

SPECTRAL AND THERMAL STUDIES OF Y(III) AND HEAVY LANTHANIDE 4-CHLOROPHTHALATES

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Complexes of heavy lanthanide(III) (Gd–Lu) and Y(III) with 4-chlorophthalic acid were prepared and their IR spectra, solubility in water at 295 K and thermal decomposition were investigated. When heated the complexes with general formula $\text{Ln}_2[\text{ClC}_6\text{H}_3(\text{CO}_2)_2]_3 \cdot n\text{H}_2\text{O}$ where $n=6$ for Tb, Dy(III), $n=4$ for Gd, Ho and Er(III), $n=2$ for Tm–Lu(III) and $n=3$ for Y(III) decompose to the oxides Ln_2O_3 , Tb_4O_7 with intermediate formation of oxochlorides LnOCl .

Keywords: 4-chlorophthalic acid–monosodium salt, IR spectra, rare earth complexes, thermal analysis

Introduction

4-Chlorobenzene-1,2-dicarboxylic acid, $\text{ClC}_6\text{H}_3(\text{COOH})_2$, 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 [1, 2, 6] sparingly soluble in water. Monopotassium salt is less soluble than the monosodium salt [2]. The solid state complexes of 4-chlorophthalic acid with rare earth elements have not been studied so far.

This work is a continuation of our study on the physico-chemical properties and thermal decomposition [7–15] of metal complexes with benzene-carboxylic acids. Its aim was to prepare solid Y(III) and lanthanide(III) carboxylates and examine some their physicochemical properties and thermal decomposition during heating in static air.

The aim of the present work was to prepare 4-chlorophthalates of Y(III) and heavy lanthanides(III) (Gd–Lu) as solids under the same conditions and examine some of their physical and chemical properties.

Experimental

4-Chlorophthalates of heavy lanthanides from Gd(III) to Lu(III) and Y(III) were prepared by adding double molar excess of 0.2 M ammonium sodium 4-chlorophthalate (pH 4.7) to a hot solution of rare earth chlorides. Precipitates formed were heated for 10 h in the mother solution, 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 PerkinElmer CHN 2400 analyser. The contents of rare earth elements were 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 of the complexes at a specific temperature. The analytical data of the complexes were in a good agreement with the theoretical calculations.

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}).

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

The powder diffraction patterns of the prepared 4-chlorophthalates are registered on a HZG (Carl-Zeiss, Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the 2θ range 5–60° by the Debye–Scherrer method.

The thermal stability of the prepared 4-chlorophthalates were investigated by TG, DTG and DTA curves, using Setsys 16/18 thermal analyzer (Setaram) at a heating rate 10 K min^{-1} . Samples were heated in air in platinum crucibles to 1673 K using $\alpha\text{-Al}_2\text{O}_3$ as a standard.

Results and discussion

4-Chlorophthalates of Y and heavy lanthanides were prepared as crystalline solids with colour characteristic

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for lanthanide(III) ions. 4-Chlorophthalate of Gd(III)–Lu(III) and Y(III) were prepared as solid complexes with a 2:3 molar ratio of metal to organic ligand and with a general formula: $\text{Ln}_2[\text{ClC}_6\text{H}_3(\text{COO})_2]_3 \cdot n\text{H}_2\text{O}$ where $n=6$ for Tb and Dy(III), $n=4$ for Gd, Ho, Er(III), $n=2$ for Tm–Lu(III) and $n=3$ for Y(III).

The prepared complexes were crystalline solids of low symmetry and large size of unit cells (Fig. 1). They have different structures and different degrees of crystallinity. Only 4-chlorophthalates of Tm–Lu(III) are isostructural.

In order to confirm the composition of the prepared complexes and to determine the metal–ligand coordination mode, the IR spectra of 4-chlorophthalic acid–monosodium salt and prepared heavy lanthanide and Y(III) 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 weak band of C=O in the COOH group at 1685 cm^{-1} , the strong band of the stretching vibration of C–O in C–OH group at 1276 cm^{-1} , the absorption bands of the asymmetrical $\nu_{\text{as}}(\text{COO})$ and symmetrical $\nu_{\text{s}}(\text{COO})$ 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} .

