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Preparation and Properties of Lanthanide Complexes with Pyridine-2,6-dicarboxylic and Thiophene-2,5-dicarboxylic Acids. Crystal Structure of Diaqua-bis(dipicolinate)lanthanum(III) Tetrahydrate

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Abstract

Lanthanum(III), gadolinium(III) and dysprosium(III) complexes with pyridine-2,6-dicarboxylic acid (H_2pdc) of composition $Na_3[Ln(pdc)_3]\cdot nH_2O$ and $Ln(pdc)(Hpdc)\cdot mH_2O$ ($n = 5-10$; $m = 5-8$) have been prepared by reaction of aqueous solutions of $Ln(NO_3)_3\cdot nH_2O$ and H_2pdc in the presence of NaOH and their physico-chemical properties studied. The thermal behaviour of $Ln(pdc)(Hpdc)\cdot mH_2O$ has been investigated and the structure of $La(pdc)(Hpdc)\cdot 6H_2O$ determined by X-ray crystallography. The compound is monoclinic, space group $P2_1/c$, with $a = 14.120(5)$, $b = 11.280(5)$, $c = 13.038(5)$ Å, $\beta = 101.67(3)°$, and $Z = 4$. Refinement of the structure based on the 3217 observed reflexions led to the final R of 0.026. The asymmetric complex unit comprises the nine-coordinate metal ion, two dipicolinato ligands and two coordinated water molecules. One dipicolinato group provides linkage with a carboxylate oxygen, allowing the formation of a polymeric chain. Selected bond distances are La–N 2.67 Å, La–O (water) 2.51 Å (mean), La–O (pdc) 2.55 Å (mean). The interaction of thiophene-2,5-dicarboxylic acid (H_2tdc) with $Ln(NO_3)_3\cdot nH_2O$ (Ln = La, Gd, Dy; $n = 6, 5, 4$) has also been studied; there is a marked difference in the complexes obtained and consequently in the coordination ability of H_2tdc towards lanthanide with respect to H_2pdc.

Introduction

The interaction of pyridine-2,6-dicarboxylic acid (H_2pdc) with several metal ions has been studied and for some complexes the crystal structure has been determined [1–12]. In these complexes pyridine-2,6-dicarboxylate acts as a tridentate ligand by coordination of the nitrogen atom and one oxygen atom from each carboxylate group. In some complexes the remaining oxygen atoms coordinate to the adjacent metal ions to form polymeric structures [9–12]. Pyridine-2,6-dicarboxylic acid is thus a polyfunctional ligand capable of forming monomeric or polymeric complexes. With lanthanides, species like $[Ln(pdc)_3]^{3-}$ have been synthesized [13–16]. The sodium salts of these complexes with the elements Ce to Dy have almost identical triclinic structures, while hexagonal, monoclinic and orthorhombic phases have been found for elements Ho to Lu.

Interest in the study of these sytems, especially in aqueous solution, comes from the possible usefulness of the lanthanide complexes in bioinorganic chemistry, as aqueous shift reagents, particularly in the study of transport of alkali-metal ions (and alkaline-earth ions) across model and real biological membranes [17, 18]. For this purpose, it is necessary to have cationic complexes and the observation of the easy preparation of $[Ln(pdc)_3]^{3-}$ has encouraged NMR investigations on these and on the similar systems obtained by chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid) [19–21]. This ligand has a tridentate coordinating ability almost identical to that of pyridine-2,6-dicarboxylic acid, but with three ionizable protons as compared to two for H_2pdc.

Moreover, solution chemistry has shown that it is possible to obtain other lanthanide complexes like $[Ln(pdc)]^+$ or $[Ln(pdc)_2]^-$, which increase the interest in products of the reaction between H_2pdc and lanthanide ions. In addition, thiophene-2,5-dicarboxylic acid (H_2tdc) would behave in a similar coordinating way, with a useful comparison between N and S ligation ability towards lanthanide ions.

We report here some results on the interaction of H_2pdc and H_2tdc with lanthanide ions, and on the crystal structure of $[La(pdc)(Hpdc)(H_2O)_2]\cdot 4H_2O$.

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Experimental

2,6-Pyridinedicarboxylic acid (BDH), dipotassium thiophene-2,5-dicarboxylate and lanthanide nitrates $Ln(NO_3)_3 \cdot xH_2O$ ($x = 4$, 5, 6 for Dy, Gd and La respectively) (Ventron) were commercial products and were used without further purification. Lanthanide salts were stored in a dessicator to prevent hydratation.

Thiophene-2,5-dicarboxylic acid was obtained as a white product by acidification (HCl) of a solution of the dipotassium salt.

Complexes with Pyridine-2,6-dicarboxylic Acid

Ln(pdc)(Hpdc)·nH_2O ($n = 5, 6, 8$; Ln = La, Gd, Dy)

Method A. To an aqueous suspension (25 ml) of 2,6-pyridinedicarboxylic acid (1 mmol), NaOH (2 mmol) in water (5 ml) was added. To the obtained solution, the appropriate $Ln(NO_3)_3 \cdot xH_2O$ (0.5 mmol), was added in water (10 ml). The solution was stirred for 20 min, then the solvent was partially evaporated and the white precipitate obtained was filtered, washed with methanol and dried *in vacuo*.

Method B. The same procedure as method A was used, except that the aqueous solution was evaporated to dryness and the residue was treated with methanol, filtered, washed with diethyl ether and dried *in vacuo*.

Crystals of La(pdc)(Hpdc)$(H_2O)_2 \cdot 4H_2O$, suitable for the X-ray work were obtained by slow evaporation of a water solution of the crude product La(pdc)(Hpdc)·$5H_2O$.

