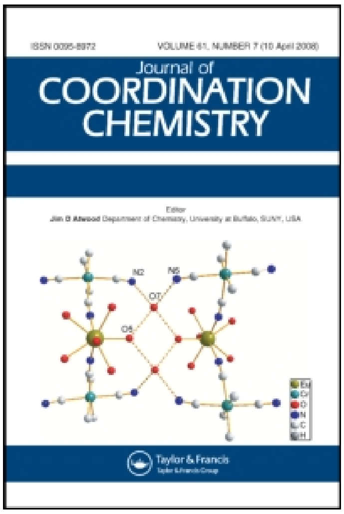

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A New Type of Lanthanide(III) Complex with 3-Hydroxybenzoic Acid, $[ML_3(H_2O)_3].2H_2O$. Crystal and Molecular Structure of Triaquatris(3-Hydroxybenzoato)-Neodymium(III) Dihydrate

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A NEW TYPE OF LANTHANIDE(III) COMPLEX WITH 3-HYDROXYBENZOIC ACID, $[ML_3(H_2O)_3].2H_2O$. CRYSTAL AND MOLECULAR STRUCTURE OF TRIAQUATRIS(3-HYDROXYBENZOATO)-NEODYMIUM(III) DIHYDRATE

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Triaquatris(3-hydroxybenzoato)neodymium(III) dihydrate, a new type of lanthanide complex with 3-hydroxybenzoic acid, crystallizes in the monoclinic space group $C2/c$ with $a = 22.220(8)$, $b = 10.007(6)$, $c = 22.086(8)$ Å, $\beta = 99.33(3)°$ and $Z = 8$. The crystal and molecular structure of the complex has been determined using X-ray diffraction data measured with MoKα radiation. The Nd^{3+} ion is coordinated to nine oxygen atoms, with Nd–O distances ranging from 2.338(7) to 2.697(6) Å. The coordinated oxygen atoms are from three water molecules and six oxygen atoms are from the 3-hydroxybezoate anions. There are three different binding modes for the anion to the Nd^{3+} ion: mono-, bi- and terdentate.

Keywords: Lanthanides; 3-hydroxybenzoic acid, complexes, X-ray structure.

INTRODUCTION

The reaction of lanthanide(III) hydroxides with an excess of 3-hydroxybenzoic acid, henceforth HL, in a hot aqueous solution gives two types of complexes depending on the size of the lanthanide cation.[1] The formulae of these complexes are (see also Fig. 1) (I) $[ML_3(H_2O)_2]\cdot HL\cdot 2H_2O$, M = La–Nd, and (II) $[ML_3(H_2O)_3]_2\cdot 2H_2O$, M = Sm, Gd, Dy, Er, Yb. The composition of the type II complexes does not depend on the $M(OH)_3 : HL$ ratio as long as an excess of HL is used. However, complex III, $[CeL_3(H_2O)]_n$, was found when a 1 : 3 mol ratio of $Ce(OH)_3$ and HL was used. The crystal structure of III has been reported.[2]

Recent solid state studies used the complexes formed in the reaction of $M(OH)_3$, M = lanthanide or yttrium, with HL in a 1 : 3 mol ratio.[3–6] In this case the analytical data suggested a new class of complexes for M = La, Pr, Nd which differed from the three classes previously reported.[1,2] Therefore, single crystal X-ray diffraction studies of the series of complexes were undertaken.

EXPERIMENTAL

The crystals of complexes of lanthanides(III) and yttrium(III) with 3-hydroxybenzoic acid were obtained by recrystallization from an aqueous solution. The crystal data

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TABLE I

Crystal data for triaquatris(3-hydroxybenzoato) lanthanide(III) hydrates $[M(C_7H_5O_3)_3(H_2O)_3].xH_2O$, $\{3 + x = n\}$.

