obtained results it is possible to state, that kind of a substituent in benzene ring of phthalic acid has influence on the change of electron density on the carbon atom of the COO^- group and causes a change of the structure and properties of rare earth 4-chlorophthalates compared to those of the corresponding 4-methyl- and 4-nitrophthalates.

The 4-chlorophthalate of light lanthanides are stable in air and can be stored for several months without change. During heating they decompose in different ways (Tables 2 and 3).

The anhydrous 4-chlorophthalates of La–Nd and Na are stable up to 562–608 K and next, in the temperature range 562–876 K, are decomposed with the strong exothermic effect to a mixture of lanthanide oxochlorides and sodium chloride (Fig. 1). Only

Table 1 Frequencies of characteristic absorption bands in IR spectra (cm^{-1}) and solubilities in water in 295 K of lanthanide 4-chlorophthalates

Complex	$\nu_{as(COO)}$	$\Delta\nu_{as}$*	$\nu_{s(COO)}$	$\Delta\nu_s$*	$\nu_{as}-\nu_s$	ν_{M-O}	Solubility/ mol dm$^{-3}\cdot10^{-3}$
$NaLaL_2$	1552/1524	–12/–40	1428	16	124/96	544	0.86
$NaCeL_2$	1552/1524	–12/–40	1428	16	124/96	544	0.86
$NaPrL_2$	1552/1524	–12/–40	1428	16	124/96	544	0.73
$NaNdL_2$	1552/1524	–12/–40	1428	16	124/96	544	0.86
$Sm_2L_3\cdot6H_2O$	1552	–12	1416	4	136	536	3.82
$Eu_2L_3\cdot6H_2O$	1552	–12	1420	8	132	536	3.59
Na_2L	1564		1412		152		

L – 4-ClC_6H_3-1,2-$(CO_2)_2^{2-}$; *Shifts of absorption bands $\nu_{as(COO)}$ and $\nu_{s(COO)}$ compared with bands of sodium 4-chlorophthalate

Table 2 Data for decomposition of $NaLnL_2$ complexes (Ln=La–Nd)

Complex	ΔT_1/K	Mass loss/%		Melting point of NaCl/K	ΔT_2/K	Mass loss/%		ΔT_3/K	Mass loss/%	
		calc.	found			calc.	found		calc.	found
$NaLaL_2$	608–865	55.49	55.0	1072	1100–1293	65.94	64.8	1293–1666	70.86	68.1
$NaCeL_2$	585–834	58.85	57.7	7069	–	–	–	1111–1380	69.28	66.0
$NaPrL_2$	585–876	55.30	55.5	1069	1096–1295	65.71	64.0	1295–1527	69.66	68.1
$NaNdL_2$	562–828	54.96	55.2	1072	1096–1275	65.32	65.7	1275–1451	70.19	70.0

L – 4-$ClC_6H_3(CO_2)_2^{2-}$; ΔT_1 – temperature range of decomposition to LnOCl+NaCl (CeO_2+NaCl); ΔT_2 – temperature range of decomposition to LnOCl (traces of NaCl);
ΔT_3 – temperature range of decomposition to oxides (Ln_2O_3, CeO_2, Pr_6O_{11}) (traces of NaCl)

Table 3 Data for dehydration and decomposition of Sm and Eu(III) complexes

Complex	ΔT_1/K	Mass loss/%		Loss of H_2O	ΔT_2/K	Mass loss/%		Loss of H_2O	ΔT_3/K	Mass loss/%		ΔT_4/K	Mass loss/%	
		calc.	found			calc.	found			calc.	found		calc.	found
$Sm_2L_3\cdot6H_2O$	315–453	7.17	7.3	4	453–654	10.76	11.0	6	654–845	59.81	60.0	1110–1456	65.29	65.2
$Eu_2L_3\cdot6H_2O$	308–475	7.15	7.0	4	475–619	10.72	10.4	6	619–797	59.62	59.8	902–1361	65.08	65.3

L – 4-$ClC_6H_3(CO_2)_2^{2-}$; ΔT_1 – temperature range of dehydration (1 stage); ΔT_2 – temperature range of dehydration (2 stage)
ΔT_3 – temperature range of decomposition to LnOCl; ΔT_4 – temperature range of decomposition to oxides

Ce(III) complex decomposes directly to the mixture of CeO_2 and NaCl (Fig. 2). The complexes of Ce(III) with other chloroorganic acids [24, 25] also decompose directly to CeO_2. The mixtures of oxochlorides and NaCl are stable between 876 and 1096 K (at about 1072 K the melting point of NaCl is observed) and next endothermically lose sodium chloride forming only LnOCl or CeO_2. The final products of decomposition are the oxides Ln_2O_3, CeO_2 and Pr_6O_{11}, which exist over 1380 (Ce)–1666 (La) K (Table 2). The oxides of La, Ce and Pr contain traces of NaCl.

The hexahydrated 4-chlorophthalates of Sm and Eu(III) are endothermically dehydrated over the range 308–654 K losing all crystallization water in two steps (first 4 and next 2 molecules) and decompose directly (with a strong exothermic effect) to LnOCl (Table 3). The formed oxochlorides are stable to 902–1110 K and next decompose to oxides Ln_2O_3 (Fig 3).

