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Preparation and properties of rare earth element complexes with pyridine-2,6-dicarboxylic acid

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Abstract

The conditions of the formation of rare earth element (Y, La–Lu) dipicolinates were studied, and their quantitative compositions and solubilities in water at 293 K were determined (10^{-2} to 10^{-3} mol dm^{-3}). The IR spectra of the hydrated complexes were recorded and their thermal decomposition in air was determined. During heating the hydrated dipicolinates $Ln_2(C_7H_3NO_4)_3 \cdot nH_2O$ ($n = 9$–25) lose some or all of their water molecules of crystallization water in one, two or three steps; then the anhydrous or hydrated complexes decompose either directly to the oxides (Y, Ce, Sm–Dy, Tm–Lu) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$ (La, Pr, Nd, Ho, Er).

Keywords: Dipicolinic acid; DTA; DTG; Lanthanon; TG

1. Introduction

Pyridine-2,6-dicarboxylic acid $C_5H_3N(COOH)_2$, known as dipicolinic acid, belongs to an interesting series of compounds with biological applications. A survey of the literature shows that dipicolinates of Mn(II), Fe(II), Cu(II), Zn(II), Ni(II) [1,2], Cr(III) [3], Co(II) [4], Pd(II) [5], Mg(II), Ca(II), Sr(II) and Ba(II) [6] have been studied in aqueous solution. Basim et al. [7] have studied the structure of lanthanide complexes with dipicolinic acid in solution using NMR. Brittain et al.

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[8–11] have studied the complexation of Tb(III) ions by dipicolinic acid in aqueous solution. The complexes of Sr [12], Cu(II) [13] and Ca(II) [14] have been prepared in the solid state and their IR spectra have been described. Dipicolinates of rare earth elements in the solid state were unknown before the present study.

The aim of this work was to prepare rare earth element(III) dipicolinates in the solid state and to examine their physico-chemical properties and thermal decomposition in air.

2. Experimental

2.1. Preparation of the complexes

Dipicolinates of Y and lanthanides from La to Lu (without Pm) were prepared by adding stoichiometric quantities of a hot 0.2 M solution of ammonium dipicolinate (pH 5.5–6.0) to a hot solution of the rare earth element chlorides (Ce(III) was used as its nitrate). The precipitate formed was heated in its mother liquor for 0.5 h at 345–353 K, and then filtered off, washed with hot water to remove Cl^- and NH_4^+ ions and dried at 303 K to a constant mass. The sodium salt was prepared by adding stoichiometric quantities of dipicolinic acid to a solution of NaOH and crystallizing at room temperature.

2.2. Elemental analysis

The carbon, hydrogen and nitrogen contents were determined by elemental analysis using V_2O_5 as oxidizing agent. The metal content was determined from the TG curve and by ignition of the complexes to the oxides at 1253 K. The content of crystallization water was determined from the TG curve and by heating the samples isothermally at 473 K to a constant mass.

2.3. IR spectra

The IR spectra of dipicolinic acid, and of the separated Y and lanthanide complexes and the sodium salt were recorded over the range 4000–400 cm^{-1} with an FT-IR 1725X Perkin-Elmer spectrophotometer. The samples were prepared as KBr discs.

2.4. Derivatograph measurements

The thermal stability of the prepared dipicolinates was determined using a Paulik–Paulik–Erdey Q 1500 D derivatograph. The TG, DTG and DTA curves were recorded. 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 1273 K at a heating rate of 10 K min^{-1}. The hydrated complexes were heated isothermally at a set temperature to constant mass and the products were confirmed by their IR spectra and elemental analysis.

2.5. Determination of solubility

The solubility of the prepared dipicolinates in water was determined at 293 K. The saturated solutions were prepared under isothermal conditions. The content of Ln(III) ions was determined by the oxalate method. The solubilities were determined on the basis of oxide mass (see Table 1).

3. Results and discussion

Dipicolinates of Y and lanthanides from La(III) to Lu(III) were prepared as crystalline solids having the color characteristic of the lanthanide(III) ions. From the elemental analyses, it was found that all complexes were prepared as hydrates with a molar ratio of metal to organic ligand of 2:3 and various degrees of hydration which do not change regularly with decreasing ionic radius of the lanthanide series (Table 1).

