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Syntheses and Crystal Structures of Diaquatris(*m*-hydroxybenzoato)lanthanoid(III) *m*-Hydroxybenzoic Acid Dihydrate (M=La, Ce, Pr, and Nd), and Di-μ-(*m*-hydroxybenzoato)bis{triaquabis(*m*-hydroxybenzoato)lanthanoid(III)} Dihydrate (M=Sm, Gd, Dy, Er, and Yb)

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Two types of lanthanoid(III) *m*-hydroxybenzoates, indicated in the title, have been synthesized, and the crystal and molecular structures of four representative complexes, where M=La (**1**), Nd (**2**), Sm (**3**), and Er (**4**), were determined by the single-crystal X-ray diffraction method. They are all triclinic, space group $P\bar{1}$, and the cell constants are as follows: (**1**) a=12.351(11), b=15.533(10), c=9.250(4) Å, α=109.86(4), β=101.40(6), γ=62.95(6)°; (**2**) a=12.287(4), b=15.542(7), c=9.194(3) Å, α=109.64(3), β=101.46(3), γ=62.83(3)°; (**3**) a=10.580(1), b=12.006(5), c=10.105(2) Å, α=111.14(2), β=90.27(1), γ=97.16(2)°; (**4**) a=10.586(4), b=11.943(6), c=10.027(5) Å, α=111.11(3), β=90.53(4), γ=97.26(4)°. The final R values obtained were (**1**) 0.039, (**2**) 0.038, (**3**) 0.030, and (**4**) 0.039. The central metal atoms of both types of complexes are octa-coordinated, and each is in a square-antiprism geometry. In **1** and **2**, one free acid molecule is present, and the molecule is hydrogen-bonded to the oxygen atoms of the coordinated water molecules through its carboxyl oxygen atoms. **1** and **2** have linear polymeric structure, and each pair of the metal atoms is bridged by a pair of the carboxylate ligands, while **3** and **4** have a dimeric structure, where metal atoms are bridged by two carboxylate ligands.

Several examples of the complicated structures of lanthanoid(III) carboxylates have already been elucidated.1–7) Among them, the tetraacetato complex of cerium(III) has the most interesting structure; four acetate ions are coordinated to the central metal atom by both of the carboxyl oxygen atoms, forming four-membered chelate rings.1) Although the structures of lanthanoid(III) aromatic carboxylates are expected to be different from those of the aliphatic ones, only a few results have been published thus far.5,8–10) This is probably due to the difficulty in obtaining good crystals for the X-ray analysis, as their solubilities are generally low. To raise the solubility of the complexes, it is thought to be effective to introduce hydroxyl groups on the phenyl group of the ligand; however, *o*- and *p*-hydroxybenzoates of lanthanoids(III) are hardly soluble in water. On the other hand, *m*-hydroxybenzoates of lanthanoid(III) are soluble enough into water, and their crystals were obtained easily. Indeed, their tetracarboxylato complexes of some lanthanoid(III), with the formula of $HML_4\cdot 4H_2O$ (where M=La, Ce, and Nd, HL=*m*-hydroxybenzoic acid) have been reported,11) though their structure has not been solved. We could obtain the tetracarboxylates of La, Ce, Pr, and Nd from an aqueous solution containing an excess of the acid: moreover, new tricarboxylate-type complexes were obtained for the heavier lanthanoids: Sm, Gd, Dy, Er, and Yb, under similar experimental conditions.

It was found, from the results of the preliminary structural studies, that the coordination geometry of both types of complexes resemble each other. It was thought to be interesting to check the variation in the bond lengths and some detailed structures of the complexes, depending on the change in the atomic number of the central metal atom. Therefore, the lanthanum(III) (**1**) and neodymium(III) (**2**) complexes of the tetracarboxylate type, as well as the samarium(III) (**3**), and erbium(III) (**4**) complexes of the tricarboxylate type, were chosen, and their structures were fully determined by the single-crystal X-ray diffraction method.

