

SPECTROSCOPIC AND THERMAL STUDIES OF RARE EARTH ELEMENT 4-METHYLPHTHALATES

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Abstract

Complexes of lanthanide(III) (La–Lu) and Y(III) with 4-methylphthalic acid were prepared and their IR spectra, solubility in water at 295 K and thermal decomposition were investigated. Rare earth complexes were obtained as solids with a 2:3 ratio of metal to organic ligand. COO[−] groups in the prepared complexes act as bidentate chelating and bidentate bridging. During heating they are dehydrated in one (La–Tm) or two steps (Yb, Lu and Y) and then decompose to the oxides Ln₂O₃, CeO₂, Pr₆O₁₁ and Tb₄O₇.

Keywords: IR spectra, 4-methylphthalic acid, rare earth complexes, thermal analysis

Introduction

4-Methylbenzene-1,2-dicarboxylic acid CH₃C₆H₃(COOH)₂, known as 4-methylphthalic acid is a white crystalline solid soluble in water (especially in hot water), ethanol, ethyl acetate and acetone and insoluble in benzene and CHCl₃ [1]. The solid-state complexes of 4-methylphthalic acid, also with rare earth elements have not been studied so far. Nair and Parthasarathy [2, 3] have determined the dissociation constants and the thermodynamic stability constants of the 1:1 complexes of some bivalent transition metal ions (Cu, Cd, Mn, Co, Ni and Zn) with 4-methylphthalic acid by a potentiometric method.

The aim of the present work was to prepare 4-methylphthalates of rare earth (Y, La–Lu, without Pm) as solids under the same conditions and to examine some of their physical and chemical properties.

Experimental

4-Methylphthalates of Y(III) and lanthanides(III) were prepared by dissolving freshly precipitated lanthanide carbonates in a 0.1 M solution of 4-methylphthalic acid. The excess of carbonates was filtered off and the 4-methylphthalate solutions

(pH 4.5–4.7) were crystallized at room temperature. The precipitates formed were filtered off, washed with water and dried at 303 K to constant mass.

The contents of carbon and hydrogen in the prepared complexes were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The content of rare earth elements was determined by the gravimetric method by transforming the complexes into oxides *via* oxalates. The content of crystallization water was determined from the TG curves by heating the samples at a set temperature.

Solubility of the prepared complexes in water at 295 K under isothermal conditions was determined spectrophotometrically using a Specord M-40 spectrophotometer, with arsenazo III.

The IR spectra of 4-methylphthalic acid, its rare earth complexes and sodium salt were recorded over the range 4000–400 cm^{-1} using a SPECORD M-80 spectrophotometer. Samples were prepared as KBr discs.

The thermal stability of the prepared 4-methylphthalates was determined using Q-1500D derivatograph at a heating range of 10°C min^{-1} . Samples (100 mg) were heated in air in platinum crucibles to 1273 K with the sensitivity TG – 100 mg, sensitivity of DTG and DTA was regulated by MOM Derill computer program. Al_2O_3 was used as a standard.

Results and discussion

4-Methylphthalates of rare earth elements (Y, La–Lu) were prepared as solids with colour characteristic for lanthanide(III) ions and as complexes with a 2:3 molar ratio of metal to organic ligand, with a general formula: $\text{Ln}_2[\text{CH}_3\text{C}_6\text{H}_3(\text{COO})_2]_3 \cdot n\text{H}_2\text{O}$, where $n=4$ for La–Gd(III); $n=6$ for Tb–Tm(III); $n=7$ for Y(III) and Lu(III) and $n=8$ for Yb(III) (Table 1).

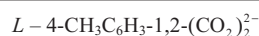
Solubility of Y(III) and lanthanide 4-methylphthalates in water at 295 K were determined (Table 1). They are of the order 10^{-2} – 10^{-3} mol dm^{-3} . Light lanthanide 4-methylphthalates are less soluble than the heavy lanthanide 4-methylphthalates. Lutetium 4-methylphthalate is the least soluble ($0.59 \cdot 10^{-2}$ mol dm^{-3}), whereas that of yttrium(III) is the best soluble one ($3.4 \cdot 10^{-2}$ mol dm^{-3}). The solubility of the prepared complexes changes with the increasing atomic number of lanthanide according the double–double effect [4]. 4-Methylphthalates of Y(III) and lanthanides are likewise soluble in water as the corresponding phthalates (10^{-3} mol dm^{-3}) [5] and more soluble than the 4-nitrophthalates (10^{-3} – 10^{-4} mol dm^{-3}) [6]. On the basis of obtained results it is possible to state that CH_3 group in benzene ring of phthalic acid (on the contrary to NO_2 group) does not influence on the change of electron density on the carbon atom in the COO^- group and its polarity.

