Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 957–964

PREPARATION, SPECTRAL AND THERMAL STUDIES OF Y(III) AND LANTHANIDE(III) 1-HYDROXY-2-NAPHTHOATES

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(Received December 11, 2001)

Abstract

Complexes of lanthanide(III) (La–Lu) and Y(III) with 1-hydroxy-2-naphthoic acid were obtained as crystalline compounds with a general formula $Ln[C_{10}H_6(OH)COO]_3 \cdot nH_2O$: n=6 for La–Tm and Y, n=2 for Yb and n=0 for Lu. IR spectra of the prepared complexes were recorded, and their thermal decomposition in air were investigated. Spectroscopic data suggest that in the coordination of metal-organic ligand only oxygen atoms from the carboxylate group take part. When heated, the complexes decompose to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 with intermediate formation of $Ln(C_{11}H_7O_3)(C_{11}H_6O_3)$.

Keywords: complexes, 1-hydroxy-2-naphthoates, IR spectra, lanthanides, synthesis, thermal analysis

Introduction

Solid complexes of rare earth elements with hydroxynaphthoic acids are not too well known. The studies concern only the complexes of some rare elements. Solid Y, La, Pr, Nd and Sm 1-hydroxy-2-naphthoates with general formula $M(C_{11}H_7O_3)_2Cl \cdot H_2O$; $M(C_{11}H_7O_3)_2(OH) \cdot 2H_2O$ and $Ce(IV)(C_{11}H_7O_3)_2(NO_3)_2 \cdot H_2O$ were prepared [1–2] and IR and UV spectra of the (OH) compounds obtained are shown [3]. In all complexes there is an indication of an O–M dative bond from the OH group of the acid. The preparation and structure of $(\mu\text{-L})_4[Nd(H_2O)(EtOH)L]_2 \cdot 2H_2O \cdot 2EtOH$, ($L$ is 1-hydroxynaphthoate ligand) are reported [4], where two ligands act as bidentates and the two other as terdentates.

The aim of the present work was to prepare the complexes of lanthanides(III) and Y(III) with 1-hydroxy-2-naphthoic acid as solids and to study their properties as well as the problem of metal-ligand coordination and to examine the influence of the OH group in naphthalene ring on the properties of the complexes.

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

1-Hydroxy-2-naphthoates Y(III) and lanthanides(III) from La(III) to Lu(III) were prepared by addition of equivalent quantities of 0.2 M ammonium 1-hydroxy-2-naphthoate (pH 4.8–5.2) to a solution of rare earth chlorides (Ce(III) was used as its nitrate) at 323 K. 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 water crystallisation was determined from TG curve and by isothermal heating of the complexes at a specified temperature. The analytical data of the complexes were in a good agreement with the theoretical calculations.

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 $2\theta=5–60°$ by the Debye-Scherrer method.

The solubility of the complexes in water at 293 K under isothermal conditions was determined spectrophotometrically using a Specord M-40 spectrophotometer, using arsenazo III.

IR spectra of 1-hydroxy-2-naphthoic 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 and the solid product of their decomposition were studied in air. TG, DTG and DTA curves were recorded by a Q 1500 D derivatograph with a Derill converter. Measurements were made at a sensitivity of 100 mg (TG). The sensitivity of DTG and DTA was regulated by the Derill computer programme. The samples (100 mg) were heated in platinum crucibles to 1273 K in a static air at a heating rate of 10 K min^{-1} with a full scale. Moreover, the process of dehydration was studied using Setsys 16/18 (Setaram) derivatograph; samples were heated to 573 K at a heating rate of 2.5 K min^{-1}.

Table 1 Solubility of Y(III) and lanthanide(III) 1-hydroxy-2-naphthoates in water at 293 K

Complex	Solubility/mol $dm^{-3}\cdot 10^{-4}$	Complex	Solubility/mol $dm^{-3}\cdot 10^{-4}$
$LaL_3^a\cdot 6H_2O$	2.81	$DyL_3\cdot 6H_2O$	6.03
$CeL_3\cdot 6H_2O$	1.93	$HoL_3\cdot 6H_2O$	5.58
$PrL_3\cdot 6H_2O$	2.56	$ErL_3\cdot 6H_2O$	5.68
$NdL_3\cdot 6H_2O$	3.40	$TmL_3\cdot 6H_2O$	6.80
$SmL_3\cdot 6H_2O$	3.00	$YbL_3\cdot 6H_2O$	4.40
$EuL_3\cdot 6H_2O$	3.03	LuL_3	3.08
$GdL_3\cdot 6H_2O$	3.18	$YL_3\cdot 6H_2O$	5.17
$TbL_3\cdot 6H_2O$	3.71		

