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Preparation and properties of Y(III) and lanthanide(III) complexes with pyridine-2,4-dicarboxylic acid

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Abstract

The conditions of the formation of Y(III) and lanthanide (III) (La–Lu) lutidinates were studied and their compositions and solubilities in water at 293 K were determined (10^{-4} mol dm^{-3}). The spectra of the hydrated complexes were recorded and their thermal decomposition in air was determined. During heating, the hydrated lutidinates $Ln_2(C_7H_3NO_4)_3 \cdot nH_2O$ ($n = 11$–29) lose some or all of their molecules of crystallization water in one (La–Nd) or two (Y, Sm–Lu) steps, and then the anhydrous (La–Nd, Lu) or hydrated (Y, Sm–Yb) complexes decompose either directly to oxides (Y, Ce, Pr, Sm–Lu) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$ (La, Nd).

Keywords: DTA; IR; Lanthanides; Lutidinic acid; TG

1. Introduction

Pyridine-2,4-dicarboxylic acid $C_5H_3N(COOH)_2$, known as lutidinic acid, is a crystalline solid sparingly soluble in water, ether and benzene, and soluble in mineral acids [1]. The acid and its derivates belong to an interesting series of compounds with biological applications [2–5]. Chiacchierini et al. [6] have determined the stability constants of Cr(III) with lutidinic acid and other pyridine dicarboxylic acids. The complexes of Mn(II), Fe(II), Cu(II), Zn(II), Ni(II) [7], Cd(II) [8] and Au(II) [9] have been prepared and their thermal stabilities have been studied. It was found that the composition of the complexes depends on the metal-to-ligand ratio and on the pH of the solution. Lutidinates of yttrium and lanthanides in the solid state were unknown before the present work.

The aim of this work was to prepare Y(III) and lanthanide(III) lutidinates in the solid state and to examine their physico-chemical properties and thermal decomposition in air.

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2. Experimental

2.1. Preparation of the complexes

Lutidinates of Y(III) and lanthanides (III) from La to Lu (without Pm) were prepared by adding stoichiometric quantities of a hot (333 K) 0.2 M solution of ammonium lutidinate (pH 5.0–5.5) to a hot solution of Y and lanthanide chlorides (Ce(III) was used as its nitrate) in a way similar to the method described previously [10].

2.2. Elemental analysis

The carbon, hydrogen and nitrogen contents were determined by elemental analysis. The metal content was determined from the TG curve and by ignition of the complexes to the oxides at 1073 K. The content of crystallization water was determined from the TG curve and by heating the samples isothermally at a set temperature to a constant mass.

2.3. IR spectra

The IR spectra of lutidinic acid and the separated rare earth element complexes and the sodium salt were recorded over the range 4000–400 cm^{-1} using an M-80 Carl Zeiss-Jena spectrophotometer. The samples were prepared as KBr discs.

2.4. Derivatograph measurements

The thermal stability and the solid products of decomposition of the prepared complexes were determined using a Paulik–Paulik–Erdey Q 1500 D derivatograph. The TG, DTG and DTA curves were recorded. The measurements were made at a sensitivity of 100 mg (TG), 500 μV (DTG) and 500 μV (DTA). Samples (100 mg) were heated in platinum crucibles to 1073 K at a heating rate $\Delta T = 10$ K min^{-1}. The hydrated complexes were heated isothermally at a set temperature to a constant mass. The products of decomposition were calculated from the TG curves and were confirmed by their IR spectra.

2.5. Determination of solubility

The solubility of the prepared lutidinates in water was determined at 293 K as described in Ref. [10].

3. Results and discussion

Complexes of Y(III) and lanthanides (III) from La to Lu with lutidinic acid were prepared as crystalline solids with the colour characteristics of the lanthanide (III) ions and with a molar ratio of metal to organic ligand of 2:3. The general formula was

$Ln_2(C_7H_3NO_4)_3 \cdot nH_2O$ ($n = 11$–29). The degree of hydration does not change regularly with increasing atomic number Z of the metal in the lanthanide series (Table 1) and has higher values than those determined for the rare earth dipicolinates [10].