The IR spectra of the complexes are similar to each other in the groups La(III)–Gd(III) and Tb(III)–Lu(III), suggesting different structures in the separate groups. In the IR spectra of free 4-methylphthalic acid there exists a strong absorption band of the C=O in the COOH group at 1692 cm^{-1} and the band of the stretching vibration of C–O in C–OH group at 1288 cm^{-1} . In the IR spectra of the complexes prepared, the

band of COOH group disappears and the bands of asymmetrical vibrations ν_{as} of COO^- at 1548–1532 cm^{-1} appear further on symmetrical vibrations ν_s of COO^- at 1428–1408 cm^{-1} (Table 2). There appear also absorption band of the OH group of the water stretching vibration with a maximum at 3432–3392 cm^{-1} and the absorption bands of the Ln–O bond at 440–426 cm^{-1} . The $\nu(\text{M–O})$ value for Yb, Lu and light lanthanides complexes is much lower than that for 4-methylphthalates of Tb–Tm and Y(III), what may suggest a different energy bond and different thermal stability [7]. The vibration of M–O are not pure ones, on account of conjugation of the C–O, M–O and C–C group vibrations, and therefore such results must be interpreted with great caution. The separation value, $\nu_{as}-\nu_s$, of the COO^- groups and the direction of the shift of these bands, when compared to sodium salt, may suggest, that organic ligand occurs as bidentate ligand in the investigated complexes [8, 9].

Table 1 Analytical data of rare earth 4-methylphthalates and solubility in water at 295 K

Complex	C/%		H/%		M/%		Solubility/ $\text{mol dm}^{-3} \cdot 10^{-2}$
	calc.	found	calc.	found	calc.	found	
$\text{La}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	36.67	36.1	2.96	2.9	31.42	31.3	0.79
$\text{Ce}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	36.57	37.0	2.95	2.8	31.60	31.0	0.76
$\text{Pr}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	36.51	36.7	2.95	2.9	31.72	31.6	0.87
$\text{Nd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	36.23	36.7	2.93	2.9	32.23	32.0	0.94
$\text{Sm}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	35.75	35.8	2.89	2.9	33.15	33.2	1.06
$\text{Eu}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	35.62	36.2	2.88	2.9	33.38	33.6	0.92
$\text{Gd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	35.21	35.0	2.85	2.8	34.15	34.1	0.26
$\text{Tb}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	33.77	33.9	3.15	2.9	33.10	33.4	0.85
$\text{Dy}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	33.52	34.1	2.92	2.9	33.59	33.9	1.17
$\text{Ho}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	33.35	33.0	3.11	2.9	33.92	33.5	1.13
$\text{Er}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	33.19	33.3	3.09	2.9	34.24	34.1	1.43
$\text{Tm}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	33.05	33.1	3.08	3.0	35.52	34.2	1.48
$\text{Yb}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	31.65	31.5	3.34	3.2	33.77	33.4	2.32
$\text{Lu}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	32.09	32.4	3.19	2.9	34.63	34.6	0.59
$\text{Y}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	38.68	39.0	3.84	3.7	21.21	21.2	3.37



The bands of asymmetrical vibrations $\nu_{as}\text{COO}^-$ of the light lanthanide complexes with 4-methylphthalic acid are shifted to lower frequencies and the bands of symmetrical vibrations $\nu_s\text{COO}^-$ do not change their position compared with the absorption band of the sodium salts. The splitting of these bands indicates that the carboxylate groups in the complex coordinate the metal ion in a different way, as bidentate chelating and bidentate bridging ligands, similarly as in the other rare earth complexes (for example 4-aminobenzoates) [10, 11]. Taking into account the high coordination number of lanthanide ion, it may be suggested, that in the studied complexes, some of water molecules are in the inner sphere.

The bands of asymmetrical vibrations $\nu_{as}\text{COO}^-$ of the Y(III) and heavy lanthanide complexes with 4-methylphthalic acid are shifted to lower frequencies and the bands of symmetrical vibrations $\nu_s\text{COO}^-$ of higher ones compared with the absorption bands of the sodium salt, which suggests, according to the spectroscopic cri-

terion [8, 9], that the carboxylate group is probably bidentate chelating. Usually, lanthanide ions are characterised by a high coordination number ($C.N.=9$ or 8), indicating that molecules of water can also be coordinated.