1	Ln(III).nH$_2$O	Y.4H$_2$O	*La.5H$_2$O	*Pr.5H$_2$O	*Nd.5H$_2$O	*Sm.4H$_2$O	Eu.4H$_2$O	Gd.4H$_2$O
2	M_w	572.31	640.33	642.33	645.66	633.76	635.39	640.66
3	space group	$P\bar{1}$	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
4	a (Å)	10.58	22.278(9)	22.278(4)	22.220(8)	10.611(2)	10.34	10.51
5	b (Å)	11.74	10.086(8)	10.014(1)	10.007(6)	12.048(4)	11.97	12.00
6	c (Å)	10.00	22.112(10)	22.100(7)	22.086(8)	10.130(1)	10.14	10.09
7	α (°)	112.0				111.14(2)	112.0	112.0
8	β (°)	90.0	99.17(3)	99.42(2)	99.33(3)	90.20(2)	91.7	90.0
9	γ (°)	92.7				97.15(2)	93.3	93.8
10	V (Å^3)	1163.5	4905.0(4.5)	4864.1(9)	4846(2)	1196.9(5)	1164.6	1176.4
11	Z	2	8	8	8	2	2	2
12	d_x (g cm^{-3})	1.63	1.74	1.754	1.77	1.76	1.81	1.81
13	d_m (g cm^{-3})	1.62	1.757	1.758	1.77	1.76	1.76	1.81

1	Tb.4H$_2$O	Dy.4H$_2$O	Ho.4H$_2$O	*Er.4H$_2$O	Tm.4H$_2$O	Yb.4H$_2$O	Lu.4H$_2$O
2	642.33	645.91	648.23	650.66	652.34	656.45	658.37
3	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
4	10.58	10.43	10.45	10.615(2)	10.45	10.45	10.42
5	11.69	12.11	11.88	11.968(1)	11.93	11.82	11.78
6	10.04	10.12	10.05	10.054(1)	9.97	9.90	10.00
7	105.0	112.0	111.0	111.10(1)	110.0	109.5	110.0
8	90.0	90.0	90.0	90.41(1)	90.0	90.0	90.0
9	97.7	98.2	92.2	97.18(1)	94.4	96.0	94.4
10	1185.9	1165.8	1163.05	1180.4(3)	1163.7	1146.0	1149.9
11	2	2	2	2	2	2	2
12	1.80	1.84	1.85	1.83	1.86	1.90	1.90
13	1.79	1.80	1.80	1.83	1.83	1.84	1.85

* Parameters obtained by least-squares refinement of the diffractometer settings for 15 independent reflections.

for these complexes (except Ce) are given in Table I. The densities were measured by flotation in a bromobenzene/ethylene bromide mixture. Unit cell parameters were obtained from oscillation and de Jong-Bouman or Weissenberg photographs or from diffractometer measurements.

Two isomorphic groups are observed. The type II complexes containing four water molecules per metal ion {$[ML_3(H_2O)_3]H_2O$, where M = Sm–Lu and Y} are dimeric and crystallize in the triclinic system with space group $P\bar{1}$. Structures of this type were described previously.[1]

The second isomorphic group includes complexes of La, Pr and Nd with the formula (IV) $[ML_3(H_2O)_3]2H_2O$, crystallizing in space group *C*2/*c*. This is a new type of lanthanide(III) complex with 3-hydroxybenzoic acid.