In order to confirm the composition of the complexes and to determine the metal–organic ligand coordination, the IR spectra of lutidinic acid, lutidinates of rare earths and sodium lutidinate were recorded. The IR spectra of the lutidinates are similar to each other and have many bands (Table 2). In the IR spectrum of free lutidinic acid, there are two strong absorption bands of COOH groups at 1706 and 1696 cm^{-1}. In the IR spectra of the prepared lutidinates, these absorption bands disappear and the bands of asymmetrical (ν_{as}) and symmetrical (ν_s) vibrations of OCO– groups appear at 1610–1650 cm^{-1}, 1385–1410 cm^{-1}, and 1365–1380 cm^{-1}, respectively. The following broad absorption bands appear: ν(OH) with maxima at 3368–3424 cm^{-1}; valency vibrations of C–N in the ring at 1280–1290 cm^{-1} and 1090–1110 cm^{-1}; C–H with maxima at 920–940 cm^{-1} and 520–540 cm^{-1}; and the Ln–O bond at 420–460 cm^{-1}. The absorption bands of C–N in the complexes are shifted insignificantly compared to the respective band of lutidinic acid. This indicates that Ln(III) ions are coordinated only by the oxygen atoms of the two carboxylic groups and that the nitrogen atom of the pyridine ring does not take part in the coordination of the metal. The separation values ($\Delta\nu$) of ν_{as}(OCO) and ν_s(OCO) in the IR spectra of the studied complexes ($\Delta\nu = 205$–240 cm^{-1}) are very similar to the value for the sodium salt ($\Delta\nu = 220\ cm^{-1}$). This indicates a notable participation of the ionic bond in the rare earth element lutidinates (Table 3). The asymmetrical (ν_{as}) and symmetrical (ν_s) bands of the OCO– groups are split, which suggests that the OCO– groups are bonded in

Table 1
Analytical data of Y and lanthanide lutidinates

Complex	% Ln		% C		% N		% H	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$Y_2L_3 \cdot 19H_2O$	17.5	17.5	24.8	25.0	4.1	4.0	4.6	4.5
$La_2L_3 \cdot 14H_2O$	27.1	27.0	24.6	24.9	4.1	4.2	3.6	3.6
$Ce_2L_3 \cdot 11H_2O$	28.7	28.8	26.9	27.0	4.3	4.3	3.2	3.2
$Pr_2L_3 \cdot 13H_2O$	26.5	26.5	23.6	24.0	3.9	4.0	3.8	3.8
$Nd_2L_3 \cdot 13H_2O$	28.3	28.0	24.8	24.9	4.1	4.4	3.4	3.5
$Sm_2L_3 \cdot 14H_2O$	28.5	28.5	23.8	23.8	3.9	4.0	3.5	3.7
$Eu_2L_3 \cdot 24H_2O$	24.7	24.8	20.5	20.6	3.4	3.5	4.6	4.5
$Gd_2L_3 \cdot 29H_2O$	23.6	23.8	18.9	20.0	3.1	3.1	5.0	4.9
$Tb_2L_3 \cdot 26H_2O$	24.8	25.0	19.7	19.8	3.3	3.4	4.9	4.9
$Dy_2L_3 \cdot 24H_2O$	26.2	26.0	20.3	20.1	3.4	3.4	4.6	4.5
$Ho_2L_3 \cdot 29H_2O$	24.5	24.5	18.7	19.0	3.1	3.2	4.9	4.8
$Er_2L_3 \cdot 29H_2O$	24.7	24.8	20.5	20.1	3.1	3.2	4.9	4.9
$Tm_2L_3 \cdot 25H_2O$	26.4	26.5	19.6	20.0	3.3	3.4	4.6	4.5
$Yb_2L_3 \cdot 26H_2O$	26.4	26.5	19.2	20.0	3.2	3.0	4.6	4.5
$Lu_2L_3 \cdot 20H_2O$	28.2	28.0	20.3	20.9	3.4	3.6	3.9	4.0

L is $C_7H_3NO_4^{2-}$.

Table 2
Frequencies of maxima for absorption bands in IR spectra of lutidine acid and lutidinates of Na, Y and lanthanides (cm^{-1})