$L^a=[C_{11}H_7O_3]^-$

Results and discussion

1-Hydroxy-2-naphthoates of lanthanides(III) from La(III) to Lu(III) and Y(III) were obtained as crystalline compounds of grey-beige colour, with a molar ratio of metal to organic ligand 1:3 and a general formula $Ln[C_{10}H_6(OH)COO]_3{\cdot}nH_2O$.Complexes of lanthanides(III) from La(III) to Tm(III) and Y(III) are found as hexahydrated and isostructural with low symmetry and they are characterised by large sizes cells. Complex of Yb(III) was found as dihydrated and Lu(III) as anhydrous one; their crystal structure are different from another. X-ray data of the complexes obtained will be published [5]. The complexes are sparingly soluble in water. Their solubility ranges from $1.93{\cdot}10^{-4}$ to $6.80{\cdot}10^{-4}$ mol dm^{-3} and changes periodically in the lanthanide series; it increases from La(III) to Tm(III) and decreases to Lu(III) (Table 1).

In order to examine the way of bonding between the ligand and lanthanide ion, the IR spectra of 1-hydroxy-2-naphthoic acid, sodium salt and lanthanide complexes of the acid were recorded and they are presented in Table 2. IR spectral data for ligand, sodium and lanthanide compounds have been interpreted on the basis of the previously reported data of hydroxycarboxylic, carboxylic and naphthoic complexes [6–17]. In the IR spectrum of the free 1-hydroxy-2-naphthoic acid there is a sharp absorption band of carboxylic group –COOH at 1632 cm^{-1}, absorption bands of δ(OH) at 1452 and at 792 cm^{-1} as well as ν(C–OH) at 1256 cm^{-1}. In the IR spectra of complexes obtained symmetric absorption bands of $\nu_s(OCO^-)$ at 1444–1440 cm^{-1} can be observed. The symmetric absorption bands are insignificantly shifted (about 4–2 cm^{-1}) or have not changed their position (for La–Eu) in comparison with sodium salt. The asymmetric vibration bands $\nu_{as}(OCO^-)$ of the hexahydrated complexes studied are split, forming a double band at 1564–1562 cm^{-1}and 1554–1552 cm^{-1}. The asymmetric vibration band of anhydrous lutetium complex at 1534 cm^{-1} is not split. The separation value, $\Delta\nu$, of the (OCO^-) group and the direction of the shifting of these bands, when compared to sodium salt, may suggest that organic ligand occurs as bidentate chelating ligand in hydrated complexes [10–11]. The splitting of the asymmetric bands $\nu_{as}(OCO^-)$, (1564–1562 and 1554–1552 cm^{-1}) indicates that the carboxylate groups in the complex coordinate the metal ion in a different way, they act as mono-, bi- or terdentate [8]. In IR spectra of hydrated complexes there exists a broad valency absorption band of the OH groups from H_2O at 3440–3332 cm^{-1} and a sharp and strong band $\delta(H_2O)$ at 1584–1576 cm^{-1}, which points to the presence of crystallisation water molecules and bands due to metal–oxygen bond at 424–394 cm^{-1}. The deformation vibrations bands of phenolic group δ(OH) at 1452 and at 792 cm^{-1} in the free acid are shifted about 4–16 cm^{-1} to the higher frequencies in the lanthanide complexes, whereas sharp and strong valency vibration band at 1256 cm^{-1} is shifted about 24–44 cm^{-1}. Generally, it is not possible on the basis of IR spectra to state if lanthanide ion forms its bond through the phenolic oxygens. Shifting bands may be a result of the disappearance of hydrogen bonding in the ligand molecule rather than participation of the phenolic group in metal coordination. Thus the conclusions were drawn from the studies of lanthanide complex structures with organic ligands with phenolic group, which were previously described. The structure of La, Nd and Sm salicylates [9] and 3-hydroxybenzoate of Nd(III) [10–12] have been determined. It was shown that in samarium salicylate only one phenolic group out of the six coordinated ligands takes part in bonding; in the case of Nd^{3+} ion, the phenolic group does not coordinate the metal. The hydrogen bond exists probably between the hydrogen atoms of the phenolic group and the oxygen atoms of the carboxylate groups and in the hydrated complexes also between hydrogen of water molecules and oxygen atoms of the carboxylate groups. The hydrogen bonds stabilize the structure of the complexes prepared.