In the IR spectra of hydrated 4-chlorophthalates there exists a broad valency absorption band of the OH group from H_2O at 3496 – 3400 cm^{-1} , which points to the presence of crystallization water molecules, the asymmetrical absorption bands of $\nu_{\text{as}}(\text{COO})$ at 1568 – 1536 cm^{-1} , symmetrical absorption bands of $\nu_{\text{s}}(\text{COO})$ at 1436 – 1416 cm^{-1} and the absorption bands of the metal–oxygen at 540 – 532 cm^{-1} (Table 1).

The $\nu(\text{M–O})$ values for all 4-chlorophthalates slightly differ to each other, what may suggest a similar

energy bond. 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 the IR spectra of all 4-chlorophthalates in comparison with the spectra of 4-chlorophthalic acid–monosodium salt suggests that the chlorine atom does not take part in coordination with the metal ion [16, 17].

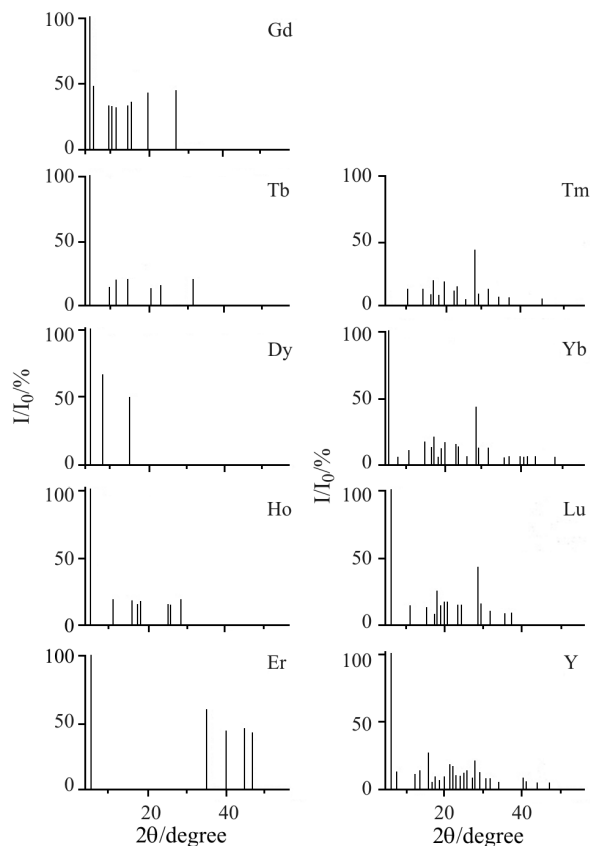


Fig. 1 Radiogram sheet of Gd–Lu(III) and Y(III) 4-chlorophthalates

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

Complex	$\nu_{\text{as}}(\text{COO})$	$\Delta\nu_{\text{as}}^*$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu_{\text{s}}^*$	$\nu_{\text{as}}-\nu_{\text{s}}$	$\nu(\text{M–O})$	Solubility/mol $\text{dm}^{-3} \cdot 10^{-3}$
Gd ₂ L ₃ ·4H ₂ O	1568	+4	1428	16	140	536	1.95
Tb ₂ L ₃ ·6H ₂ O	1552	–12	1420	8	132	532	4.90
Dy ₂ L ₃ ·6H ₂ O	1548	–16	1416	4	132	536	4.25
Ho ₂ L ₃ ·4H ₂ O	1568	+4	1428	16	140	540	5.20
Er ₂ L ₃ ·4H ₂ O	1548	–16	1420	8	128	540	7.85
Tm ₂ L ₃ ·2H ₂ O	1536	–28	1436	24	100	540	2.83
Yb ₂ L ₃ ·2H ₂ O	1536	–28	1436	24	100	540	2.98
Lu ₂ L ₃ ·2H ₂ O	1540	–24	1436	24	104	540	1.79
Y ₂ L ₃ ·3H ₂ O	1568	+4	1436	24	132	532	2.70
Na ₂ L	1564		1412		152		

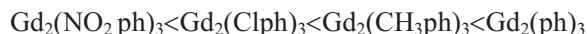
L – 4-ClC₆H₃-1,2-(CO₂)₂²⁻; * Shifts of absorption bands $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ compared with bands of sodium 4-chlorophthalate

The positions of absorption bands of aromatic ring vibrations in the IR spectra of heavy lanthanide 4-chlorophthalates are slightly shifted (8 cm^{-1}) in comparison with the spectra of disodium salt, what indicate that kind of metal ion has very little influence on the change of electron density in the aromatic ring [18].