Complex	$\nu(OH)$	$\sigma(OH)$	$\nu(CO)$	$\nu_{as}(OCO)$	$\nu_s(OCO)$	$\nu(CN)$	$\nu(CH)$	$\nu(MO)$
$C_7H_5NO_4$			1706, 1696	1650, 1610	1420, 1380	1290, 1090	940, 520	
$Y_2L_3 \cdot 19H_2O$	3416	1260, 1200	–	1640, 1610	1400, 1370	1290, 1100	930, 540	460
$La_2L_3 \cdot 14H_2O$	3368	1240, 1220	–	1610, 1590	1410, 1380	1290, 1100	920, 520	450
$Ce_2L_3 \cdot 11H_2O$	3400	1260, 1210	–	1640, 1600	1410, 1380	1290, 1100	920, 540	450
$Pr_2L_3 \cdot 13H_2O$	3400	1250, 1200	–	1610, 1580	1400, 1370	1290, 1100	930, 540	450
$Nd_2L_3 \cdot 13H_2O$	3416	1250, 1200	–	1620, 1590	1400, 1370	1290, 1100	930, 540	450
$Sm_2L_3 \cdot 14H_2O$	3416	1260, 1200	–	1640, 1610	1410, 1380	1290, 1100	920, 540	450
$Eu_2L_3 \cdot 24H_2O$	3424	1250, 1200	–	1630, 1600	1400, 1370	1280, 1100	920, 540	450
$Gd_2L_3 \cdot 29H_2O$	3392	1260, 1210	–	1640, 1600	1400, 1370	1290, 1100	930, 540	450
$Tb_2L_3 \cdot 26H_2O$	3400	1250, 1200	–	1640, 1600	1400, 1370	1280, 1100	930, 530	450
$Dy_2L_3 \cdot 24H_2O$	3416	1250, 1200	–	1650, 1600	1400, 1370	1290, 1100	930, 540	450
$Ho_2L_3 \cdot 29H_2O$	3392	1250, 1200	–	1650, 1600	1400, 1370	1280, 1100	925, 530	450
$Er_2L_3 \cdot 29H_2O$	3392	1250, 1200	–	1650, 1600	1400, 1370	1290, 1100	930, 540	450
$Tm_2L_3 \cdot 25H_2O$	3384	1250, 1200	–	1650, 1600	1400, 1370	1290, 1100	930, 540	450
$Yb_2L_3 \cdot 26H_2O$	3392	1260, 1210	–	1650, 1600	1400, 1370	1290, 1100	930, 540	450
$Lu_2L_3 \cdot 20H_2O$	3392	1260, 1210	–	1650, 1600	1400, 1370	1290, 1100	930, 540	450
$Na_2L \cdot xH_2O$	3420	1240, 1200	–	1610, 1580	1385, 1365	1280, 1090	940, 520	420

different ways within the same complex molecule. The nature of the metal–ligand bonding can be explained in detail after determination of the crystal and molecular structure of the monocrystals.

The rare earth hydrated lutidinates are stable up to 313 K and when heated in air, decompose in various ways (Figs. 1–8, Table 4). During heating, the hydrated complexes of La(III)–Nd(III) are dehydrated in one step and then decompose directly to the oxides (Ce, Pr) or with the intermediate formation of oxocarbonates (La, Nd). The hydrated complex of Lu(III), when heated, loses its water of crystallization in two steps forming the anhydrous state at 625 K and then decomposes directly to the oxide. The hydrated complexes of Y(III) and Sm(III)–Yb(III) decompose in three steps. During heating they lose some of their waters of crystallization in two steps and then simultaneously lose their remaining water molecules and decompose directly to the oxides. The results indicate that the thermal decomposition of hydrated rare earth lutidinates can be presented as

$$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3 \quad \text{for } Ln = La, Nd$$

$$Ce_2L_3 \cdot 11H_2O \rightarrow Ce_2L_3 \rightarrow CeO_2$$

$$Pr_2L_3 \cdot 13H_2O \rightarrow Pr_2L_3 \rightarrow Pr_6O_{11}$$

$$Lu_2L_3 \cdot 20H_2O \rightarrow Lu_2L_3 \cdot 6H_2O \rightarrow Lu_2L_3 \rightarrow Lu_2O_3$$

$$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2L_3 \cdot zH_2O \rightarrow Ln_2O_3, Tb_4O_7$$

for $Ln = Y, Sm\text{–}Yb, x > y > z$

where L is $C_7H_3NO_4^{2-}$.

Table 3
Absorption bands for $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ of Na, Y and lanthanide lutidinates (cm^{-1})

Complex	$\bar{\nu}_{as}(OCO)$	$\Delta\nu_{as}(OCO)$	$\bar{\nu}_s(OCO)$	$\Delta\nu_s(OCO)$	$\bar{\nu}_{as}-\bar{\nu}_s(OCO)$
$Na_2L \cdot xH_2O$	1595	–	1375	–	220
$Y_2L_3 \cdot 19H_2O$	1625	30	1385	10	240
$La_2L_3 \cdot 14H_2O$	1600	5	1395	20	205
$Ce_2L_3 \cdot 11H_2O$	1620	25	1395	20	225
$Pr_2L_3 \cdot 13H_2O$	1595	0	1385	10	210
$Nd_2L_3 \cdot 13H_2O$	1605	10	1385	10	220
$Sm_2L_3 \cdot 14H_2O$	1625	30	1395	20	230
$Eu_2L_3 \cdot 24H_2O$	1615	20	1385	10	230
$Gd_2L_3 \cdot 29H_2O$	1620	25	1385	10	235
$Tb_2L_3 \cdot 26H_2O$	1620	25	1385	10	235
$Dy_2L_3 \cdot 24H_2O$	1625	30	1385	10	240
$Ho_2L_3 \cdot 29H_2O$	1625	30	1385	10	240
$Er_2L_3 \cdot 29H_2O$	1625	30	1385	10	240
$Tm_2L_3 \cdot 25H_2O$	1625	30	1385	10	240
$Yb_2L_3 \cdot 26H_2O$	1625	30	1385	10	240
$Lu_2L_3 \cdot 20H_2O$	1625	30	1385	10	240