Na_3[Ln(pdc)$_3$]·nH_2O ($n = 6, 8, 10$; Ln = La, Gd, Dy)

To an aqueous (25 ml) suspension of H_2pdc (3 mmol), NaOH (6 mmol) in water (10 ml) was added. To the obtained solution, the appropriate $Ln(NO_3)_3 \cdot xH_2O$ in water (10 ml) was added. The solution was stirred for 30 min and then evaporated to dryness. The residue was stirred in methanol (25 ml) for 1 h, then filtered, washed with methanol and dried *in vacuo*.

Physico-Chemical Measurements

IR spectra were carried out as KBr pellets by using a Perkin-Elmer 580B model spectrophotometer equipped with a data station.

Elemental analyses and infrared data of the prepared complexes are reported in Tables I and II.

The thermogravimetric and differential thermoanalysis curves were obtained by a Netzsch STA 429 thermoanalytical equipment. The tests were performed in a nitrogen atmosphere (flux rate 250 ml min^{-1}; heating rate 5 min^{-1}) and in air flux under the same conditions. Neutral alumina (C. Erba) was used as reference material.

X-ray fluorescence analyses were performed by using a Philips SEM 505 model scanning electron microscope equipped with a scanning electron microprobe; metal ratios were approximated by integration of back-scattered X-rays by using an EDAX data station.

X-ray Data for La(pdc)(Hpdc)$(H_2O)_2 \cdot 4H_2O$

A well formed crystal of maximum dimension 0.2 mm was mounted on a glass fibre and covered with epoxy adhesive. Cell constants were determined from a least-squares refinement of the setting angles of 25 medium angle reflections, which had been carefully centered on a Philips PW 1100 diffractometer. The observed intensities were corrected for Lp and for absorption [23]. Scattering factors for neutral atoms were taken from ref. 24. Crystal and intensity data are summarized in Table III. The structure was solved by standard methods and refined by full-matrix least-squares to the final conventional R factor of 2.6%. At convergence the maximum shift was 0.3σ and 0.5σ on the coordinates and the thermal parameters of the non-hydrogen atoms and 0.5σ on the coordinates of the hydrogen atoms. The temperature factors for the H atoms were held constant ($U = 0.07$ Å^2) during the refinement. The maximum residual electronic density on the final

TABLE I. Elemental Analyses for the Prepared Compounds

Compound	Found (%)			Calculated (%)		
	C	H	N	C	H	N
La(Hpdc)(pdc)·$6H_2O$	29.07	2.48	4.83	29.08	3.31	4.84
Dy(Hpdc)(pdc)·$6H_2O$	27.76	2.48	4.57	27.94	3.18	4.65
Gd(Hpdc)(pdc)·$8H_2O$	26.50	2.73	4.41	26.58	3.66	4.43
$Na_3La(pdc)_3 \cdot 5H_2O$	31.40	1.92	5.51	31.80	2.41	5.30
$Na_3Dy(pdc)_3 \cdot 10H_2O$	27.61	2.84	4.57	27.81	3.22	4.63
$Na_3Gd(pdc)_3 \cdot 8H_2O$	28.48	2.15	5.43	29.14	2.91	4.85

TABLE II. Infrared Data for the Prepared Compounds (cm^{-1})

Compound	COO^- asymm and symm
$La(Hpdc)(pdc)\cdot6H_2O$	1670sh, 1619b, 1572b, 1393
$Dy(Hpdc)(pdc)\cdot6H_2O$	1660sh, 1626s, 1616s, 1588s, 1574s, 1396
$Gd(Hpdc)(pdc)\cdot8H_2O$	1670sh, 1625sh, 1607b, 1570b, 1404
$Na_3La(pdc)_3\cdot5H_2O$	1625s, 1585s, 1389s
$Na_3Dy(pdc)_3\cdot10H_2O$	1631s, 1590s, 1396s
$Na_3Gd(pdc)_3\cdot8H_2O$	1626s, 1589s, 1396s

Fourier difference map was 0.9 e/Å^3. Positional and thermal parameters are reported in Table IV, distances and angles in Tables V and VI, and the equations of selected mean planes in Table VII.

TABLE III. Crystal and Intensity Data for $[La(pdc)(Hpdc)(H_2O)_2]\cdot4H_2O$

Monoclinic	$C_{14}H_{15}N_2O_{14}La$
Formula weight	574
Space group	$P2_1/c$
a (Å)	14.120(5)
b (Å)	11.280(5)
c (Å)	13.038(5)
β (°)	101.67(3)
Z	4
D_c	1.87 g cm^{-1}
λ(Mo Kα)	0.7107 Å
(MoKα)	23.2 cm^{-1}
Scan method	ϑ–2ϑ
Total reflections	3964
Observed reflextions	3217
2ϑ limit	50°
Criterion for observed reflexions	$I > 3\sigma(I)$