In order to confirm the composition of the prepared dipicolinates and to determine the metal–ligand coordination, the IR spectra of dipicolinic acid, and of the prepared Y, lanthanide and sodium dipicolinates were recorded. The IR spectra of the dipicolinates are similar to each other and have many bands (Table 2). In the IR spectrum of free dipicolinic acid, there is a single strong absorption band at 1697 cm^{-1} of COOH groups, which confirms their equivalent character. In the IR spectra of the prepared complexes, this absorption band disappears and the bands of asymmetrical (ν_{as}) and symmetrical (ν_s) vibrations of the OCO^- group appear at 1627–1608 and 1588–1572 cm^{-1}, and 1444–1430 and 1403–1370 cm^{-1}, respectively, the broad absorption bands of ν(OH) appear with maxima at 3463–3100 cm^{-1}, the bands of valency vibrations of C–N in the ring appear at 1299–1273 and 1083–1074 cm^{-1}, the bands of C–H appear with maxima at 959–910 and 595–513 cm^{-1}, and the bands of the Ln–O bond appear at 447–424 cm^{-1}. The absorption bands of C–N in the prepared complexes are shifted insignificantly compared to the respective band of dipicolinic acid, which indicates that Ln(III) ions are coordinated only by the oxygen atoms of two carboxylate group 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 prepared complexes ($\Delta\nu = 180$ cm^{-1}) are very similar to this value in the sodium salt ($\Delta\nu = 187.5$ cm^{-1}), which indicates a notable participation of the ionic bond in the rare earth element dipicolinates (Table 2). The asymmetrical (ν_{as}) and symmetrical (ν_s) bands of the OCO^- group are split which suggests that OCO^- groups are bonded in different ways in 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 element hydrates are stable up to 313–483 K and, when heated in air, decompose in various ways (Table 3, Figs. 1–5).

Table 1
Analytical data and solubilities of yttrium and lanthanide dipicolinates in water at 293 K

Complex	Ln in %		C in %		N in %		H in %		Solubility × 10^{-3} in mol dm^{-3}
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$Y_2(C_7H_3NO_4)_3 \cdot 12H_2O$	20.0	20.0	28.3	28.0	4.7	5.0	3.7	3.7	23.8
$La_2(C_7H_3NO_4)_3 \cdot 19H_2O$	21.5	21.5	22.6	22.5	3.8	3.6	4.2	4.4	6.7
$Ce_2(C_7H_3NO_4)_3 \cdot 9H_2O$	29.9	30.0	26.9	27.0	4.5	4.6	2.9	3.0	6.1
$Pr_2(C_7H_3NO_4)_3 \cdot 20H_2O$	24.8	24.5	22.2	22.0	3.7	3.9	4.3	4.5	4.2
$Nd_2(C_7H_3NO_4)_3 \cdot 20H_2O$	25.2	25.0	22.0	22.4	3.7	3.9	4.3	4.3	5.1
$Sm_2(C_7H_3NO_4)_3 \cdot 24H_2O$	24.5	24.5	20.5	20.9	3.4	3.5	4.6	4.4	2.7
$Eu_2(C_7H_3NO_4)_3 \cdot 12H_2O$	29.9	30.0	24.8	25.0	4.1	4.0	3.2	3.3	8.6
$Gd_2(C_7H_3NO_4)_3 \cdot 9H_2O$	32.3	32.5	25.9	30.0	4.3	4.2	2.8	2.9	8.1
$Tb_2(C_7H_3NO_4)_3 \cdot 9H_2O$	32.6	32.5	25.8	26.0	4.3	4.5	2.8	2.9	20.3
$Dy_2(C_7H_3NO_4)_3 \cdot 25H_2O$	25.6	25.5	19.8	19.5	3.3	3.2	4.6	4.5	32.0
$Ho_2(C_7H_3NO_4)_3 \cdot 9H_2O$	33.4	33.5	25.5	25.9	4.3	4.3	2.8	3.0	33.8
$Er_2(C_7H_3NO_4)_3 \cdot 12H_2O$	32.0	32.0	24.1	24.0	4.0	4.1	3.1	3.0	16.0
$Tm_2(C_7H_3NO_4)_3 \cdot 25H_2O$	26.3	26.0	17.6	17.5	3.3	3.5	4.6	4.5	48.5
$Yb_2(C_7H_3NO_4)_3 \cdot 12H_2O$	32.7	33.0	23.8	24.1	3.9	3.9	3.1	3.1	32.0
$Lu_2(C_7H_3NO_4)_3 \cdot 25H_2O$	27.0	27.0	19.4	19.5	3.2	3.0	4.5	4.6	14.5