Table 2 Frequencies of absorption bands of OCO^- and OH groups of 1-hydroxy-2-napthoic acid and its compounds (cm^{-1})

Compound	$\nu_{as}OCO^-$	ν_sOCO^-	$\nu_{as}–\nu_s$	δOH	νCOH	δOH	νM–O
HL^a				1452	1256	792	
NaL	1578	1440	138	1460	1258	796	428
$LaL_3·6H_2O$	1562 1552	1440	122 112	1468	1300	800	424
$CeL_3·6H_2O$	1562 1552	1440	122 112	1468	1296	800	424
$PrL_3·6H_2O$	1562 1552	1440	122 112	1468	1300	800	424
$NdL_3·6H_2O$	1562 1552	1440	122 112	1468	1296	792	424
$SmL_3·6H_2O$	1564 1554	1442	122 112	1464	1296	800	420
$EuL_3·6H_2O$	1564 1554	1440	124 114	1464	1296	792	420
$GdL_3·6H_2O$	1564 1554	1444	120 110	1468	1296	792	420
$TbL_3·6H_2O$	1564 1554	1444	120 110	1468	1296	796	420
$DyL_3·6H_2O$	1564 1554	1444	120 110	1468	1296	792	416
$HoL_3·6H_2O$	1564 1554	1444	120 110	1468	1296	792	416
$ErL_3·6H_2O$	1564 1554	1444	120 110	1468	1296	792	416
$TmL_3·6H_2O$	1564 1554	1444	120 110	1468	1292	796	420
$YbL_3·6H_2O$	1544 1536	1442	102 94	1468	1280	796	394
LuL_3	1534	1442	92	1468	1280	796	404
$YL_3·6H_2O$	1562 1552	1440	122 112	1468	1296	792	424

$L^a=C_{10}H_6(OH)COO^-$

The thermal stability of the compounds was studied and is presented in Table 3. The hexahydrated complexes of lanthanides(III) and Y(III) are stable in air to 323–345 K, dihydrated complex of Yb(III) is stable to 356 K and anhydrous complex of Lu(III) is stable to 480 K. The complexes of lanthanides(III) decompose in various ways when heated (Figs 1 and 2). The hexahydrated complexes of La(III) to Tm(III) lose six water molecules at 323–398 K. After dehydration the anhydrous complexes are stable to 415–432 K. The temperature of dehydration in hexahydrated complexes are similar, due to isostructural properties. Dihydrated complex of Yb(III) is dehydrated at 356–400 K. Anhydrous lanthanide complexes are stable to 415–480 K,

Table 3 Data of decomposition of yttrium(III) and lanthanide(III) 1-hydroxy-2-naphthoates in air

Complex	LnL_3					$LnLL'$			Ln_2O_3		
	ΔT_1	Mass loss/%		nH_2O	T_c	T_u	Mass loss/%		Mass loss/%		T_0
		calc.	found				calc.	found	calc.	found	
$LaL_3{}^a\cdot 6H_2O$	335–395	13.35	13.2	6	424	476	36.60	35.9	79.84	80.5	1063
$CeL_3\cdot 6H_2O$	341–394	13.36	12.9	6	415	483	36.58	36.0	78.84	78.6	1026
$PrL_3\cdot 6H_2O$	333–387	13.32	13.3	6	423	489	36.54	36.2	78.99	79.0	1000
$NdL_3\cdot 6H_2O$	333–387	13.27	13.2	6	423	483	36.39	36.0	79.32	79.4	1060
$SmL_3\cdot 6H_2O$	330–398	13.17	12.9	6	424	488	36.12	36.0	78.72	78.5	1000
$EuL_3\cdot 6H_2O$	338–390	13.14	13.1	6	420	488	36.06	35.7	78.58	78.8	933
$GdL_3\cdot 6H_2O$	335–385	13.06	13.0	6	432	490	35.81	35.3	78.07	78.1	927
$TbL_3\cdot 6H_2O$	337–391	13.03	12.8	6	423	493	35.75	35.1	77.43	77.3	1011
$DyL_3\cdot 6H_2O$	335–385	12.98	12.7	6	425	513	35.59	35.6	77.58	77.9	933
$HoL_3\cdot 6H_2O$	323–391	12.94	12.6	6	427	498	35.49	35.4	77.35	77.3	986
$ErL_3\cdot 6H_2O$	328–396	12.91	12.8	6	428	500	35.40	35.2	77.13	77.1	950
$TmL_3\cdot 6H_2O$	345–392	12.88	12.8	6	429	503	35.31	35.0	76.93	77.0	923
$YbL_3\cdot 2H_2O$	356–400	4.67	4.5	2	434	508	29.09	28.5	74.43	74.4	1040
LuL_3					480	547	25.55	25.6	72.98	72.9	1080
$YL_3\cdot 6H_2O$	333–385	14.24	14.0	6	435	498	39.05	38.4	85.11	85.3	990