TABLE IV. Atomic Parameters for $[La(pdc)(Hpdc)(H_2O)_2]\cdot4H_2O$

Atom	x/a	y/b	z/c
Atomic coordinates			
La1	0.26836(2)	0.20768(2)	0.14835(2)
O1	0.34697(20)	0.40477(25)	0.12653(24)
O2	0.47256(23)	0.52285(28)	0.12453(28)
O3	0.35858(22)	0.01011(26)	0.13334(24)
O4	0.49013(27)	−0.09567(30)	0.12616(31)
O5	0.15064(22)	0.07031(27)	0.21596(22)
O6	0.07781(25)	−0.10581(28)	0.21399(23)
O7	0.26998(20)	0.21738(26)	−0.04903(20)
O8	0.21717(22)	0.16291(26)	−0.21536(20)
O9	0.12246(23)	0.32029(31)	0.06002(24)
O10	0.36384(25)	0.15356(35)	0.32716(24)
O11	0.04056(22)	0.30863(29)	−0.15023(22)
O12	0.03198(29)	−0.05783(34)	0.40107(28)
O13	0.38152(36)	0.72912(38)	0.11509(43)
O14	0.79235(38)	0.09981(43)	0.42193(57)
N1	0.45398(23)	0.21247(31)	0.13167(25)
N2	0.16591(22)	0.05024(28)	0.01877(23)
C1	0.50492(30)	0.11191(38)	0.13400(32)
C2	0.60374(40)	0.11143(53)	0.13922(43)
C3	0.64995(47)	0.21903(59)	0.13908(49)
C4	0.59741(40)	0.32428(51)	0.13429(42)
C5	0.49884(30)	0.31614(37)	0.13067(32)
C6	0.43476(30)	0.42358(38)	0.12675(32)
C7	0.44490(32)	0.00278(39)	0.13119(34)
C8	0.17225(26)	0.04649(34)	−0.08290(28)
C9	0.13705(29)	−0.04730(38)	−0.14716(33)
C10	0.09703(31)	−0.14264(40)	−0.10474(34)
C11	0.09101(30)	−0.13974(39)	0.00021(33)
C12	0.12453(27)	−0.04048(35)	0.05860(29)
C13	0.11716(29)	−0.02492(37)	0.17264(31)
C14	0.22368(27)	0.15067(34)	−0.11869(29)
H2	0.6359(42)	0.0261(54)	0.1467(44)
H3	0.7286(42)	0.2306(52)	0.1460(43)
H4	0.6274(41)	0.4113(54)	0.1419(44)

(continued)

TABLE IV. *(continued)*

Atom	x/a	y/b	z/c
H9	0.1425(40)	−0.0409(53)	−0.2157(45)
H10	0.0728(40)	−0.2172(53)	−0.1522(44)
H11	0.0612(40)	−0.2093(54)	0.0295(43)
H41	0.4532(44)	−0.1633(57)	0.1179(48)
H91	0.0837(44)	0.3597(58)	0.0803(48)
H92	0.1023(43)	0.3143(56)	−0.0050(50)
H101	0.4077(45)	0.1043(57)	0.3411(48)
H102	0.3484(44)	0.1817(57)	0.3785(49)
H122	0.0248(44)	0.0191(60)	0.3911(48)
H121	0.0382(45)	−0.0713(59)	0.3431(49)
H132	0.4097(45)	0.6565(59)	0.1100(48)
H131	0.3188(47)	0.7187(58)	0.1008(48)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters[a] $U_{i,j} \times 10^{-4}$						
La1	202(1)	191(1)	146(1)	−10(1)	57(1)	−1(1)
O1	238(15)	249(16)	448(18)	−15(13)	93(13)	−11(12)
O2	318(17)	284(17)	648(23)	7(16)	96(16)	−72(14)
O3	356(17)	266(16)	406(18)	−21(14)	76(14)	31(13)
O4	521(22)	286(18)	628(24)	−64(17)	147(18)	148(16)
O5	443(18)	322(17)	238(15)	−65(13)	164(13)	−111(14)
O6	625(22)	365(18)	295(16)	6(14)	242(15)	−199(16)
O7	363(16)	316(16)	172(13)	−1(12)	83(11)	−103(13)
O8	420(17)	343(16)	155(13)	24(12)	80(12)	−86(14)
O9	363(18)	470(21)	223(15)	−42(14)	21(13)	161(15)
O10	439(20)	591(23)	194(15)	−10(15)	36(14)	283(17)
O11	396(17)	432(19)	262(15)	−4(14)	92(13)	12(15)
O12	670(24)	389(20)	396(19)	−41(17)	287(18)	−136(18)
O13	651(28)	371(24)	1125(39)	−44(24)	174(28)	52(22)
O14	770(35)	474(28)	2057(67)	−30(30)	−161(39)	72(26)
N1	257(17)	284(18)	226(16)	5(15)	80(13)	16(15)
N2	220(16)	229(17)	176(15)	2(13)	69(13)	15(14)
C1	288(9)					
C2	493(13)					
C3	614(15)					
C4	479(13)					
C5	285(9)					
C6	276(9)					
C7	308(10)					
C8	204(8)					
C9	271(9)					
C10	309(9)					
C11	290(9)					
C12	226(8)					
C13	263(9)					
C14	222(8)					

[a] Anisotropic thermal parameters are in the form $T = \exp - [2\pi^2(U_{ij}H_iH_jA^*_iA^*_j)]$.

Results and Discussion

Complexes with Pyridine-2,6-dicarboxylic Acid

It was reported that in aqueous solution lanthanide ions form $[Ln(pdc)_3]^{3-}$, $[Ln(pdc)_2(H_2O)_3]^-$ and $[Ln(pdc)(H_2O)_2]^+$ species [22], and for the former complex the crystal structure is also known [13–16]. For the Ln(III)–bis-dipicolinate complexes (Ln = Ce–Dy), NMR studies in aqueous solution have shown a structure with three water molecules bonded to the central metal ions and with two dipicolinate anions acting as tridentate [22] (Fig. 1).