Table 2
Frequencies of the most important absorption bands for IR spectra of dipicolinic acid and dipicolinates of Na, Y and lanthanides (cm^{-1})

Complex [a]	ν(OH)	σ(OH)	ν(CO)	ν_{as}(OCO)	ν_s(OCO)	ν(CN)	ν(CH)	ν(Mc–O)
$C_7H_5NO_4$			1697	1575	1415	1299 1082	997–513	
$Y_2L_3 \cdot 12H_2O$	3408 3166	1190 1158	–	1625 1583	1435 1392	1279 1076	920–527	438
$La_2L_3 \cdot 19H_2O$	3407 3169	1175 1158	–	1620 1581	1435 1392	1277 1083	959–524	431
$Ce_2L_3 \cdot 9H_2O$	3378 3225	1188 1148	–	1619 1571	1436 1386	1275 1078	924–527	434
$Pr_2L_3 \cdot 20H_2O$	3143 3046	1185 1159	–	1618 1582	1428 1382	1275 1075	918–522	429
$Nd_2L_3 \cdot 20H_2O$	3421 3179	1186 1158	–	1620 1581	1431 1386	1274 1075	917–520	431
$Sm_2L_3 \cdot 24H_2O$	3289 3080	1196 1156	–	1608 1572	1442 1397	1281 1083	920–519	434
$Eu_2L_3 \cdot 12H_2O$	3280 3100	1195 1155	–	1608 1572	1441 1397	1281 1083	921–519	440
$Gd_2L_3 \cdot 9H_2O$	3143 3046	1188 1147	–	1613 1583	1440 1397	1278 1076	919–521	434
$Tb_2L_3 \cdot 9H_2O$	3375 3179	1188 1146	–	1621 1588	1436 1370	1279 1075	915–517	436
$Dy_2L_3 \cdot 25H_2O$	3143 3045	1188 1158	–	1620 1581	1430 1397	1281 1075	920–529	436
$Ho_2L_3 \cdot 9H_2O$	3406 3182	1195 1150	–	1602 1572	1444 1403	1284 1075	927–478	443
$Er_2L_3 \cdot 12H_2O$	3428 3170	1189 1147	–	1622 1585	1434 1387	1278 1074	920–527	439
$Tm_2L_3 \cdot 25H_2O$	3418 3180	1188 1148	–	1620 1580	1435 1380	1281 1075	921–529	436
$Yb_2L_3 \cdot 12H_2O$	3418 3168	1197 1148	–	1627 1603	1443 1391	1284 1074	929–595	447
$Lu_2L_3 \cdot 25H_2O$	3411 3187	1189 1148	–	1620 1572	1436 1381	1282 1074	923–533	438
$Na_2L \cdot xH_2O$	3463 3088	1191	–	1622 1580	1441 1386	1273 1078	910–596	424

[a] L is $C_7H_3NO_4^{2-}$.