The splitting of the absorption bands arising from the vibrations $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ ($\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$) are for complexes of Gd, Ho almost the same and for the 4-chlorophthalates of Tb, Dy, Er–Lu(III) and Y(III) a far smaller ($132\text{--}100\text{ cm}^{-1}$) 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 $\nu_{\text{as}}(\text{COO})$ in the IR spectra of the prepared complexes are shifted to lower frequencies ($\Delta\nu_{\text{as}} = 12\text{--}28\text{ cm}^{-1}$) (only for salts of Gd, Ho and Y do not almost change their position) and the bands of $\nu_{\text{s}}(\text{COO})$ are shifted to higher frequencies ($\Delta\nu_{\text{s}} = 4\text{--}24\text{ cm}^{-1}$) compared to corresponding bands for the sodium salt. Due to the spectroscopic criterion [19–21], the carboxylic group in the studied complexes is probably bidentate symmetrical chelating (only in the 4-chlorophthalates of Gd, Ho and Y(III) – bidentate asymmetrical chelating). The similar way of coordination of carboxylate groups is in 4-methylphthalates [22] and 4-nitrophthalates [23] of heavy lanthanide and Y(III).

4-Chlorophthalates of yttrium and heavy lanthanides are sparingly soluble in water. Their solubilities at 295 K are of the order $10^{-3}\text{ mol dm}^{-3}$ and change irregularly in the lanthanide series (Table 1). The best soluble is 4-chlorophthalate of Er(III) and the least soluble are complexes of Lu(III) and Gd(III). 4-chlorophthalates of Gd(III)–Lu(III) and Y(III) are less soluble in water than the corresponding 4-methylphthalates ($10^{-2}\text{ mol dm}^{-3}$) [22] and more soluble (without salts of Yb and Lu) than 4-nitrophthalates ($10^{-4}\text{ mol dm}^{-3}$) [23] and likewise soluble than phthalates ($10^{-3}\text{ mol dm}^{-3}$) [24]. The solubility of 4-Rphthalates (where $R = \text{CH}_3, \text{Cl}, \text{NO}_2$) complexes, for example, for Gd salts increases in the order:



On the basis of the obtained results it is possible to suggest that kind of the substituent in benzene ring of phthalic (ph) acid have influence on the change of electron density on the carbon atom of the COO^- group and causes a change in the structure and properties of rare earth 4-chlorophthalates as compared to those of the corresponding 4-methyl- and 4-nitrophthalates.

The 4-chlorophthalate of rare earth elements are stable in air and can be stored for several months without change. During heating the hydrated complexes decompose in various ways (Table 2).

The hexahydrated 4-chlorophthalates of Tb and Dy(III) are endothermically dehydrated in two steps over the temperature range of 303–632 K losing all crystallization water molecules (first 4 and next 2 molecules) and decompose directly (with the strong exothermic effect) to LnOCl . The forming oxochlorides are stable up to 920–1110 K and next decompose to oxides Ln_2O_3 , Tb_4O_7 (Fig. 2).

The tetrahydrated complexes of Gd and Ho(III) lose endothermically 3 water molecules (over the temperature range of 301–470 K) transforming into monohydrate compounds stable up to 621 and 660 K, respectively, and next decompose to Ln_2O_3 with intermediate formation oxochlorides (stable at 849–960 K) (Fig. 3).

The tetrahydrate 4-chlorophthalate of Er(III) decomposes otherwise. During heating loses 4 water molecules in two steps (first 3 and next 1 molecule) and next decomposes (through ErOCl) to Er_2O_3 (Fig. 4).

The dihydrated complexes of Tm–Lu(III), stable up to 437–451 K, are dehydrated endothermically in one step over the temperature range of 437–542 K forming anhydrous 4-chlorophthalates, stable to 641–681 K and then they decompose (with strong exothermic effect) to oxochlorides and finally to oxides Ln_2O_3 (Fig. 5).

Trihydrated complex of Y(III) lose the crystallization water over the range 349–462 K transforming into anhydrous salt stable at 462–626 K and next decomposes to YOCl stable at 840–918 K. The finally product of decomposition is Y_2O_3 (Fig. 6).