By reacting $Ln(NO_3)_3 \cdot nH_2O$ (Ln = La, Dy, Gd; n = 6, 5, 4 respectively) with H_2pdc in water in the presence of NaOH (in a Ln/H_2pdc/NaOH molar ratio

TABLE V. Interatomic Distances (Å)[a]

Coordination			
La–O(1)	2.526(3)	La–O(8$^{\mathrm{I}}$)	2.516(3)
La–O(3)	2.594(3)	La–O(9)	2.495(3)
La–O(5)	2.556(3)	La–O(10)	2.521(3)
La–O(7)	2.580(2)	La–N(1)	2.674(3)
		La–N(2)	2.667(3)
pdc(1)		pdc(2)	
C(6)–O(1)	1.257(5)	C(13)–O(5)	1.260(5)
C(6)–O(2)	1.243(5)	C(13)–O(6)	1.246(5)
C(7)–O(3)	1.228(5)	C(14)–O(7)	1.256(5)
C(7)–O(4)	1.289(5)	C(14)–O(8)	1.253(5)
N(1)–C(1)	1.340(5)	N(2)–C(2)	1.347(5)
N(1)–C(5)	1.331(5)	N(2)–C(12)	1.335(5)
C(1)–C(2)	1.383(7)	C(8)–C(9)	1.378(6)
C(2)–C(3)	1.378(8)	C(9)–C(10)	1.381(6)
C(3)–C(4)	1.395(8)	C(10)–C(11)	1.388(6)
C(4)–C(5)	1.386(7)	C(11)–C(12)	1.382(6)
C(5)–C(6)	1.507(6)	C(12)–C(13)	1.521(5)
Possible hydrogen bonds			
O(2)···O(13)	2.65	O(7)···O(10$^{\mathrm{I}}$)	2.71
O(2)···O(10$^{\mathrm{III}}$)	2.70	O(8)···O(9$^{\mathrm{I}}$)	2.97
O(4$^{\mathrm{IV}}$)···O(13)	2.49	O(8)···O(10$^{\mathrm{I}}$)	2.90
O(5)···O(11$^{\mathrm{I}}$)	2.90	O(9)···O(11)	2.75
O(6)···O(12)	2.70	O(9)···O(12$^{\mathrm{I}}$)	2.71
O(6)···O(11$^{\mathrm{II}}$)	2.86	O(11)···O(12$^{\mathrm{I}}$)	2.90
O(7)···O(9)	2.98	O(13)···O(14)	3.06
		O(13)···O(14$^{\mathrm{III}}$)	2.81

[a] $\mathrm{I} = x, \frac{1}{2} - y, \frac{1}{2} + z$; $\mathrm{II} = 1 - x, 1 - y, z$; $\mathrm{III} = 1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\mathrm{IV} = x, 1 - y, z$.

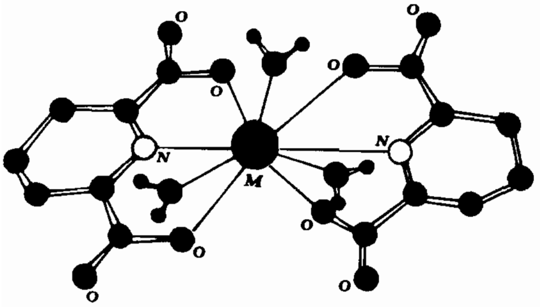

Fig. 1. The structure of $[\mathrm{Lu(pdc)_2(H_2O)_3}]^-$ in water from NMR data [22].

of 1.3:6 and 1:2:4 respectively), $\mathrm{Na_3[Ln(pdc)_3]\cdot}$$n\mathrm{H_2O}$ and $\mathrm{Ln(pdc)(Hpdc)\cdot}$$m\mathrm{H_2O}$ have been synthesized. The tris-complexes are soluble in cold water, while the bis-complexes are solubilized only by hot water. All the bis- and tris-complexes prepared behave as electrolytes in water solution, suggesting that also for $\mathrm{Ln(pdc)(Hpdc)\cdot}$$n\mathrm{H_2O}$ a dissociation occurs. A comparison of the X-ray fluorescence spectra of the two types of complexes has shown that the bis-dipicolinate complexes do not contain sodium ions. In the tris-complexes a 3:1 sodium/lanthanide ratio

TABLE VI. Bond Angles (deg) (E.s.d.s refer to the last significant digit)

Coordination			
N(1)–La–O(1)	60.8(1)	O(3)–La–O(5)	82.5(1)
N(1)–La–O(3)	60.4(1)	O(1)–La–O(7)	76.0(1)
N(2)–La–O(5)	60.5(1)	O(3)–La–O(7)	81.8(1)
N(2)–La–O(7)	60.6(1)	O(1)–La–O(9)	80.8(1)
N(1)–La–O(7)	73.2(1)	O(7)–La–O(9)	72.0(1)
N(1)–La–O(10)	74.4(1)	O(3)–La–O(10)	71.5(1)
N(2)–La–O(3)	65.9(1)	O(5)–La–O(10)	78.3(1)
N(2)–La–O(9)	75.8(1)	O(5)–La–O(9)	86.2
O(8$^{\mathrm{I}}$)–La–O(1)	76.4(1)	N(1)–La–N(2)	112.1(1)
O(8$^{\mathrm{I}}$)–La–O(10)	70.3(1)	N(1)–La–O(8$^{\mathrm{I}}$)	118.2(1)
O(8$^{\mathrm{I}}$)–La–O(5)	78.9(1)	N(2)–La–O(8$^{\mathrm{I}}$)	129.6(1)
O(8$^{\mathrm{I}}$)–La–O(9)	72.7(1)		
pdc(1)		pdc(2)	
La–O(1)–C(6)	127.1(3)	La–O(5)–C(13)	125.0(2)
La–O(3)–C(7)	124.4(3)	La–O(7)–C(14)	126.0(2)
C(1)–C(7)–O(3)	120.4(4)	C(12)–C(13)–O(5)	116.3(4)
C(1)–C(7)–O(4)	115.3(4)	C(12)–C(13)–O(6)	117.6(4)
O(3)–O(7)–O(4)	124.3(4)	O(5)–C(13)–O(6)	126.1(4)
C(5)–C(6)–O(11)	116.7(4)	C(8)–C(14)–O(7)	117.2(4)
C(5)–C(6)–O(2)	117.9(4)	C(2)–C(14)–O(8)	117.2(3)
O(1)–O(6)–O(2)	125.4(4)	O(7)–C(14)–O(8)	125.4(4)
		La–O(8$^{\mathrm{I}}$)–C(14$^{\mathrm{I}}$)	143.3(3)