Table 3
Data on dehydration and decomposition of Y and lanthanide dipicolinates

Complex	Temp. range of dehydration in K	Mass loss in %		Loss of H_2O in mol	Temp. range of decomposition in K	Mass loss in %		Temp. of Ln_2O_3 formation in K
		Calcd.	Found			Calcd.	Found	
$Y_2L_3 \cdot 12H_2O$	313–363	4.0	4.0	2	603–993	74.5	75.0	993
	403–488	12.0	12.0	6				
	553–593	3.0	2.9	1				
$La_2L_3 \cdot 19H_2O$	338–453	17.8	18.0	11	533–1063	70.7	71.0	1063
$Ce_2L_3 \cdot 9H_2O$	313–483	17.3	17.0	9	518–953	63.3	63.5	953
$Pr_2L_3 \cdot 20H_2O$	333–513	18.1	18.0	11	518–953	69.7	70.0	953
$Nd_2L_3 \cdot 20H_2O$	483–553	12.6	13.0	8	563–1003	70.7	71.0	1003
$Sm_2L_3 \cdot 24H_2O$	313–443	20.5	20.0	14	513–963	71.6	71.5	963
$Eu_2L_3 \cdot 12H_2O$	308–463	21.2	21.0	12	573–973	65.3	66.0	973
$Gd_2L_3 \cdot 9H_2O$	313–533	16.6	16.5	9	573–1003	62.7	63.0	1003
$Tb_2L_3 \cdot 9H_2O$	313–523	16.6	17.0	9	663–1003	61.7	62.0	1003
$Dy_2L_3 \cdot 25H_2O$	313–523	19.8	19.5	14	563–923	70.6	71.0	923
$Ho_2L_3 \cdot 9H_2O$	308–513	16.5	17.0	9	663–963	61.7	62.0	963
$Er_2L_3 \cdot 12H_2O$	413–633	20.6	20.5	12	642–1053	63.4	63.5	1053
$Tm_2L_3 \cdot 25H_2O$	393–633	35.0	34.5	25	643–1003	69.8	70.0	1003
$Yb_2L_3 \cdot 12H_2O$	308–493	15.3	15.0	9	623–993	62.7	63.0	993
	533–613	20.4	20.5	3				
$Lu_2L_3 \cdot 25H_2O$	313–403	4.1	4.0	3	583–953	69.2	70.0	953
	543–573	34.7	35.0	22				

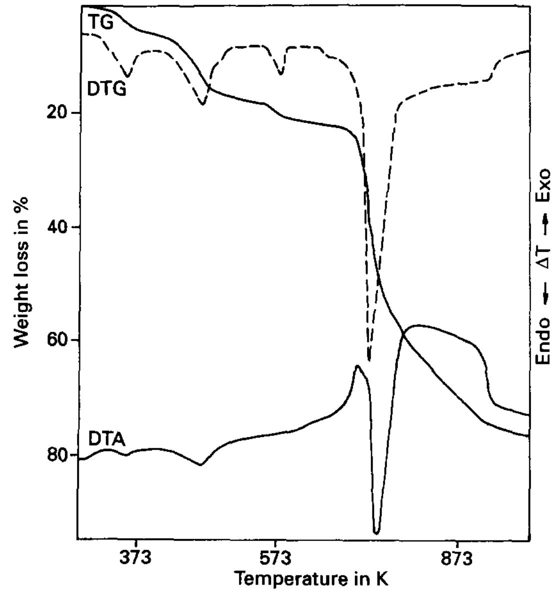

Fig. 1. TG, DTG and DTA curves of $Y_2(C_7H_3NO_4)_3 \cdot 12H_2O$.

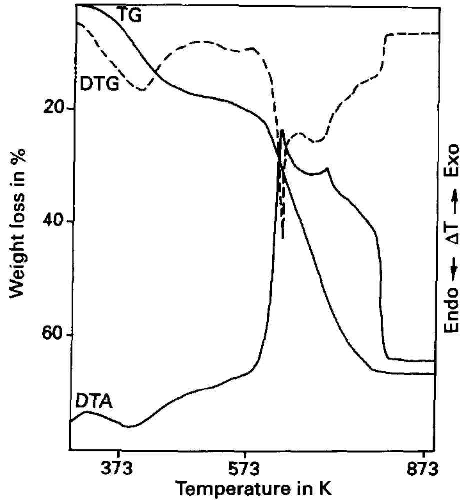

Fig. 2. TG, DTG and DTA curves of $Ce_2(C_7H_3NO_4)_3 \cdot 9H_2O$.