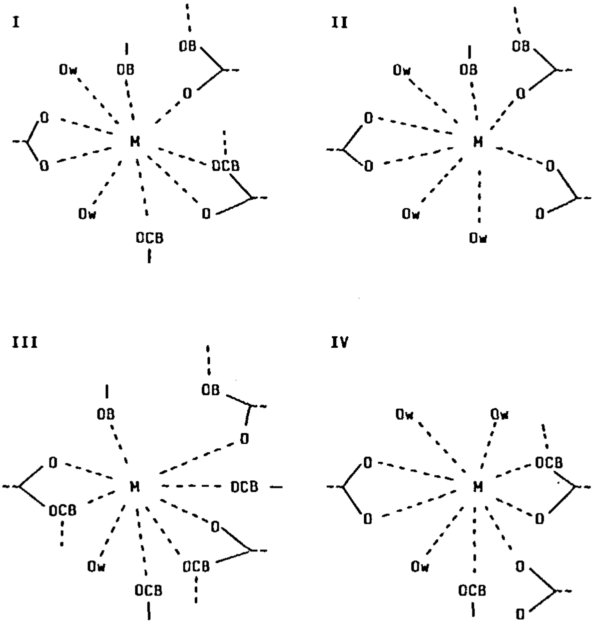


FIGURE 1 General stereochemistry of lanthanide(III) and yttrium(III) complexes with 3-hydroxybenzoic acid; I: $[ML_3(H_2O)_2]{\cdot}HL{\cdot}2H_2O$ (ref. 1), M = La–Nd, coordination number 9; II:$[ML_3(H_2O)_3]_2{\cdot}2H_2O$ (ref. 1 and this paper), M = Sm–Lu and Y, coordination number 8; III:$[ML_3(H_2O)]_n$ (ref. 2), M = Ce, coordination number 9; IV:$[ML_3(H_2O)_3]{\cdot}2H_2O$ (this paper), M = La, Pr, Nd; coordination number 9 (OB-bridging oxygen atom; OCB-chelating and bridging oxygen atom).

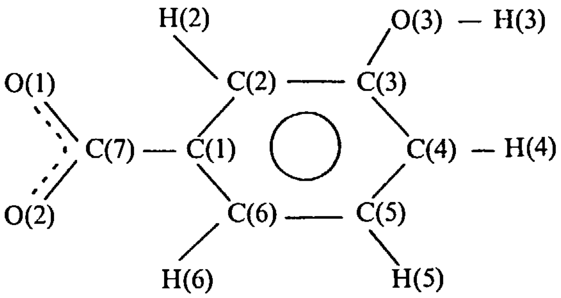
A set of three-dimensional X-ray diffraction data was collected for the Nd complex, triaquatris(3-hydroxybenzoato)neodymium(III) dihydrate. The crystal had dimensions 0.42 × 0.32 × 0.20 mm. Intensities of reflections were measured on a Nicolet R3m diffractometer at room temperature (T = 295K), using MoKα graphite-monochromated radiation ($\lambda = 0.71069$ Å, $\mu = 22.1\ \mathrm{cm}^{-1}$). A variable speed (2.0–29.3° min^{-1}), θ–2θ scan technique, was used in the 2θ range 4–47°. Stationary background counts were recorded on each side of the reflection. Two standard reflections monitored after every 50 reflections showed no intensity variations. A total of 3825 unique reflections was collected; range *h* 0–24, *k* 0–11, *l* ±25. The Patterson synthesis gave the position of the Nd ion. The positions of the ligand atoms were obtained from subsequent Fourier syntheses. The model was refined by

TABLE II

Atomic coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^3) for the heavy atoms.

	x/a	*y/b*	*z/c*	*U**
Nd	307(1)	2031(1)	−19(1)	18(1)
Ow(1)	340(3)	4076(6)	−673(3)	25(2)
Ow(2)	1360(3)	2071(8)	−298(3)	42(3)
Ow(3)	1022(3)	637(6)	711(3)	27(2)
Ow(4)	4052(4)	1302(8)	1788(4)	51(3)
Ow(5)	614(4)	7492(7)	2011(3)	48(3)
C(1A)	−1608(4)	3310(9)	−393(4)	28(3)
C(2A)	−1824(4)	4217(10)	−10(5)	31(4)
C(3A)	−2441(5)	4587(11)	−134(5)	39(4)
C(4A)	−2819(5)	4080(12)	−632(5)	42(4)
C(5A)	−2599(5)	3197(12)	−1020(6)	50(4)
C(6A)	−1994(5)	2786(11)	−899(5)	38(4)
C(7A)	−956(4)	2908(9)	−272(4)	21(3)
O(1A)	−597(3)	3474(6)	145(3)	23(2)
O(2A)	−773(3)	1980(6)	−577(3)	29(2)
O(3A)	−2688(3)	5479(9)	233(4)	63(4)
C(1B)	−546(4)	712(9)	1530(4)	25(3)
C(2B)	−697(4)	47(10)	2035(4)	25(3)
C(3B)	−881(5)	752(11)	2507(4)	36(4)
C(4B)	−914(8)	2126(13)	2479(5)	71(6)
C(5B)	−752(9)	2793(12)	1981(6)	90(8)
C(6B)	−586(7)	2083(12)	1504(5)	61(5)
C(7B)	−367(4)	−93(10)	1027(4)	24(3)
O(1B)	−311(3)	430(6)	515(3)	28(2)
O(2B)	−286(3)	−1338(6)	1105(3)	29(2)
O(3B)	−1036(4)	139(8)	3014(3)	49(3)
C(1C)	1645(4)	3987(10)	1474(4)	25(3)
C(2C)	2002(4)	3050(11)	1233(4)	34(3)
C(3C)	2579(5)	2740(11)	1538(5)	38(4)
C(4C)	2805(5)	3348(12)	2090(5)	45(4)
C(5C)	2448(5)	4294(12)	2334(5)	49(5)
C(6C)	1881(5)	4630(11)	2024(5)	40(4)
C(7C)	1009(5)	4276(9)	1155(4)	27(3)
O(1C)	779(3)	3504(7)	733(3)	36(2)
O(2C)	728(3)	5253(7)	1330(3)	33(2)
O(3C)	2915(4)	1805(9)	1276(4)	61(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.