The different way of decomposition process points to the different way of bonding of water molecules. The low temperature of dehydration of yttrium 4-chlorophthalate indicates that the crystallization water is probably outer sphere water. In the complexes of Tm–Lu(III) there exists, probably, inner sphere water molecules only, whereas in the other hydrated complexes there act

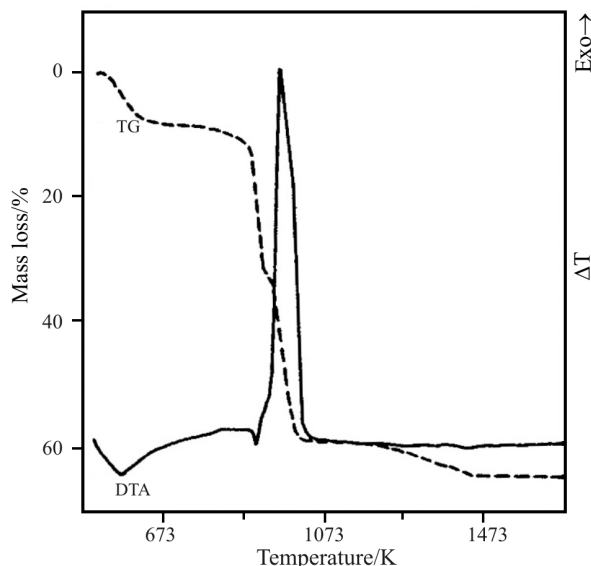


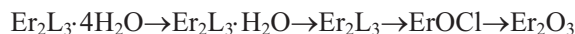
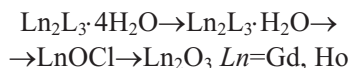
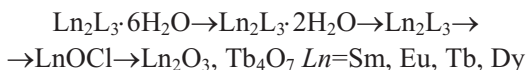
Fig. 2 TG and DTA curves of $\text{Dy}_2(\text{C}_8\text{H}_3\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$

Table 2 Data for dehydration and decomposition of 4-chlorophthalates of Gd–Lu and Y(III)

Complex	$\Delta T_1/K$	Mass loss/%		Loss of H ₂ O	$\Delta T_2/K$	Mass loss/%		Loss of H ₂ O	$\Delta T_3/K$	Mass loss/%		$\Delta T_4/K$	Mass loss/%	
		calc.	found			calc.	found			calc.	found		calc.	found
Gd ₂ L ₃ :4H ₂ O	301–470	5.50	5.6	3	–	–	–	–	621–801	57.49	56.8	1030–1359	63.10	62.9
Tb ₂ L ₃ :6H ₂ O	303–461	7.05	6.9	4	461–632	10.58	10.2	6	632–801	58.81	58.8	980–1214	63.41	64.0
Dy ₂ L ₃ :6H ₂ O	308–463	7.00	7.3	4	463–632	10.50	10.0	6	632–819	58.40	58.8	994–1245	63.75	63.9
Ho ₂ L ₃ :4H ₂ O	304–460	5.42	5.6	3	–	–	–	–	660–877	56.61	56.9	960–1186	62.12	61.9
Er ₂ L ₃ :4H ₂ O	313–464	5.39	5.4	3	464–623	7.19	7.2	4	623–867	56.36	56.8	867–1188	61.82	62.1
Tm ₂ L ₃ :2H ₂ O	–	–	–	–	438–537	3.71	3.5	2	681–852	54.53	54.4	852–1116	60.20	59.7
Yb ₂ L ₃ :2H ₂ O	–	–	–	–	451–533	3.68	3.7	2	671–845	54.07	54.5	845–1132	59.70	59.5
Lu ₂ L ₃ :2H ₂ O	–	–	–	–	437–542	3.67	3.7	2	641–880	53.86	53.9	880–1188	59.46	59.5
Y ₂ L ₃ :3H ₂ O	349–462	6.53	6.2	3	–	–	–	–	626–840	66.07	66.3	918–1232	72.71	72.8

L – 4-ClC₆H₃(CO₂)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

inner and outer sphere water molecules. The results suggest the following schemes of the thermal decomposition of rare earth elements 4-chlorophthalates:



The temperatures of dehydration (T_0) (Fig. 7) of 4-chlorophthalates of Gd–Er(III) (301–313 K) are lower than for Tm–Lu(III) (438–451 K) like the temperatures

of decomposition of anhydrous complexes (T_d) (632, 641–681, respectively). The temperatures of LnOCl formation (T) are lower for complexes of Gd–Dy(III) (801–819 K) than for Ho–Lu(III) (845–880 K), whereas the temperatures of the end of the decomposition (T_K) change irregularly in the heavy lanthanide series.