During heating, the hydrated complexes of Ce(III), Eu(III)–Tb(III), Ho and Lu are dehydrated in one (Ce, Eu–Tb) or two (Ho–Lu) steps. The anhydrous complexes are stable up to 518–663 K and then decompose directly to the oxides (Ce, Eu–Dy, Tm–Lu) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$

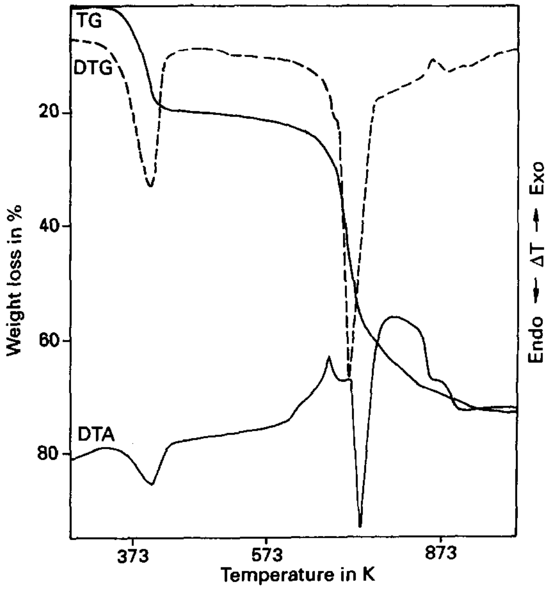

Fig. 3. TG, DTG and DTA curves of $Sm_2(C_7H_3NO_4)_3 \cdot 24H_2O$.

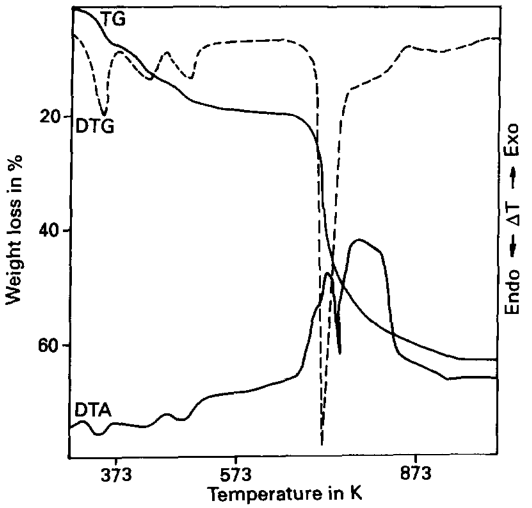

Fig. 4. TG, DTG and DTA curves of $Ho_2(C_7H_3NO_4)_3 \cdot 9H_2O$.

(Ho, Er). The complex hydrates of Y, Pr–Sm and Dy when heated lose some crystallization water molecules, and then simultaneously lose their remaining water molecules in one (Pr–Sm, Dy) or three (Y) steps, and decompose either directly to oxides (Y, Sm, Dy) or with intermediate formation of oxocarbonates (La, Pr, Nd).

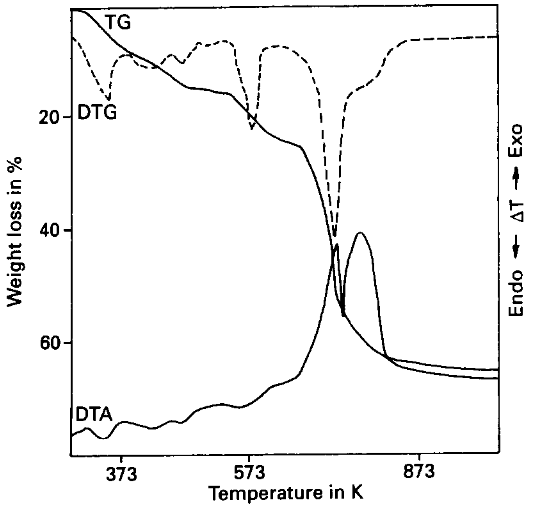

Fig. 5. TG, DTG and DTA curves of $Yb_2(C_7H_3NO_4)_3 \cdot 12H_2O$.