$L^a = [C_{11}H_7O_3]^-$; $L' = [C_{11}H_6O_3]^{2-}$
ΔT_1 – temperature range of dehydration
T_c – temperature of decomposition of anhydrous complex
T_u – temperature of formation of the unstable intermediate product
T_0 – temperature of oxide formation (Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7)

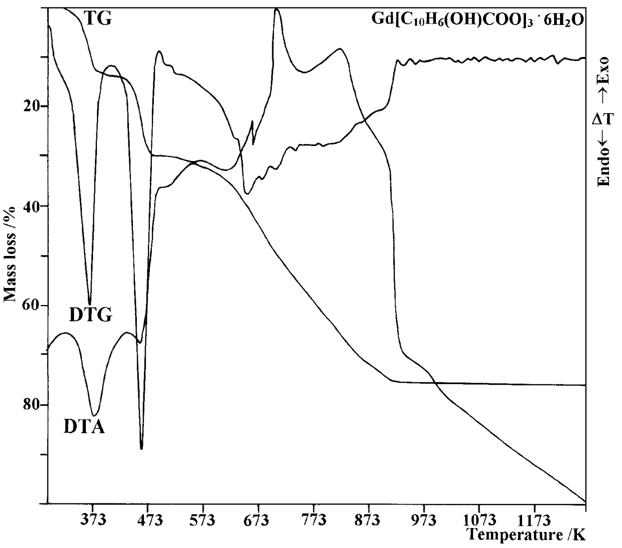

Fig. 1 TG, DTG and DTA curves of Gd[$C_{10}H_6$(OH)COO]$_3$·6H_2O (in air)

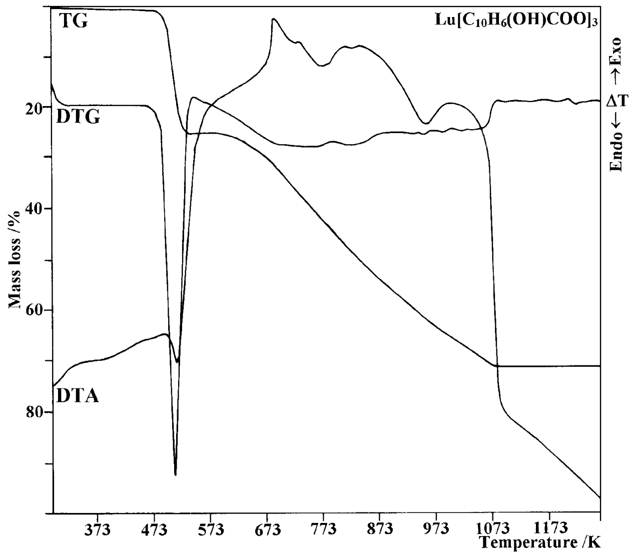

Fig. 2 TG, DTG and DTA curves of Lu[$C_{10}H_6$(OH)COO]$_3$ (in air)

when heated they decompose to oxides Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7 with an intermediate formation of unstable products [LnLL′], in which molar ratio of metal to organic ligand is 1:2. Similarly, as in the case of 2,6-dihydroxybenzoates of rare earth elements [13–15] and Pb(II) and Cu(II) [16], the metal ion are bound to one hydroxynaphthoate(–1) ligand and hydroxynaphthoate(–2) ligand, which is formed by deprotonation of both carboxylic and phenolic groups. Complexes La(III) and