TABLE VII. Selected Mean Planes[a]

Plane I: O(1), O(5), O(9), O(10) [La]
$0.457X - 0.574Y - 0.679Z = -1.737$ Å
[O(1) 0.11, O(5) 0.12, O(9) –0.14, O(10) –0.14, La 0.66]

Plane II: N(1), N(2), O(3), O(7) [La]
$0.511X - 0.533Y - 0.674Z = 0.951$ Å
[N(1) – 0.26, N(2) – 0.24, O(3) 0.25, O(7) 0.18, La – 1.74]

Plane III: O(3), O(5), O(10) [La]
$0.003X - 0.837Y + 0.548Z = 0.851$ Å
[La 1.76]

Plane IV: O(1), O(7), O(9) [La]
$-0.040X + 0.732Y - 0.679Z = 2.062$ Å
[La –1.77]

Plane V: O(1), C(6), C(5), N(1), C(1), C(7), O(3) [La]
$0.013X - 0.017Y - 0.999Z = -1.631$ Å
O(1) 0.00, C(6) 0.01, C(5) –0.01, N(1) –0.01,
[C(1) –0.01, C(7) 0.03, O(3) –0.01, La –0.26]

Plane VI: O(5), C(13), C(12), N(2), C(8), C(14), O(7) [La]
$0.807X - 0.530Y + 0.259Z = 1.629$ Å
[O(5) 0.08, C(13) –0.06, C(12) –0.10, N(2) 0.02,
C(8) 0.04, C(14) 0.12, O(7) –0.09, La –0.36]

Planes	Angle (deg)
1–2	3.9
3–4	9.9
5–6	76.1

[a] X, Y and Z are orthogonal coorinates which are related to the fractional coordinates by the expression: $X = 14.120x - 2.637z$; $Y = 11.280y$; $Z = 12.768z$.

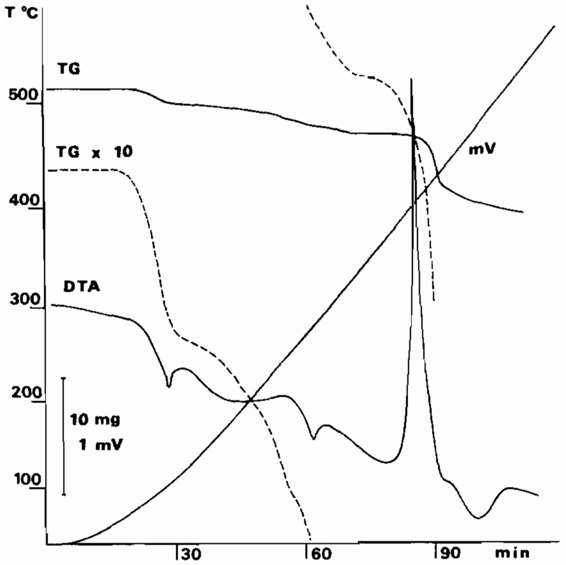

Fig. 2. Thermograms of La(pdc)(Hpdc)$(H_2O)_2 \cdot 4H_2O$ (23.44 mg).

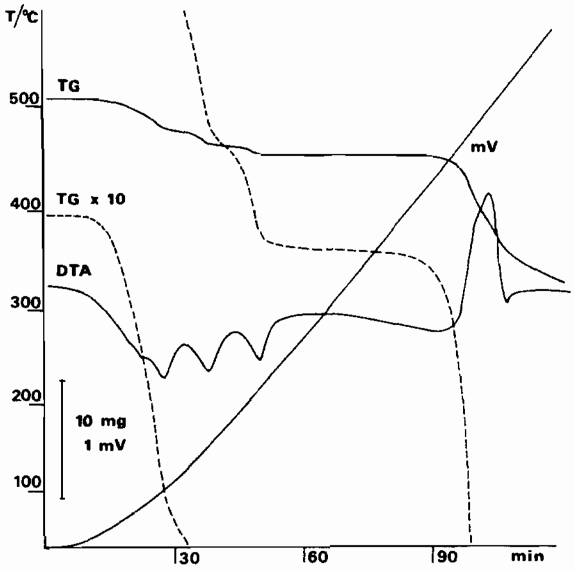

Fig. 3. Thermograms of Dy(pdc)(Hpdc)$\cdot 6H_2O$ (31.00 mg).

was observed by integration of back-scattered X-rays by using a scanning electron microprobe [25].

A comparison of the IR spectra of the bis- and tris-complexes does not show significative differences except for an additional shoulder at about 1660–1670 cm^{-1} for the bis-complexes, which render the peaks broader due to $\nu_{asym}COO^-$; it must be noted that in pyridine-2,6-dicarboxylic acid the band ν(C=O) lies at 1703 cm^{-1} and the ν(C–O) can be associated with the band at $\simeq 1300$ cm^{-1}.

The thermal behaviour of crystals of La(pdc)(Hpdc)$\cdot 6H_2O$, grown from water, has shown the loss of the water molecules in three distinct, well detectable steps (Fig. 2).

Two water molecules are lost at about 87 °C, another two in the 120–200 °C temperature range and the last two molecules at about 300 °C. Above 300 °C there is decomposition of the sample, which does not allow further studies on the anhydrous complex. This decomposition is probably (possibly) also due to a coordination change about the lanthanum ion. Also the thermal behaviour of powders of La(pdc)(Hpdc)$\cdot 6H_2O$ shows a step-by-step loss of the water molecules; two water molecules are also lost under dry gas flux at room temperature, two at 110 °C and the last two at 170 °C. It must be noted that different samples, obtained by the same experimental procedures, contain variable amounts of water (4, 5 or 6), in agreement with the thermal behaviour observed. Powder samples produce anhydrous complexes stable in the 200–300 °C temperature range. The IR spectrum of these compounds is almost identical to that of the starting complex La(pdc)(Hpdc)$\cdot 6H_2O$, obviously with the absence of the absorption band due to the water molecules.