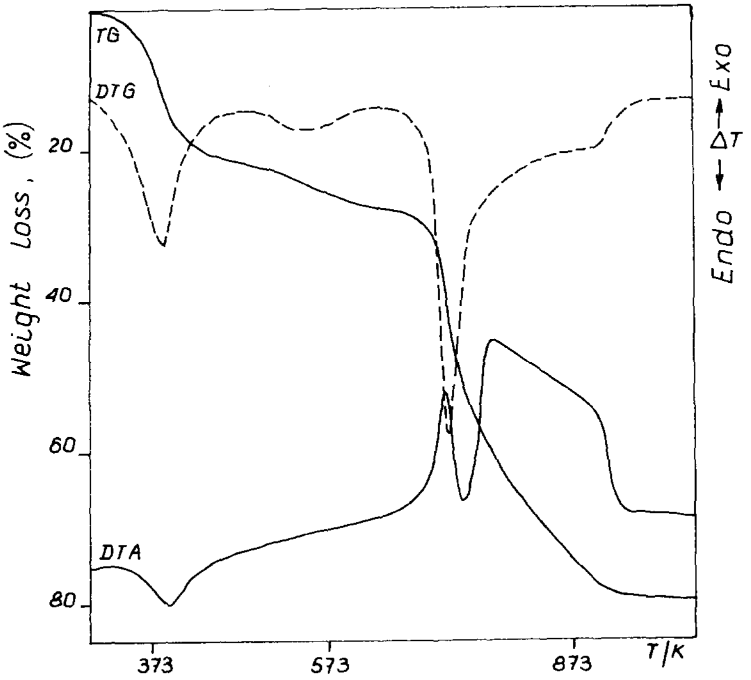

Fig. 1. TG, DTG and DTA curves for $Y_2(C_7H_3NO_4)_3 \cdot 19H_2O$.

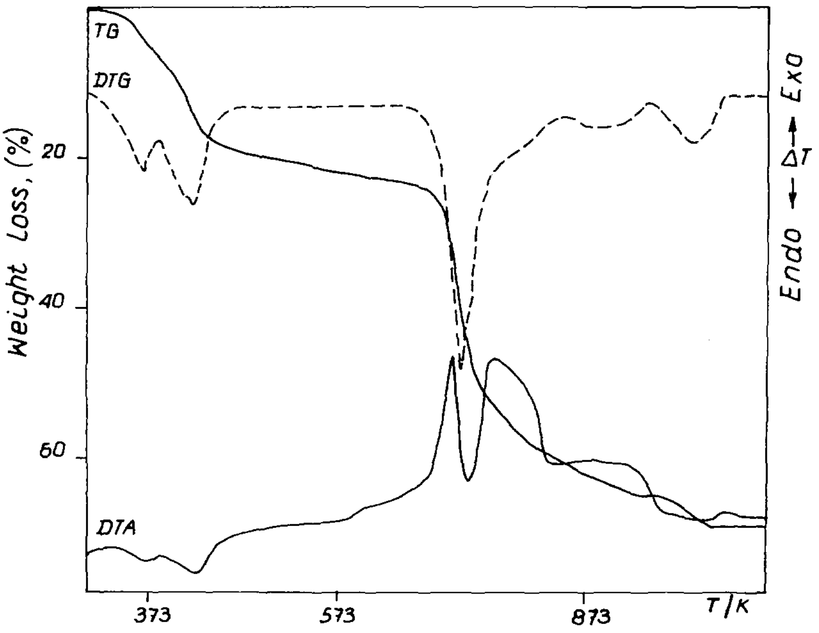

Fig. 2. TG, DTG and DTA curves for $La_2(C_7H_3NO_4)_3 \cdot 14H_2O$.