"blocked cascade" least-squares. First, isotropic temperature factors and positional parameters were refined for all nonhydrogen atoms. After that, refinement with anisotropic temperature factors followed. A difference Fourier map then showed positions of all H-atoms. The H-atom contributions were included in the structure factor calculations but their parameters were not refined.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; final $R = 0.052$, $wR = 0.062, S = 5.52$ for 3468 observed reflections $|F_o/\sigma(F_o) \geqslant 2|$ and 325 variables. The maximum shift/σ ratio in the last cycle was 0.01 and the final difference electron density map showed residual peaks in the range from −2.40 to 2.15 $e\text{Å}^{-3}$, the highest near the Nd ion.

All calculations were carried out using the SHELXTL crystallographic computer system on a DG Model 30 Desktop Eclipse.[7] The final atomic parameters are given in Tables II and III. Lists of observed and calculated structure factors and anistropic thermal parameters for the nonhydrogen atoms can be obtained from the Editor on request.

TABLE III

H-Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$).

	x/a	*y/b*	*z/c*	*U*
H(2A)	−1567	4664	367	50
H(3A)	−2286	6101	435	50
H(4A)	−3231	4398	−734	50
H(5A)	−2924	2746	−1374	50
H(6A)	−1784	2058	−1187	50
H(2B)	−876	−996	2052	50
H(3B)	−841	−788	3033	50
H(4B)	−864	2708	2926	50
H(5B)	−966	3806	1891	50
H(6B)	−513	2500	1169	50
H(2C)	1920	2738	800	50
H(3C)	3490	1608	1414	50
H(4C)	3218	3095	2361	50
H(5C)	2664	4959	2675	50
H(6C)	1595	5361	2230	50
H(1W1)	−32	4225	−830	50
H(2W1)	600	4490	−672	50
H(1W2)	1510	1952	−633	50
H(2W2)	1721	1695	−70	50
H(1W3)	1017	732	1121	50
H(2W3)	988	−379	681	50
H(1W4)	4354	1556	2114	50
H(2W4)	4079	1402	1509	50
H(1W5)	288	7886	1776	50
H(2W5)	697	7136	1714	50

RESULTS AND DISCUSSION

The triaquatris(3-hydroxybenzoato)neodymium(III) dihydrate structure is illustrated in Fig. 2. The distances and angles involving the Nd^{3+} ion and 3-hydroxybenzoate anions are given in Table IV. The Nd^{3+} ion is coordinated to nine oxygens, six

TABLE IV

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Nd(C_7H_5O_3)_3(H_2O)_3].2H_2O$