These data seem to suggest that the crystals represent one of the possible structural forms of La(pdc)(Hpdc)$\cdot 6H_2O$. Anhydrous La(pdc)(Hpdc), obtained by thermal heating of the powders, retakes four water molecules in air. The additional two water molecules are too labile, in agreement with thermal results. The elemental analysis agrees with the formulation La(pdc)(Hpdc)$\cdot 4H_2O$.

Dy(pdc)(Hpdc)$\cdot 6H_2O$ loses water molecules in three distinct steps. The first loss of three water molecules is observed also at room temperature only by maintaining the sample in a dry gas flux. On heating, this loss was observed at about 90 °C.

Two additional water molecules are lost at 150 °C and the remaining sixth molecule is lost at 211 °C. The anhydrous complex obtained is stable in the 245–420 °C temperature range and its IR spectrum is completely comparable, with the exception of the water absorption bands, to that of the hydrate starting complex. In air the anhydrous complex retakes four water molecules as the lanthanum analogue. Again the elemental analysis agrees with the formulation Dy(pdc)(Hpdc)$\cdot 4H_2O$.

On the basis of these results, only one water molecule should be directly coordinated to dysprosium (Fig. 3).

The thermal analysis of Gd(pdc)(Hpdc)$\cdot 8H_2O$ shows that the water molecules are lost in one step with a maximum at 120 °C. The anhydrous complex obtained is stable in the 200–435 °C temperature range; it has an IR spectrum comparable to those of the lanthanum and gadolinium analogues, but significantly different from the starting complex Gd(pdc)(Hpdc)$\cdot 8H_2O$. It should be noted that the hydrogen percentage has always been found to be less than ex-

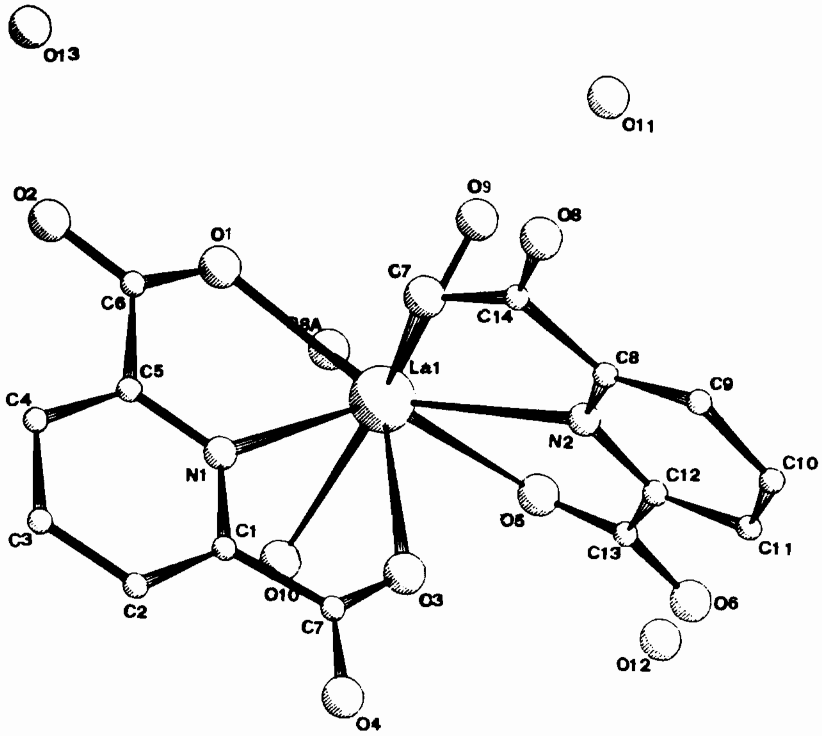

Fig. 4. Crystal structure of $[La(pdc)(Hpdc)(H_2O)_2]\cdot 4H_2O$.

pected, possibly owing to a partial loss of water of crystallization.

X-ray Structure of $[La(pdc)(Hpdc)(H_2O)_2]\cdot 4H_2O$

The crystal structure determination shows the complex to be $\{[La(pdc)(Hpdc)(H_2O)_2]\cdot 4H_2O\}_n$, the lanthanum atom being nine-coordinate.

Figure 4 shows the asymmetric unit with the atom numbering scheme. In each unit two dipicolinate ions are chelated to the metal atom through the nitrogen and two carboxylate oxygens, and one of them links a further La atom by a multidentate bridging bond with one remaining carboxylate oxygen (the O(8) atom). Thus the repeating units are linked to form a polymeric chain which extends along the *c* axis of the cell, as shown in Fig. 5. Two of the six formula water molecules are directly bonded to La. The coordination polyhedron around La can be considered to be a monocapped square-antiprism with $O(8^I)$ in the apical position, as shown in Fig. 6. Mean planes for the atoms comprising the base of the polyhedron and those comprising the base of the pyramidal cap are given in Table VII with the displacement from these planes. The La atom lies 0.66 Å below the base of the pyramidal cap and 1.74 Å above the base of the coordination polyhedron. However, as shown in Fig. 7, the coordination geometry approaches also that of the tricapped trigonal prism, where N(1), N(2) and $O(8^I)$ form the caps.