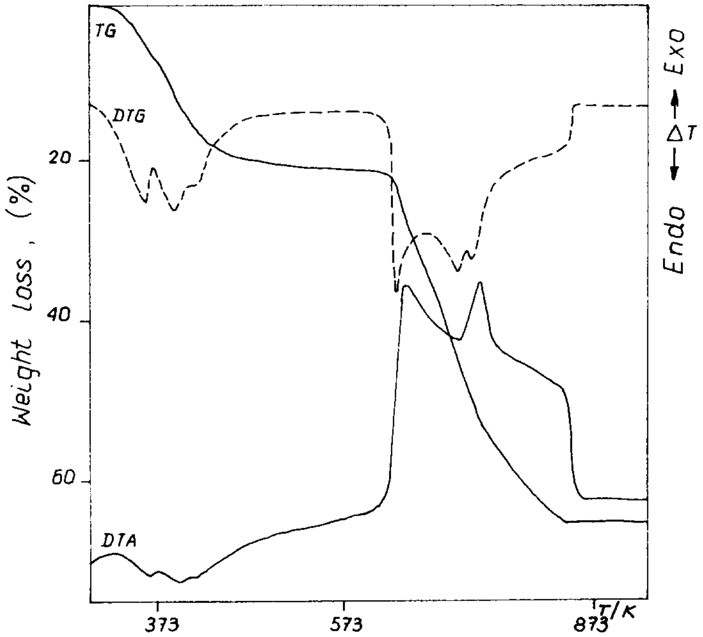

Fig. 3. TG, DTG and DTA curves for $Ce_2(C_7H_3NO_4)_3 \cdot 11H_2O$.

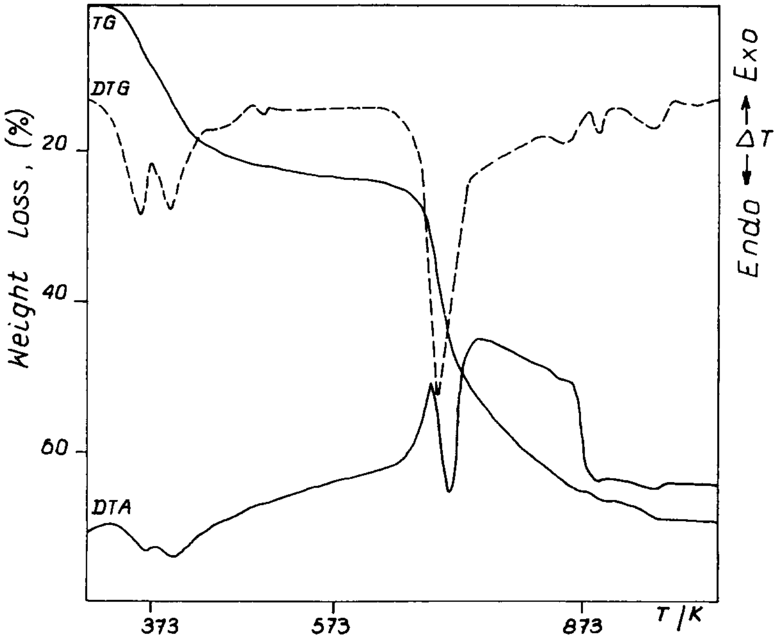

Fig. 4. TG, DTG and DTA curves for $Nd_2(C_7H_3NO_4)_3 \cdot 13H_2O$.

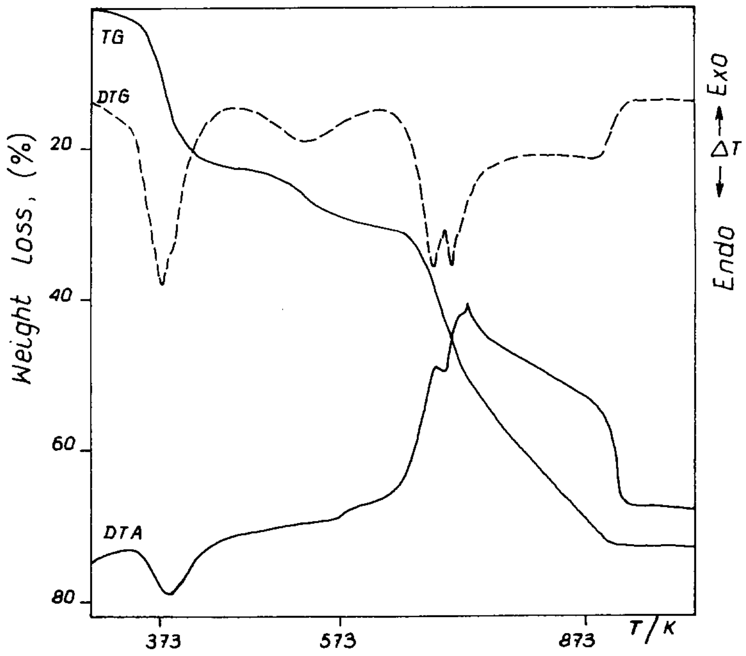

Fig. 5. TG, DTG and DTA curves for $Eu_2(C_7H_3NO_4)_3 \cdot 24H_2O$.