Table 2 Frequencies of the absorption bands of asymmetrical and symmetrical vibrations of the COO^- groups and metal–oxygen bond in lanthanide 4-methylphthalates (cm^{-1})

Complex	$\nu_{\text{as}}(\text{COO})^-$	$\Delta\nu_{\text{as}}^*$	$\nu_{\text{s}}(\text{COO})^-$	$\Delta\nu_{\text{s}}^*$	$\nu_{\text{as}}-\nu_{\text{s}}$	$\nu(\text{M}-\text{O})$
Na_2L	1552		1408		144	
$\text{La}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1536	-16	1408	0	128	416
$\text{Ce}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1536	-16	1408	0	128	416
$\text{Pr}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1536	-16	1408	0	128	424
$\text{Nd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1536	-16	1408	0	128	424
$\text{Sm}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1532	-20	1408	0	124	424
$\text{Eu}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1536	-16	1408	0	128	424
$\text{Gd}_2\text{L}_3 \cdot 4\text{H}_2\text{O}$	1532	-20	1408	0	124	424
$\text{Tb}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	1540	-12	1416	8	124	440
$\text{Dy}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	1536	-16	1412	4	124	440
$\text{Ho}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	1544	-8	1412	4	132	440
$\text{Er}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	1536	-16	1416	8	120	440
$\text{Tm}_2\text{L}_3 \cdot 6\text{H}_2\text{O}$	1548	-4	1420	12	128	440
$\text{Yb}_2\text{L}_3 \cdot 8\text{H}_2\text{O}$	1548	-4	1420	12	128	424
$\text{Lu}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	1536	-16	1424	16	112	424
$\text{Y}_2\text{L}_3 \cdot 7\text{H}_2\text{O}$	1536	-16	1428	20	108	436

$L = 4\text{-CH}_3\text{C}_6\text{H}_3\text{-1,2-(CO}_2\text{)}_2^{2-}$

*Shifts of absorption bands $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ compared with bands of sodium 4-methylphthalate

4-Methylphthalates of lanthanides are stable in air up to 313–358 K and can be stored for several months without change. The complexes decompose in various ways during heating (Table 3, Figs 1 and 2). The tetrahydrated complexes of La–Gd(III) are endothermically dehydrated in one step over the range 318–483 K, forming anhydrous compounds stable to 483–608 K and then decompose (with the strong exothermic effect) to oxides Ln_2O_3 , CeO_2 and Pr_6O_{11} (Fig. 1). The hexahydrated complexes of Tb–Tm(III) are dehydrated in one step, too, but the temperatures of dehydration of these complexes are higher (348–583 K) than the temperatures of dehydration of 4-methylphthalates of light lanthanides and after the dehydration these complexes decompose directly to oxides Ln_2O_3 and Tb_4O_7 . The octahydrated complex of Yb(III) and heptahydrated complexes of Lu(III) and Y(III) dehydrated in two steps within the range of 313–643 K losing all crystallization water molecules and decompose directly to oxides Ln_2O_3 (Fig. 2).

The different way of the decomposition process points to the different way of bonding of water molecules. The low temperature of dehydration of light lanthanide 4-methylphthalates indicates that the crystallization water is, probably, outer sphere water. In the complexes of Tb(III)–Tm(III) there exists, probably, inner sphere water molecules only, whereas in the complexes of Yb(III), Lu(III) and Y(III) there act inner and outer sphere water molecules. The anhydrous complexes of 4-methylphthalates of Y(III) and heavy lanthanide are unstable, in opposition to anhydrous

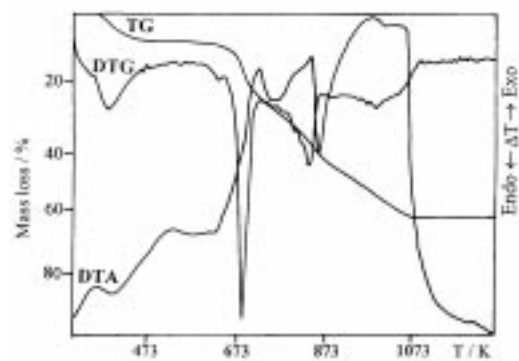


Fig. 1 TG, DTG and DTA curves of $\text{Nd}_2(\text{C}_9\text{H}_6\text{O}_4)_3 \cdot 4\text{H}_2\text{O}$

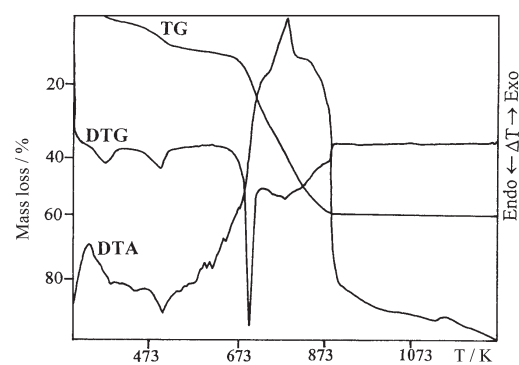


Fig. 2 TG, DTG and DTA curves of $\text{Lu}_2(\text{C}_9\text{H}_6\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$