The low temperature of dehydration of 4 water molecules for Sm and Eu(III) 4-chlorophthalates indicates that this water molecules are, probably, in outer sphere and other 2 water molecules are in inner sphere of the complexes. According to Nikolaev *et al.* [26] and Singh *et al.* [27] water released below 423 K can be considered as water of crystallization, whereas water eliminated above 423 K is chemically bonded to central ions through coordination bond, but generally it is possible to say that temperature of dehydration is not connected directly with position of water molecules in inner or outer sphere [28, 29]. The results suggest the following schemes of the thermal decomposition of light lanthanide 4-chlorophthalates:

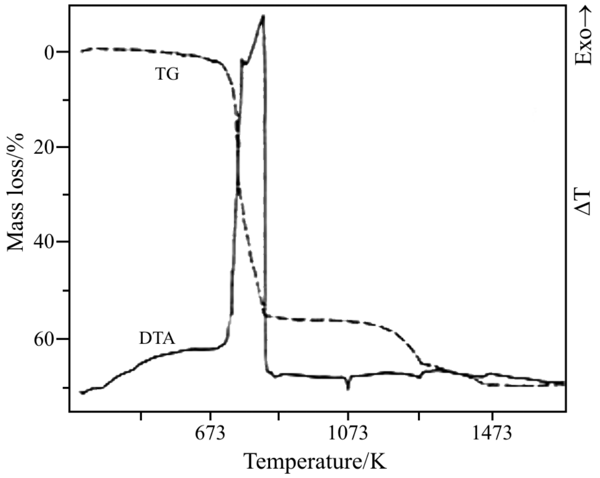

Fig. 1 TG and DTA curves of $Na[Nd(C_8H_3ClO_4)_2]$

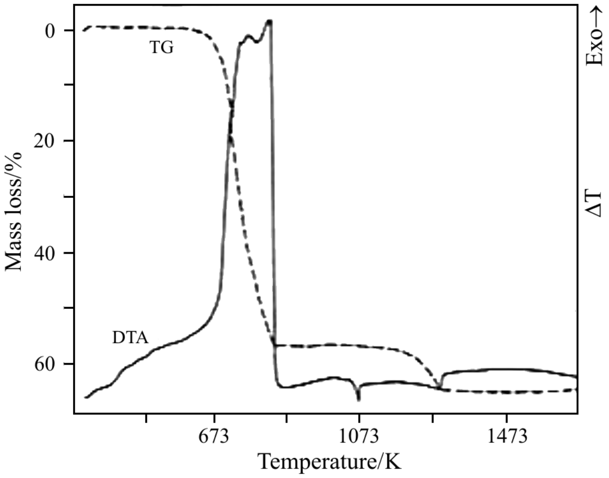

Fig. 2 TG and DTA curves of $Na[Ce(C_8H_3ClO_4)_2]$

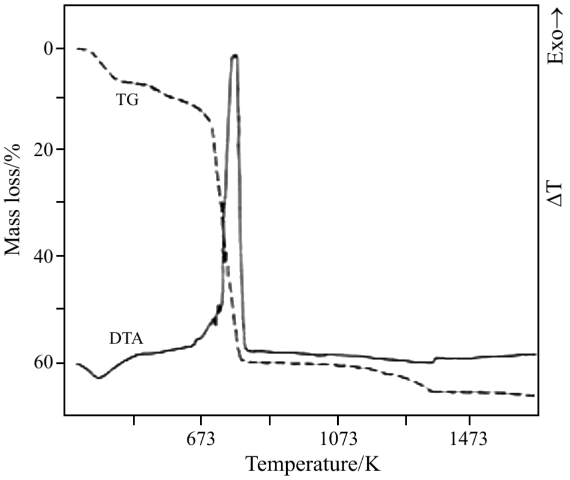

Fig. 3 TG and DTA curves of $Eu_2(C_8H_3ClO_4)_3{\cdot}6H_2O$

$$NaLnL_2 \rightarrow LnOCl+NaCl \rightarrow LnOCl \rightarrow Ln_2O_3,\ Pr_6O_{11}$$

Ln=La, Nd, Pr

$$NaCeL_2 \rightarrow CeO_2+NaCl \rightarrow CeO_2$$

$$Ln_2L_3{\cdot}6H_2O \rightarrow Ln_2L_3{\cdot}2H_2O \rightarrow Ln_2L_3 \rightarrow LnOCl \rightarrow Ln_2O_3$$

Ln=Sm, Eu

The temperature over which the oxides exist (without CeO_2 – 1380 K) are higher for the complexes of La–Nd (1451–1666 K) than for the complexes of Sm and Eu (1452, 1361 K). The temperature of oxides formation are higher for light lanthanides (1666–1361 K) than for heavy lanthanides (1359–1116 K) [7]. The hydrated 4-chlorophthalates of lanthanides are decomposed likewise the complexes with 4-chlorobenzoic acid [24].

Conclusions

4-Chlorophthalates of La–Nd(III) were prepared as anhydrous complexes with a 1:1:2 molar ratio of sodium to lanthanide and to organic ligand and general formula $NaLn[ClC_6H_3(COO)_2]_2$ whereas the compounds of Sm and Eu(III) were obtained as hexahydrates with a 2:3 molar ratio of metal to organic ligand with formula $Ln_2[ClC_6H_3(COO)_2]_3\cdot 6H_2O$ with colour characteristic for metal ion. The prepared complexes are crystalline solids of different structures (complexes of Ce–Nd(III) are iso-structural). The solubilities of the prepared complexes in water at 295 K are of the order 10^{-2} mol dm^{-3} for La–Nd(III) and 10^{-3} mol dm^{-3} for Sm, Eu(III). The COO groups in studied complexes act as bidentate bridging (Sm, Eu) or bidentate chelating and bridging (La–Nd). During heating all complexes decompose to oxides with intermediate formation of oxochlorides.

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