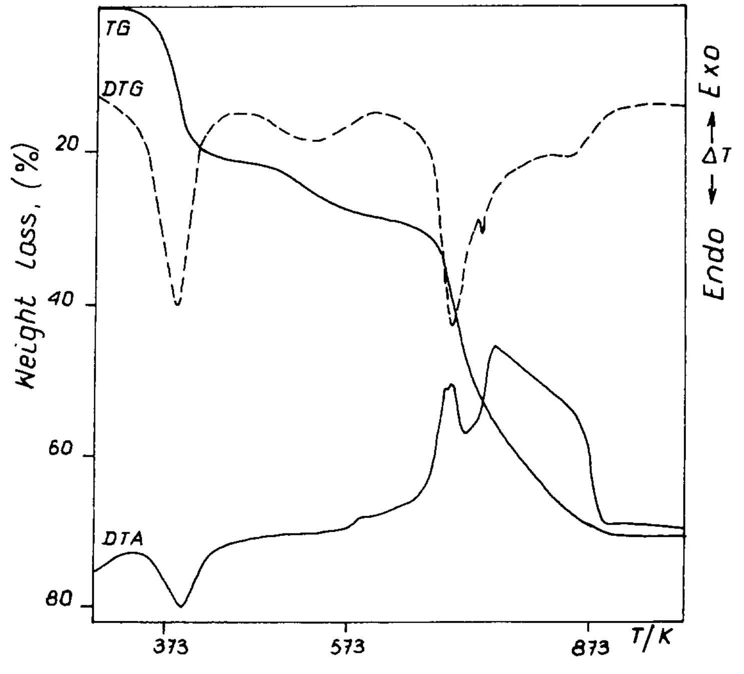

Fig. 6. TG, DTG and DTA curves for $Dy_2(C_7H_3NO_4)_3 \cdot 24H_2O$.

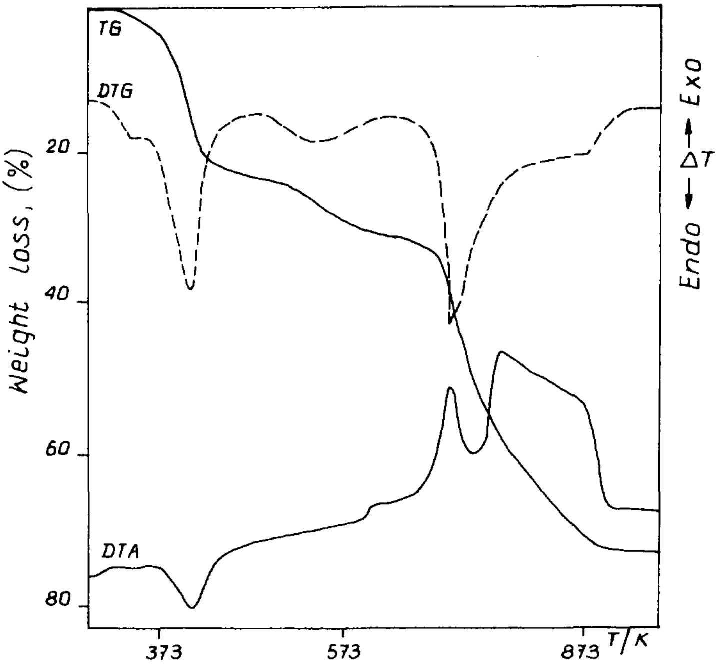

Fig. 7. TG, DTG and DTA curves for $Er_2(C_7H_3NO_4)_3 \cdot 29H_2O$.

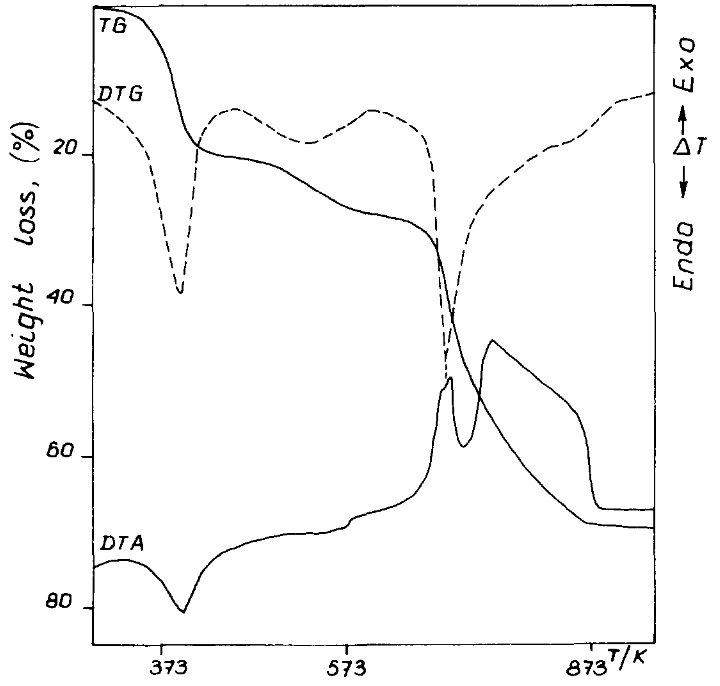

Fig. 8. TG, DTG and DTA curves for $Lu_2(C_7H_3NO_4)_3 \cdot 20H_2O$.