Bond lengths (Å)			
		coordination polyhedron	
Nd–Ow(1)	2.513(6)	Nd–O(1B)	2.524(7)
Nd–Ow(2)	2.515(7)	Nd–O(1B)*	2.697(6)
Nd–Ow(3)	2.498(6)	Nd–O(2B)*	2.490(7)
Nd–O(1A)	2.546(6)	Nd–O(1C)	2.338(7)
Nd–O(2A)	2.514(6)		
	anion A	anion B	anion C
C(1)–C(2)	1.380(14)	1.386(14)	1.389(15)
C(2)–C(3)	1.403(14)	1.374(15)	1.383(15)
C(3)–C(4)	1.370(15)	1.379(17)	1.382(15)
C(4)–C(5)	1.374(18)	1.383(20)	1.399(17)
C(5)–C(6)	1.389(15)	1.369(19)	1.374(15)
C(1)–C(6)	1.396(13)	1.375(15)	1.399(14)
C(1)–C(7)	1.484(13)	1.476(14)	1.500(13)
C(7)–O(1)	1.252(10)	1.271(12)	1.254(11)
C(7)–O(2)	1.253(11)	1.266(12)	1.254(12)
C(3)–O(3)	1.378(15)	1.370(13)	1.381(14)
Bond angles (°)			
		coordination polyhedron	
Ow(1)–Nd–Ow(2)	74.4(2)	Ow(3)–Nd–O(1B)*	73.1(2)
Ow(1)–Nd–Ow(3)	138.7(2)	Ow(3)–Nd–O(2B)*	112.1(2)
Ow(1)–Nd–O(1A)	73.6(2)	Ow(3)–Nd–O(1C)	74.3(2)
Ow(1)–Nd–O(2A)	81.3(2)	O(1A)–Nd–O(2A)	50.9(2)
Ow(1)–Nd–O(1B)	148.7(2)	O(1A)–Nd–O(1B)	78.0(2)
Ow(1)–Nd–O(1B)*	120.5(2)	O(1A)–Nd–O(1B)*	129.1(2)
Ow(1)–Nd–O(2B)*	70.8(2)	O(1A)–Nd–O(2B)*	113.8(2)
Ow(1)–Nd–O(1C)	81.0(2)	O(1A)–Nd–O(1C)	79.3(2)
Ow(2)–Nd–Ow(3)	69.4(2)	O(2A)–Nd–O(1B)	70.6(2)
Ow(2)–Nd–O(1A)	144.3(2)	O(2A)–Nd–O(1B)*	81.3(2)
Ow(2)–Nd–O(2A)	137.1(2)	O(2A)–Nd–O(2B)*	69.8(2)
Ow(2)–Nd–O(1B)	136.3(2)	O(2A)–Nd–O(1C)	130.1(2)
Ow(2)–Nd–O(1B)*	81.4(2)	O(1B)–Nd–O(1B)*	69.4(3)
Ow(2)–Nd–O(2B)*	69.0(2)	O(1B)–Nd–O(2B)*	110.3(2)
Ow(2)–Nd–O(1C)	80.6(2)	O(1B)–Nd–O(1C)	106.5(2)
Ow(3)–Nd–O(1A)	131.2(2)	O(1B)*–Nd–O(2B)*	49.8(2)
Ow(3)–Nd–O(2A)	139.6(2)	O(1C)–Nd–O(1B)*	146.5(2)
Ow(3)–Nd–O(1B)	71.4(2)	O(1C)–Nd–O(2B)*	142.7(2)
	anion A	anion B	anion C
C(2)–C(1)–C(6)	120.5(9)	119.3(9)	119.1(9)
C(2)–C(1)–C(7)	119.6(8)	118.2(8)	120.2(8)
C(6)–C(1)–C(7)	119.9(9)	122.5(9)	120.7(9)
C(1)–C(2)–C(3)	118.6(9)	120.3(9)	120.5(9)
C(2)–C(3)–C(4)	120.9(10)	119.9(10)	120.4(10)
C(2)–C(3)–O(3)	121.7(9)	122.4(10)	117.9(9)
C(4)–C(3)–O(3)	117.5(9)	117.7(10)	121.6(9)
C(3)–C(4)–C(5)	120.3(10)	119.8(12)	119.3(10)
C(4)–C(5)–C(6)	120.2(10)	119.9(11)	120.3(10)
C(1)–C(6)–C(5)	119.5(10)	120.6(11)	120.3(10)
C(1)–C(7)–O(1)	119.8(8)	121.4(8)	118.0(8)
C(1)–C(7)–O(2)	119.8(8)	119.0(8)	118.9(8)
O(1)–C(7)–O(2)	120.4(8)	119.5(9)	123.0(9)