Mean planes for the atoms comprising the two trigonal faces, which are twisted by 15° from one another, are reported in Table VII. The La atom lies 1.76 Å below the plane formed by O(3), O(10) and O(5), and 1.77 Å above the plane formed by O(1), O(7) and O(9). The four La–O bonds of the organic ligands to the same La atom are in the range 2.526–2.594 Å, with a mean value of 2.564 Å, which is significantly longer than the two La–O(water) distances (mean 2.508 Å). This feature suggests that factors related to the geometry of the polydentate ligands should also play a role in determining the length of the four above mentioned La–O(pdc) bonds; the fact that the length of the La–$O(8^I)$ bond (2.516(3) Å) with the external bridging oxygen of the next repeating unit is fully comparable to that of the La–O(water) bonds seems to confirm this view. The La–N bonds agree well themselves and, as usual, are considerably longer (mean 2.670 Å) than the La–O bonds.

One of the two pdc ligands, bridged through the O(8) atom, is bianionic, while the other is monoanionic, having one protonated –COOH and one ionized $-COO^-$ group. This feature, which provides the electroneutrality of the compound, is directly supported by the circumstance that the presence and the position of the carboxylic hydrogen atom H(4) were determined with sufficient confidence and confirmed during the structure refinement, and indirectly by structural details. In fact, the C–O bond

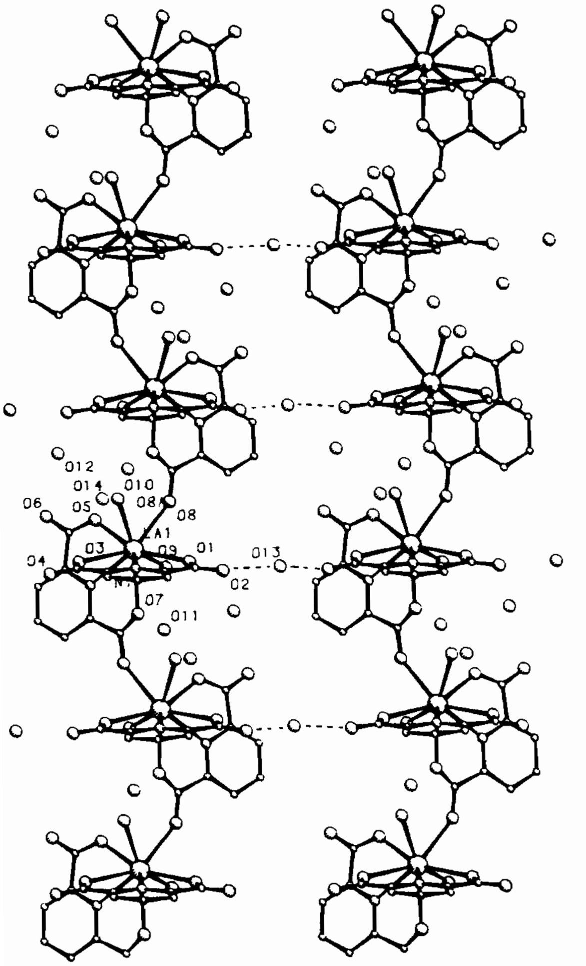

Fig. 5. The polymeric chain of $[La(pdc)(Hpdc)(H_2O)_2] \cdot 4H_2O$. Projection along the *a* axis.

lengths in the anionic carboxylates are in the range 1.24–1.26 Å, showing delocalization of the negative charge with formation of partial double C–O bonds; on the contrary, these distances are 1.23 Å and 1.29 Å in the carboxylic group, which is coordinated to La through O(3), the ketonic oxygen atom.

As shown in Table V, the two coordinated and the four clathrate water molecules are involved in a rather complicated network of hydrogen bonds which link together adjacent polymeric chains of the complex and provide compactness and stability to the crystal packing (Fig. 5).

Complexes with Thiophene-2,5-dicarboxylic Acid

The interaction of thiophene-2,5-dicarboxylic acid with lanthanide(III) nitrates gives rise to different systems. Complexes, formulable on the basis of elemental analyses as $Ln_2(tdc)_3 \cdot nH_2O$ (Ln = La, Gd, Dy), have been found by reaction of H_2tdc, NaOH and the appropriate lanthanide nitrate hydrate in water. White powders or microcrystalline compounds have been obtained. With samarium(III) nitrate, under similar conditions, only $Sm(tdc)OH \cdot H_2O$ was obtained. Both compounds have been synthesized with gadolinium. Metal and sulphur ratios and the homogeneity of the samples were determined also by using a scanning electron microprobe.

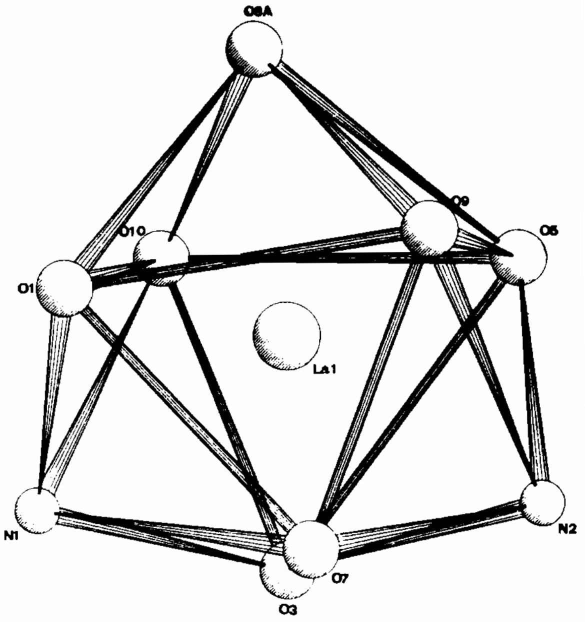

Fig. 6. The monocapped square-antiprism around La.