The results indicate that the thermal decomposition of Y and lanthanide dipicolinates can be presented in the following manner

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3, CeO_2, Tb_4O_7$ for Ln is Ce, Eu-Tb

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3$ for Ln is Tm, Yb, Lu

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$ for Ln is Ho, Er

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2O_3CO_3 \rightarrow Ln_2O_3, Pr_6O_{11}$ for Ln is La-Nd

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot yH_2O \rightarrow Ln_2O_3$ for Ln is Sm, Dy

$Y_2L_3 \cdot 12H_2O \rightarrow Y_2L_3 \cdot 10H_2O \rightarrow Y_2L_3 \cdot 4H_2O \rightarrow Y_2L_3 \cdot H_2O \rightarrow Y_2O_3$

In general, it can be suggested that hydrated rare earth element dipicolinates when heated in air lose all or some water molecules, and then decompose to the oxides either directly or with intermediate formation of oxocarbonates.

The dehydration and decomposition of the complexes are connected with a strong endothermic effect, whereas the combustion of the organic ligand shows an exothermic effect. The endothermic effect (DTA) associated with dehydration and simultaneous decomposition is larger than that for the dehydration alone.

On the basis of the IR spectra and the thermal curves, it is possible to suggest that the water molecules present in rare earth element dipicolinates are bonded in different ways. The water molecules in the Ce, and Eu-Tb complexes are probably outer-sphere water, and those in the complexes of Y, La, Pr-Sm, and Dy-Lu are outer and inner sphere water.

The temperatures of dehydration (T_0), the temperatures of decomposition (T) of the complexes and the temperatures of oxide formation (T_K) change irregularly with

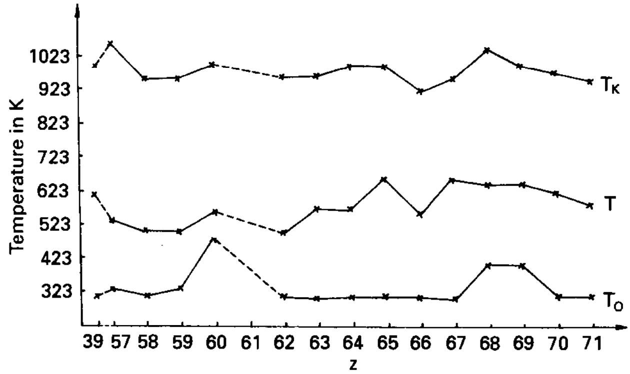

Fig. 6. Relationship between T_0, T, T_K and Z.

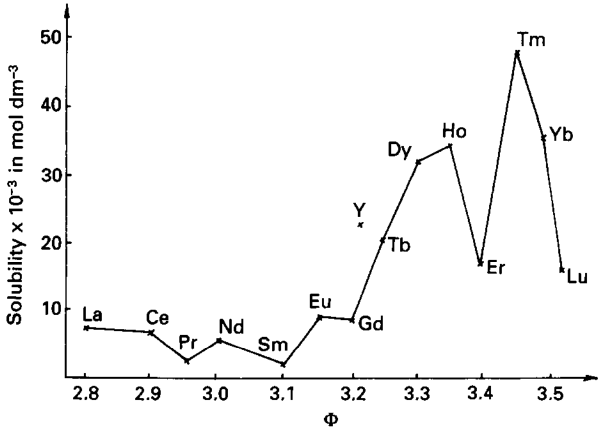

Fig. 7. Relationship between solubility and ionic potential Φ of Ln(III).

increasing atomic number Z of the metal (Fig. 6). The T_0 values are similar to each other (313–333 K) except for the hydrated complexes of Nd, Er and Tm, which are stable up to 483, 413 and 393 K, respectively. The decomposition of the anhydrous complexes begins at 518–663 K, and that of the hydrates at 513–643 K. The temperature of oxide formation changes insignificantly in the lanthanide series; La_2O_3 forms at the highest temperature (1063 K) and Dy_2O_3 at the lowest (923 K). These results are listed in Table 3.

Dipicolinates of Y and lanthanides are soluble in water. Their solubilities are in the range 10^{-2}–10^{-3} mol dm^{-3} (Table 1) and change irregularly with change in the ionic potential Φ (Fig. 7). The solubilities of Y and heavy lanthanide dipicolinates are almost ten times greater than those of light lanthanide complexes. The Tm complex is most soluble and that of Sm the least.

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