(*) $\bar{x},\bar{y},\bar{z}$

carboxylate oxygen atoms and three water oxygen atoms. The Nd–O distances range from 2.338(7) to 2.697(6) Å. The shortest distance is Nd–O(1c) involving the monodentate anion while the longest distance is to the bridging oxygen atom O(1b′). The Nd–O bond lengths are in agreement with values reported for other nine-coordinate Nd^{3+}-carboxylic acid complexes: *e.g.*, 2.428–2.532 Å in tris(oxydiacetato)neodymium(III),[8] 2.35–2.72 Å in hexaaquatris(malonato)dineodymium(III),[9,10] 2.43–2.62 Å in hexaaqua(fumarato)dimaleatodineodymium(III),[11] and 2.417–2.634 Å in aquatrisacetatoneodymium(III)[12] complexes.

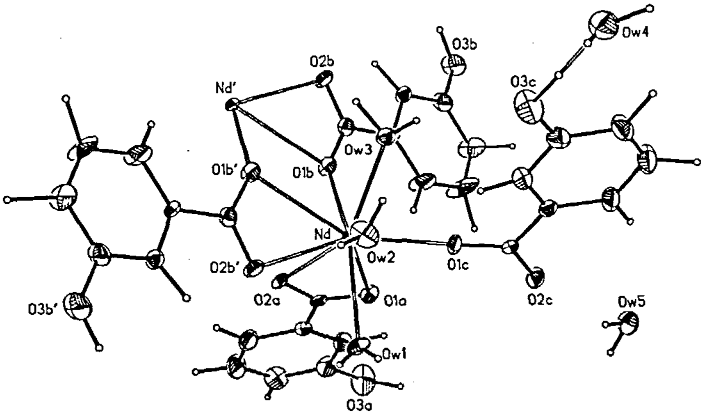


FIGURE 2 Perspective view of the Nd complex. Primed atoms are those of the anion B related by the symmetry operation $\bar{x},\bar{y},\bar{z}$.

The irregular coordination polyhedron around the Nd^{3+} ion can be described as a distorted tricapped trigonal prism. The Ow(1), O(1a), O(2a), Ow(3), and O(1b′) atoms form a trigonal prism with the O(1b), O(1c) and O(2b′) atoms capping the rectangular faces. One edge of the polyhedron, O(1b)–O(1b′), is shared with a second Nd^{3+} ion related by a centre of symmetry to give a centrosymmetric dimer with a Nd–Nd separation of 4.293 Å.

Each of the three anions bonds to the Nd^{3+} ion in a different way. Anion A forms a bidentate chelate, anion B is terdentate, and anion C is monodentate. In all cases the bonding is through the anionic carboxylate groups with no interactions involving the hydroxyl groups. The bond lengths in the carboxylate groups appear to depend on the mode of coordination, with the longest C–O bond distances found in anion B. The carboxylate groups are rotated slightly about the C(1)–C(7) bond. The dihedral angles between the COO group and the phenyl ring are 7.8, 9.4 and 12.8°, respectively in anions A, B and C. The bond lengths in the phenyl rings and the hydroxyl C–O bond distances are normal.

The crystal structure consists of a three-dimensional hydrogen bonded network involving the $NdL_3(H_2O)_3$ dimers and the two waters of hydration (Figure 3). The dimensions of the various hydrogen bonds are given in Table V. The water molecules coordinated to the Nd^{3+} ion function only as hydrogen donors while the uncoordinated water molecules and hydroxy groups are both donors and acceptors. The coordinated carboxylate groups are only acceptors.

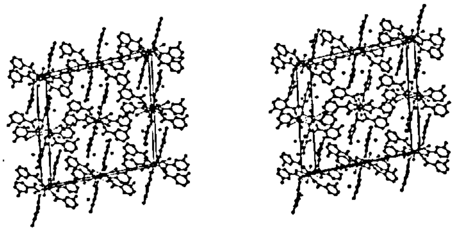


FIGURE 3 Stereoview down the *b* axis showing the crystal packing.

TABLE V

Geometry of hydrogen bonds.