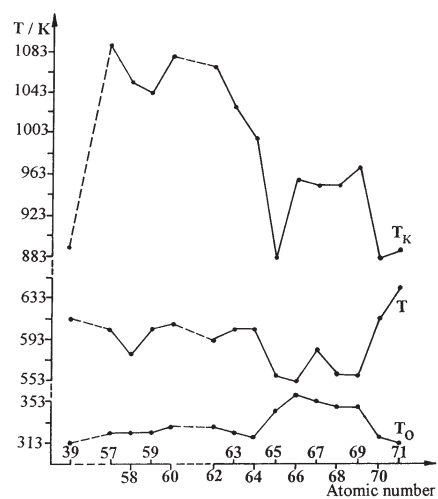


Fig. 3 Relationship between T_0 , T , T_K and the atomic number of the metal

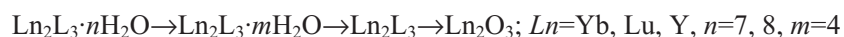
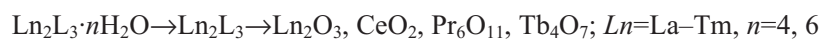
Table 3 Thermal data of dehydration and decomposition of yttrium and lanthanide 4-methylphthalates in an air atmosphere

Complex	Temperature range of dehydration/K	Mass loss/%		Loss of H ₂ O/n	Temperature range of decomposition/K	Mass loss/%		T _K /K
		calc.	found			calc.	found	
La ₂ L ₃ ·4H ₂ O	323–483	8.15	8.0	4	603–1088	63.16	63.3	1088
Ce ₂ L ₃ ·4H ₂ O	323–483	8.13	8.3	4	578–1053	61.18	61.2	1053
Pr ₂ L ₃ ·4H ₂ O	323–483	8.11	8.1	4	603–1043	61.66	62.0	1043
Nd ₂ L ₃ ·4H ₂ O	328–483	8.05	8.0	4	608–1078	62.40	62.6	1078
Sm ₂ L ₃ ·4H ₂ O	328–478	7.94	8.0	4	593–1068	61.56	61.5	1068
Eu ₂ L ₃ ·4H ₂ O	323–483	7.91	8.0	4	603–1028	61.34	61.1	1028
Gd ₂ L ₃ ·4H ₂ O	318–483	7.82	8.0	4	603–998	60.64	60.6	998
Tb ₂ L ₃ ·6H ₂ O	343–558	11.25	11.3	6	558–883	61.07	61.0	883
Dy ₂ L ₃ ·6H ₂ O	358–553	11.17	11.0	6	553–958	61.45	61.3	958
Ho ₂ L ₃ ·6H ₂ O	353–583	11.11	11.0	6	583–953	61.14	61.3	953
Er ₂ L ₃ ·6H ₂ O	348–558	11.06	11.0	6	558–953	60.85	61.0	953
Tm ₂ L ₃ ·6H ₂ O	348–583	11.02	11.0	6	558–968	60.68	61.2	968
Yb ₂ L ₃ ·8H ₂ O	318–613	14.06	14.0	8	613–883	61.54	61.6	883
Lu ₂ L ₃ ·7H ₂ O	313–643	12.48	12.3	7	643–888	60.62	60.7	888
Y ₂ L ₃ ·7H ₂ O	313–613	15.04	15.0	7	613–893	73.06	73.0	893

L – 4-CH₃C₆H₃(CO₂)₂²⁻

T_K – temperature of the end of the decomposition

compounds of light lanthanide with 4-methylphthalic acid. The results suggest the following scheme of the thermal decomposition of rare earth 4-methylphthalates:



The temperatures of dehydration (T_0) (Fig. 3) of 4-methylphthalates of light lanthanide and Yb(III), Lu(III) and Y(III) are lower than for heavy lanthanides (343–358 K), whereas the value of temperatures of decomposition (T) of anhydrous complexes are inverted: lower for heavy lanthanide complexes (553–558 K) and higher for 4-methylphthalates of light lanthanide and Yb(III), Lu(III) and Y(III) (578–643 K). The temperature of the end of the decomposition (T_k) are higher for light lanthanides (998–1088 K), than for the heavy lanthanides (883–968 K) (Fig. 3). The temperature of the end of the decomposition of Y-complex (893 K) is similar to that of heavy lanthanide oxide formation, which can be explained by the similarity of ionic radii.

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