The temperature of formation of Y_2O_3 (1232 K) is similar to that of Dy_2O_3 formation, which can be explained by the similarity of ionic radii.

The temperatures of decomposition of the anhydrous 4-chlorophthalates of heavy lanthanides are higher and the temperatures of oxides formation are lower than those of the 4-methylphthalate [22]. 4-Nitrophthalates decompose explosively [23].

The hydrated 4-chlorophthalates of rare earth elements decompose likewise the complexes with 4-chlorobenzoic acid, with intermediate formation

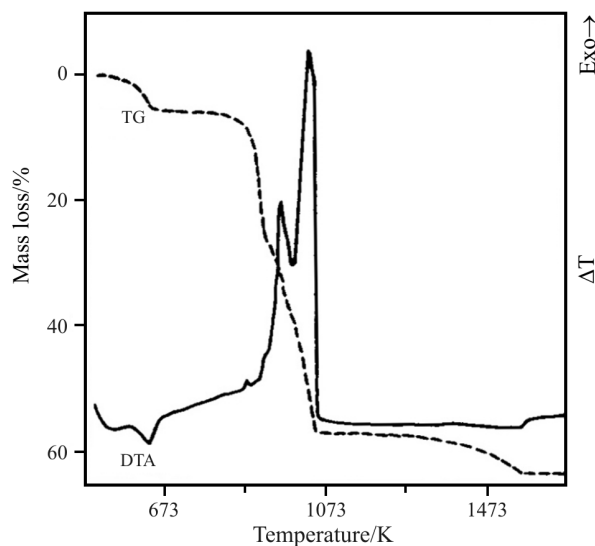


Fig. 3 TG and DTA curves of $\text{Gd}_2(\text{C}_8\text{H}_3\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$

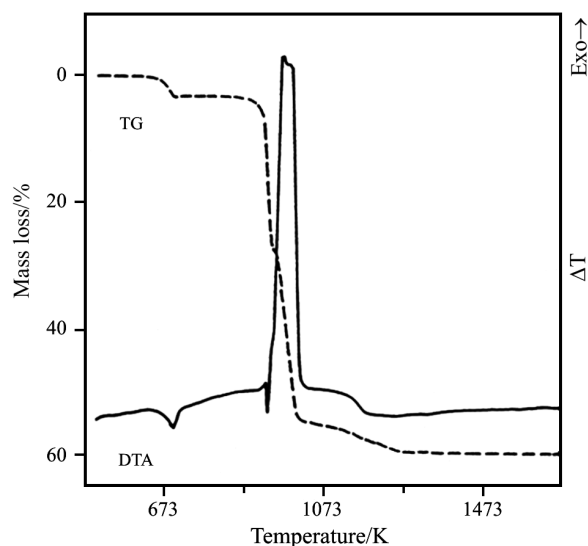


Fig. 5 TG and DTA curves of $\text{Yb}_2(\text{C}_8\text{H}_3\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$

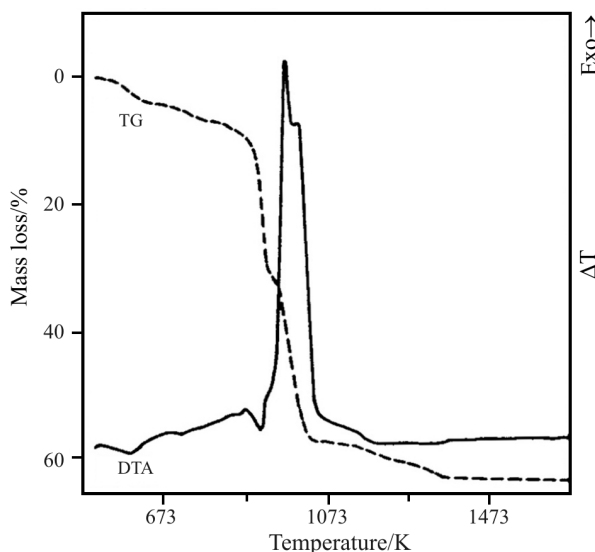


Fig. 4 TG and DTA curves of $\text{Er}_2(\text{C}_8\text{H}_3\text{ClO}_4)_3 \cdot 4\text{H}_2\text{O}$