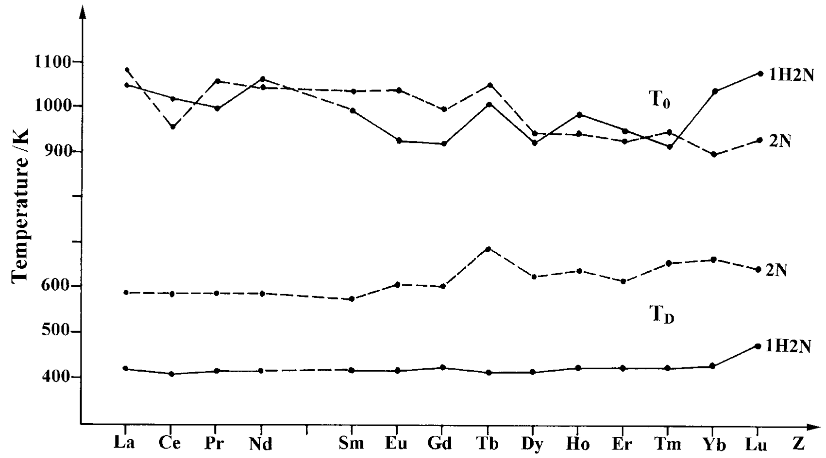

Fig. 3 Relationship between temperature of anhydrous complexes decomposition (T_D) and oxide formation (T_0) for lanthanide complexes with 2-naphthoic acid (2N) and 1-hydroxy-2-naphthoic acid (1H2N) and Z

Nd(III) decompose to Ln_2O_3, with intermediate formation of unstable [LnLL′] and oxocarbonates $Ln_2O_2CO_3$ stable up at 920–1010 K. The temperature of oxides formation are high and change periodically in lanthanide series. The thermal decomposition of obtained 1-hydroxy-2-naphthoates of lanthanides(III) and Y(III) can be presented:

$LnL_3{\cdot}nH_2O \rightarrow LnL_3 \rightarrow LnLL' \rightarrow Ln_2O_3$ *Ln*=Ce–Pr, Sm–Yb and Y

$LnL_3{\cdot}nH_2O \rightarrow LnL_3 \rightarrow LnLL' \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$ *Ln*=La and Nd

$LuL_3 \rightarrow LnLL' \rightarrow Lu_2O_3$

On the basis of current and previous studies of 2-naphthoates [17] there were attempts to determine the influence of the OH group in naphthalene ring on the properties of the lanthanide complexes. The presence of the OH group in the naphthalene ring results in: the increase in the number of crystallisation water molecules (6 molecules in 1-hydroxy-2-naphthoates; and 3–2 or 0 in 2-naphthoates); the increase of solubility in water at 293 K (10^{-4} mol dm^{-3} for 1-hydroxy-2-naphthoates; and 10^{-5} mol dm^{-3} for 2-naphthoates); spliting of the $\nu_{as}(OCO^-)$ absorption bands (which points to the presence of different bonding modes of metal–ligand); lowering of the decomposition temperature of anhydrous complexes (180–200 K) (Fig. 3.). The OH group has an insignificant influence on the temperature of oxide formation.

References

1 Y. H. Desphande and V. R. Rao, Indian J. Chem., 7 (1969) 1051.
2 Y. H. Desphande, D. V. Jahagirdar and V. R. Rao, Proc. 2nd Chem. Symp. Madras, 1970, 1 (1971) 275.
3 Y. H. Desphande and V. R. Rao, J. Inorg. Nucl. Chem., 35 (1973) 3626.

4 Ohki Yoshiyuki, Suzuki Yasuo, Takenchi Toshio, Shimoi Mamoru and Ouchi Akira, Bull. Chem. Soc. Jpn, 59 (1986)1015.
5 A. Kula, Powder Diffraction File (in press).
6 B. S. Manhans and A. K. Trikha, J. Ind. Chem. Soc., 59 (1982) 315.
7 K. Moore and G. S. Vige, Inorg. Chim. Acta, 91 (1984) 53.
8 W. Brzyska, Z. Rzączyńska and A. Kula, Monatsh. Chem., 120 (1989) 211.
9 J. H. Burns and W. H. Baldwin, Inorg. Chem., 16 (1977) 289.
10 W. Brzyska, A. Kula and M. Dąbkowska, J. Thermal Anal., 31 (1986) 1037.
11 W. Brzyska and A. Kula, Polish J. Chem., 60 (1986) 411.
12 A. E. Kozioł, W. Brzyska, B. Klimek, A. Kula, G. J. Palenik and K. Stępniak, J. Coord. Chem., 21 (1990) 183.
13 W. Brzyska, Z. Rzączyńska, A. Kula and M. Jaroniec, Polish J. Chem., 72 (1998) 2087.
14 W. Brzyska, Z. Rzączyńska, A. Kula and J. Jaroniec, Polish J. Chem., 72 (1998) 2524.
15 T. Glowiak, W. Brzyska, A. Kula and Z. Rzączyńska, J. Coord. Chem., 48 (1999) 477.
16 T. Głowiak, H. Kozłowski, L. Erre Strinna, G. Micera and B. Gulinotti, Inorg. Chim. Acta, 202 (1992) 43.
17 W. Brzyska and A. Kula, J. Thermal Anal., 44 (1995) 1159.