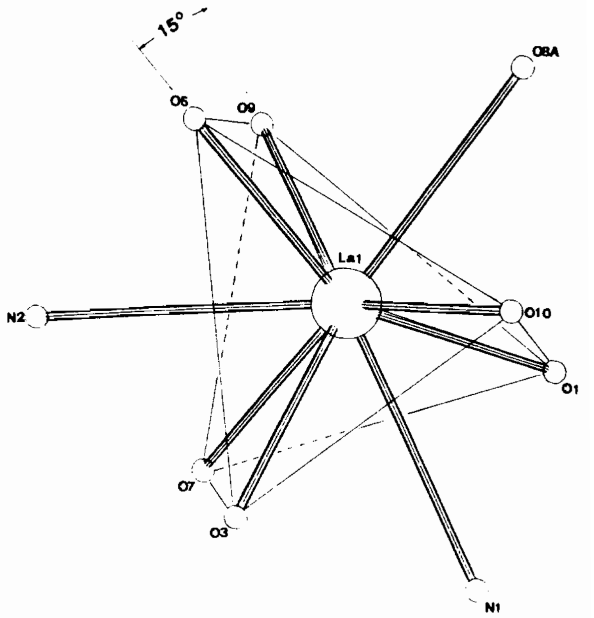

Fig. 7. The tricapped trigonal prism around La.

The compounds obtained are insoluble in common organic solvents, thus preventing any correct assignment of their structural configuration. The infrared spectrum of H_2tdc shows ν(C=O) at 1764 cm^{-1} as a shoulder and at 1666 cm^{-1} as a strong band and the ν(C–O) at 1279 cm^{-1}. In the spectrum of Na_2tdc, the $\nu_{asym}(COO^-)$ lies at 1569 cm^{-1} and the ν_{symm}-(COO) at 1386 cm^{-1}; the ν_{asym}(COO) is lowered at 1558–1547 cm^{-1} while the ν_{symm}(COO) is unchanged by coordination to lanthanide ions.

It seems that, on changing nitrogen with sulphur, the stoichiometry of the prepared complexes and perhaps the coordination ability of the ligand drastically change. This behaviour could reflect the more pronounced tendency of hard ions to link to nitrogen rather than sulphur; it must be noted, however, that Schiff bases containing a thioetheric sulphur in the aliphatic chain, give Ln–S and UO_2–S bonds easily.

In contrast to the lanthanide compounds synthesized with pyridine-2,6-dicarboxylic acid, we were not successful in the preparation of bis- or tris-lanthanide thiophene-2,5-dicarboxylate complexes.

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References

1 G. den Baef and H. Hoppa, *Talanta, 15*, 1058 (1968).
2 D. V. Naik and C. Curran, *Inorg. Chem., 10*, 1017 (1971).
3 G. Strahs and R. E. Dickerson, *Acta Crystallogr., Sect. B, 24*, 571 (1968).
4 G. H. Bershed, R. L. Berford and I. C. Paul, *Inorg. Chem., 8*, 1557 (1968).
5 M. G. B. Drew, R. W. Mathews and R. A. Walton, *J. Chem. Soc. A*, 1405 (1970).
6 G. Gaw, W. R. Robinson and R. A. Walton, *Inorg. Nucl. Chem. Lett., 7*, 695 (1971).
7 K. J. Palmer, R. Y. Wang and J. C. Lewis, *Acta Crystallogr., Sect. B, 28*, 223 (1972).
8 G. Marangoni, S. Degetto and U. Croatto, *Talanta, 20*, 1217 (1973).
9 G. Marangoni, S. Degetto, R. Graziani, G. Bombieri and E. Forsellini, *J. Inorg. Nucl. Chem., 36*, 1787 (1974).
10 S. Degetto, G. Marangon, L. Baracco, S. Gurrieri and G. Siracusa, *J. Inorg. Nucl. Chem., 37*, 1185 (1975), and references therein.
11 L. Cattalini, L. Baracco, S. Degetto, G. Marangoni, L. Maresca and L. Sindellari, *Gazz. Chim. Ital., 104*, 905 (1974).
12 S. Degetto, L. Baracco, R. Graziani and E. Celon, *Transition Met. Chem., 3*, 351 (1978).
13 J. Albertsson, *Acta Chem. Scand., 24*, 1213 (1970).
14 J. Albertsson, *Acta Chem. Scand., 26*, 985 (1972).
15 J. Albertsson, *Acta Chem. Scand., 26*, 1005 (1972).
16 J. Albertsson, *Acta Chem. Scand., 26*, 1023 (1972).
17 M. M. Pike, S. R. Simon, J. A. Balschi and C. S. Springer, *Proc. Natl. Acad. Sci. U.S.A., 79*, 810 (1982).
18 J. A. Balschi, V. P. Cirillo and C. S. Springer, *J. Biophys., 38*, 323 (1982).
19 M. M. Pike and C. S. Springer, *J. Magn. Reson., 46*, 348 (1982).
20 J. A. Balschi, V. P. Cirillo, W. J. Le Noble, E. C. Schreiber, S. R. Simon and C. S. Springer, *Rare Earth Mod. Sci. Technol., 3*, 15 (1982).
21 M. M. Pike, D. M. Yarmuch, J. A. Balschi, R. E. Lenkinski and C. S. Springer, *Inorg. Chem., 22*, 2388 (1983).
22 R. J. P. Williams, 'Structure and Bonding', Vol. 50, Springer Verlag, Berlin, 1982, p. 79.
23 A. C. T. North, D. C. Phillips and F. S. Matheus, *Acta Crystallogr., Sect. A, 24*, 351 (1968).
24 D. T. Cromer and D. Libermann, *J. Chem. Phys., 53*, 1891 (1970).
25 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 119*, 215 (1986).