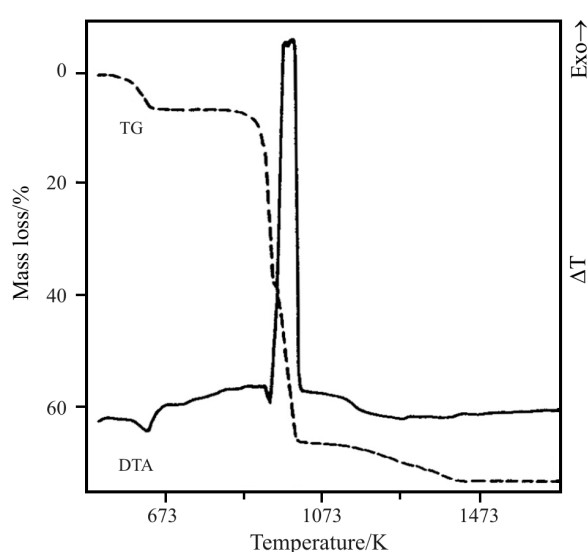


Fig. 6 TG and DTA curves of $\text{Y}_2(\text{C}_8\text{H}_3\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

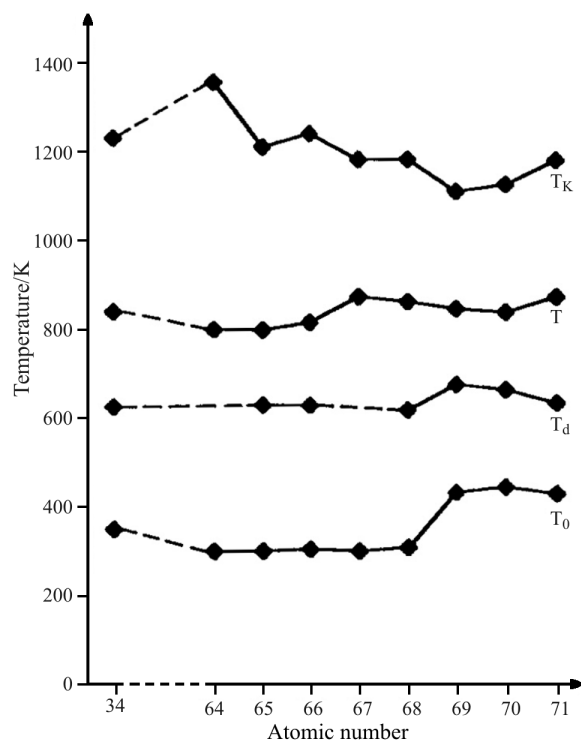


Fig. 7 Relationship between T_0 , T_d , T , T_{κ} and the atomic number of the metal

oxochlorides, but the temperatures of LnOCl and oxides formation are lower for complexes of 4-chlorophthalates than for 4-chlorobenzoates [25].

Conclusions

4-Chlorophthalates of heavy lanthanides(III) (Gd–Lu) and Y(III) were prepared as hydrates with molar ratio of metal to organic ligand 2:3 and general formula $\text{Ln}_2[\text{ClC}_6\text{H}_3(\text{CO})_2]_3 \cdot n\text{H}_2\text{O}$ where $n=6$ for Tb, Dy(III), $n=4$ for Gd, Ho and Er(III), $n=2$ for Tm–Lu(III) and $n=3$ for Y(III) with colour characteristic for metal ion. The prepared complexes are crystalline solids of different structures (complexes of Tm–Lu(III) are isostructural). The solubilities of the prepared complexes in water at 295 K are of the order $10^{-3} \text{ mol dm}^{-3}$. The carboxylate groups in studied complexes act as bidentate chelating. The hydrate complexes are stable in air at room temperature. During heating they decompose in different ways. They are dehydrated in one (Gd, Ho, Tm–Lu, Y) or two (Tb, Dy, Er) steps forming anhydrous or monohydrate (Gd, Ho) compounds and next decompose to oxides with intermediate formation of oxochlorides.

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Received: January 10, 2005

In revised form: April 14, 2005

DOI: 10.1007/s10973-005-6871-9