Table 4
Thermoanalytical data for Y and lanthanide lutidinates

Complex	Temp. range of dehyd./K	Mass loss %		Loss H_2O mol	Temp. range of decomp/K	Mass loss %		Temp of oxide form/K
		Calcd.	Found			Calcd.	Found	
$Y_2L_3 \cdot 19H_2O$	313–473	19.5	19.5	11	533–983	77.7	78.0	983
	493–523	7.7	7.5	4				
$La_2L_3 \cdot 14H_2O$	313–543	24.6	24.5	14	633–1033	68.2	68.5	1033
$Ce_2L_3 \cdot 11H_2O$	313–493	20.6	20.5	11	593–853	64.6	65.0	853
$Pr_2L_3 \cdot 13H_2O$	313–493	23.0	23.0	13	633–923	69.3	69.0	923
$Nd_2L_3 \cdot 13H_2O$	313–463	23.0	23.0	13	633–983	66.9	67.0	983
$Sm_2L_3 \cdot 14H_2O$	313–473	15.3	15.0	9				
	493–633	6.0	6.0	3	643–963	66.9	67.0	963
$Eu_2L_3 \cdot 24H_2O$	313–453	20.5	20.5	14				
	473–593	11.0	11.0	6	613–923	71.4	71.5	923
$Gd_2L_3 \cdot 29H_2O$	313–453	21.6	21.5	16				
	483–603	9.4	9.5	7	613–953	72.7	73.0	953
$Tb_2L_3 \cdot 26H_2O$	313–463	22.5	22.5	16				
	473–593	8.4	8.5	6	603–933	70.8	71.0	933
$Dy_2L_3 \cdot 24H_2O$	313–463	21.7	22.0	15				
	483–613	7.2	7.0	5	623–953	69.9	70.0	953
$Ho_2L_3 \cdot 29H_2O$	313–473	22.7	23.0	17				
	493–623	8.0	8.0	6	633–973	71.9	72.0	973
$Er_2L_3 \cdot 29H_2O$	313–453	22.6	22.5	17				
	493–633	8.0	8.0	6	643–993	71.7	72.0	993
$Tm_2L_3 \cdot 25H_2O$	313–473	21.0	21.0	15				
	493–633	8.5	8.5	6	643–943	69.8	70.0	943
$Yb_2L_3 \cdot 26H_2O$	313–463	22.0	22.0	16				
		8.2	8.0	6	633–933	69.9	70.0	933
$Lu_2L_3 \cdot 20H_2O$	313–453	20.3	20.5	14				
	483–625	8.7	8.5	6	633–913	67.9	68.0	913

In general, it can be suggested that hydrated rare earth lutidinates when heated lose all or some water molecules, and then decompose to the oxides either directly or with the intermediate formation of oxocarbonates. The dehydration and decomposition of the prepared complexes are connected with a strong endothermic effect, whereas the combustion of the organic ligand and the products of its decomposition show an exothermic effect. On the basis of the results obtained, it is possible to suggest that the water molecules present in rare earth lutidinates are bonded in different ways. The water molecules lost at 313 K are probably outer-sphere water, and those lost simultaneously with decomposition of the complexes are inner-sphere ones. The relationship between the temperatures at the beginning of dehydration (T_0), the beginning of decomposition (T) for the complexes, and the temperatures of oxide formation (T_K) are presented in Fig. 9. The temperatures of dehydration, T_0, have the same values (313 K) as for dipicolinates [10]. The temperatures of decomposition for the hydrated and anhydrous complexes and the temperatures of oxide formation