D-H...A	D...A(Å)	D-H(Å)	H...A(Å)	< D-H...A(°)
O(3A)-H(3A)...O(3C) $(-1/2+x, 1/2+y, z)$	2.803	1.12	1.97	128
O(3B)-H(3B)...Ow(5) $(-x, -1+y, 1/2-z)$	2.813	1.02	1.80	171
O(3C)-H(3C)...Ow(4)	2.643	1.28	1.41	158
Ow(1)-H(1W1)...O(2C) $(-x, 1-y, -z)$	2.659	0.86	1.83	165
-H(2W1)...O(1A) $(-x, 1-y, -z)$	2.735	0.71	2.35	116
Ow(2)-H(1W2)...O(3C) $(1/2-x, 1/2-y, -z)$	3.106	0.87	2.40	138
-H(2W2)...O(3A) $(1/2+x, -1/2+y, z)$	2.754	0.95	1.84	161
Ow(3)-H(1W3)...O(3B) $(-x, y, 1/2-z)$	2.854	0.91	1.99	157
-H(2W3)...O(2A) $(-x, -y, -z)$	2.683	1.02	1.68	168
Ow(4)-H(1W4)...Ow(5) $(1/2-x, -1/2+y, 1/2-z)$	2.893	0.94	2.14	137
-H(2W4)...Ow(1) $(1/2-x, 1/2-y, -z)$	3.018	0.64	2.46	147
Ow(5)-H(1W5)...O(2B) $(x, 1+y, z)$	2.843	0.91	1.95	165
-H(2W5)...O(2C)	2.733	0.79	2.07	141

The lanthanide(III) ions form four different types of complexes with 3-hydroxybenzoic acid. In all cases the ratio of the metal ion to the coordinated anionic ligand is 1 : 3. However, the four types differ in the metal to H_2O ratio. There are differences in the number of water molecules coordinated to the metal ion and in the number of water molecules of hydration. Since the structures of all four types of complexes have now been determined, there is an opportunity to establish relationships between these four different types.

A simple relationship exists between type **II** complexes of Sm to Lu and Y with a coordination number of 8 and type **IV** complexes of La, Pr and Nd with coordination number 9. Both complexes are dimeric with a formula of $ML_3(H_2O)_3$ for the dimeric unit. However, the larger lanthanides La, Pr and Nd show an increased interaction with an oxygen of the bridging ligand which expands the coordination number to 9. The larger dimer unit requires two waters of hydration for crystal packing rather than one found in type **II** complexes.

The transformation of type **IV** to **III** can be visualized (Fig. 4) as involving the removal of two water molecules, Ow(1) and Ow(3), from the coordination sphere, thus requiring the bridging oxygen atoms to maintain a high coordination number. The result is a linear infinite chain in the crystal with hydrogen bonding involving the uncoordinated hydroxyl groups rather than water.

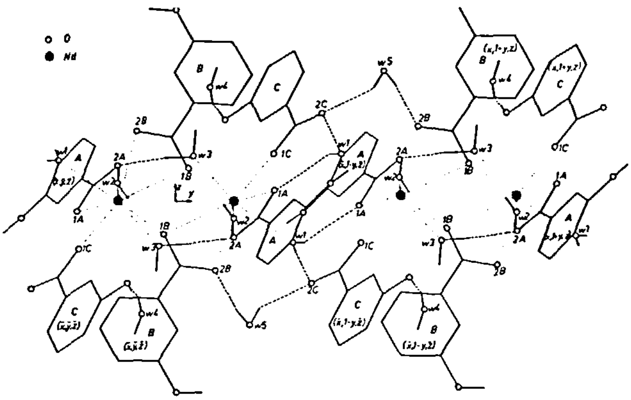


FIGURE 4 Projection of a part of the crystal structure showing the hydrogen bonds between the $NdL_3(H_2O)_3$ dimers along the *b* axis. H-atoms of the phenyl ring are omitted for clarity.

If a water molecule is removed from IV, the coordination number would be reduced to 8. However, if the dimers are linked *via* the uncoordinated O(3c) atom, the polymer chain in I is found. Now the four waters per dimer found in IV are replaced by two waters and the one free acid group found in I. In essence, the small bite of the carboxylate ligand coupled with the relatively large size of the lanthanides produces a series of complexes where the numbers of chelating carboxylates are minimized as much as possible.

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