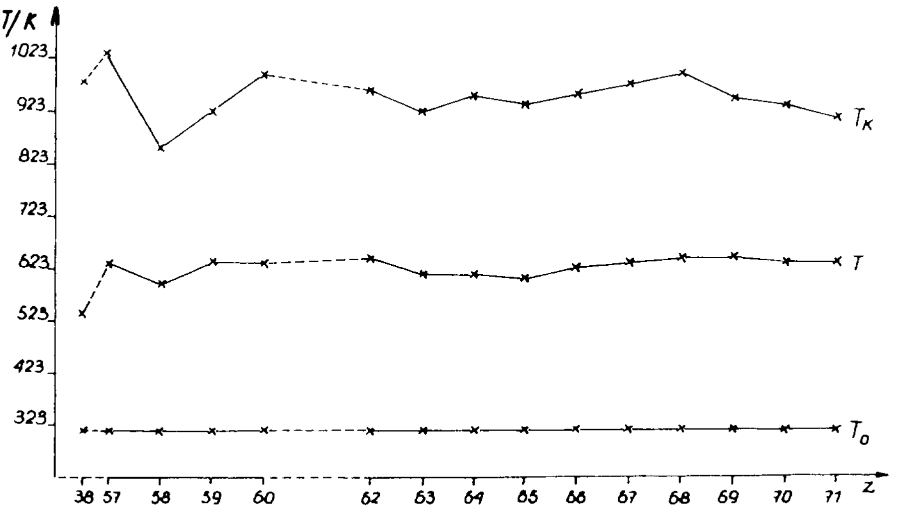

Fig. 9. Relationship between T_0, T, T_K, and Z for Ln(III).

change insignificantly for the lanthanide series. La_2O_3 forms at the highest temperature (1033 K) and CeO_2 at the lowest (853 K).

Lutidinates of rare earth elements are sparingly soluble in water (Table 5). Their solubilities are of the order of 10^{-4} mol dm^{-3} and change irregularly in the lanthanide series (Fig. 10). The solubility of Y(III) lutidinate is ten times greater than those of the lanthanide complexes. The Sm(III) complex is the most soluble and that of Ce(III) the least in the lanthanide series. Rare earth lutidinates are sparingly soluble in water (10^{-4} mol dm^{-3}) whereas the corresponding dipicolinates are soluble in water (10^{-1} mol dm^{-3}) [10]. On this basis it is possible to confirm that the position of the two COOH groups in the pyridine ring influences the electron cloud density on the carbon

Table 5
Solubilities of rare earth lutidinates in mol dm^{-3} × 10^{-4} in water at 293 K

Complex	Solubility	Complex	Solubility
Y_2L_3	24.80	Gd_2L_3	2.04
La_2L_3	1.78	Tb_2L_3	5.75
Ce_2L_3	0.46	Dy_2L_3	2.36
Pr_2L_3	5.28	Ho_2L_3	2.22
Nd_2L_3	3.10	Er_2L_3	2.61
Sm_2L_3	8.14	Tm_2L_3	2.27
Eu_2L_3	1.87	Yb_2L_3	5.17
		Lu_2L_3	1.61

L is $C_7H_3NO_4^{2-}$.

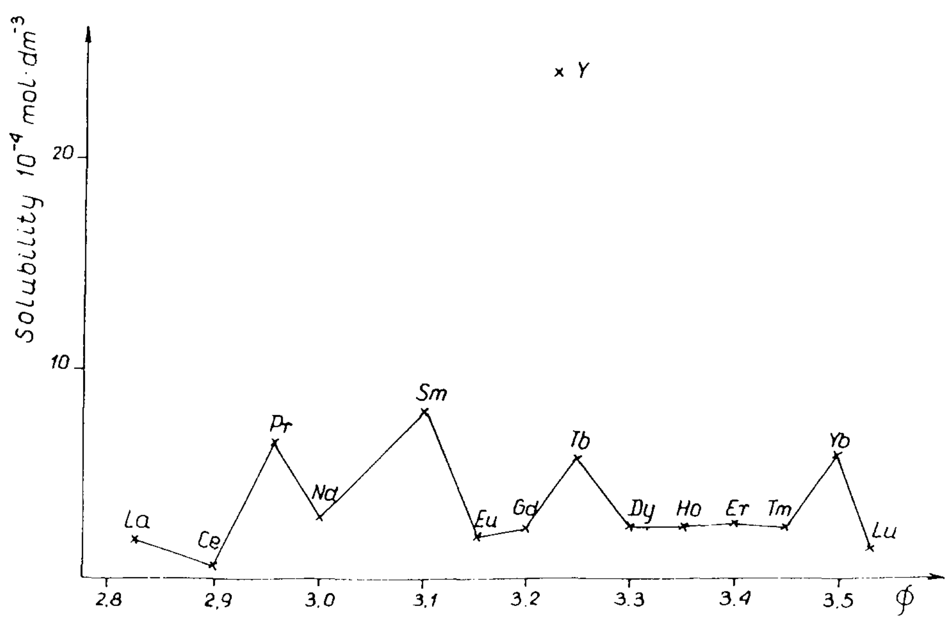

Fig. 10. Relationship between solubility and ionic potential ϕ for Ln(III).

atom of the OCO- group and causes a change in the structure and properties of rare earth lutidinates compared to those of the corresponding picolinates.

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