Experimental

*Synthesis of Diaquatris(*m*-hydroxybenzoato)lanthanum(III)-(*m*-hydroxybenzoic acid) dihydrate polymer (**1**).* About 1.3 g (9.4 mmol) of *m*-hydroxybenzoic acid and fresh lanthanum(III) hydroxide, prepared from 0.75 g (2.0 mmol) of lanthanum(III) chloride heptahydrate, were mixed in hot water (about 20 cm^3). The solution was then cooled and left standing in a silica-gel desiccator overnight; the crystalline product was thus obtained. The product was washed with water and diethyl ether successively to remove the excess free acid. The crude product thus obtained could be recrystallized from the aqueous solution by leaving it in a silica-gel desiccator for several days. The yield was about 0.9 g (about 60%).

A similar synthetic technique is applicable to obtain the isomorphous cerium(III), and praseodymium(III) complexes; their yields were about the same. In the case of neodymium(III) **2**, as the tetracarboxylate is hardly precipitated at all, a little more free acid was added to the more dilute aqueous solution, and it was left standing in the desiccator longer. The coprecipitated free acid was removed by washing the product with diethyl ether repeatedly.

*Synthesis of Di-μ-(*m*-hydroxybenzoato)bis{triaquabis-(*m*-hydroxybenzoato)erbium(III)} Dihydrate (**4**).* When the procedure used for the former type of complexes was applied to erbium(III) hydroxide, the titled complex was obtained as single crystals; even when the mole ratio of the added acid to the metal salt was increased, the precipitate obtained was a mixture of the titled tricarboxylate complex and the free acid. Similarly, this type of tricarboxylate complex was obtained for samarium(III) (**3**), gadolinium(III), dysprosium(III), and ytterbium(III). The yields were all about 60%.

The results of the elemental analyses of the products are shown in Table 1.

Table 1. Analyses of the complexes

Type[a)]	Ln		Ln(%)	C(%)	H(%)
1	La	Found	18.05	43.96	3.82
		Calcd	18.27	44.23	3.84
1	Ce	Found	18.10	43.91	3.81
		Calcd	18.40	44.16	3.84
1	Pr	Found	18.78	43.89	3.81
		Calcd	18.48	44.11	3.83
1	Nd	Found	19.02	43.67	3.78
		Calcd	18.84	43.92	3.82
2	Sm	Found	24.00	39.84	3.60
		Calcd	23.72	39.80	3.66
2	Gd	Found	24.80	39.43	3.58
		Calcd	24.55	39.37	3.62
2	Dy	Found	25.49	39.30	3.58
		Calcd	25.16	39.05	3.59
2	Er	Found	25.91	38.77	3.50
		Calcd	25.71	38.77	3.56
2	Yb	Found	26.63	38.61	3.41
		Calcd	26.63	38.42	3.53

a) The chemical formulae of the complexes: Type 1: $[LnL_3(H_2O)_2]\cdot HL\cdot 2H_2O$; Type 2: $[LnL_3(H_2O)_3]_2\cdot 2H_2O$ (where HL=*m*-hydroxybenzoic acid).

Single-crystal X-Ray Analysis. Crystals 0.4×0.3×0.3 mm³ in size were used as the samples of **1**, **2**, and **3**, while a crystal 0.3×0.3×0.3 mm³ in size was used as the sample of **4**. The reflections were collected on a Rigaku AFC-6A automated four-circle diffractometer with graphite monochromated Mo *Kα* radiation (0.7107 Å), the θ-2θ scan technique being employed (scan speed 4° min^{-1}; scan width $1.03+0.5\tan\theta°$). These crystals are all triclinic, space group $P\bar{1}$; their crystallographic data are shown in Table 2. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. All the calculations were carried out on a HITAC M-200H computer of the Computer Center of the University of Tokyo, using the local version of the UNICS program.[12)] The atomic-scattering factors were taken from the tables.[13)]

Structure Determination. The structure of each complex was solved by the heavy-atom method. In the case of the **1** and **4** complexes, the central metal and some oxygen atoms were deduced from the three-dimensional Patterson maps, while all the other non-hydrogen atoms were located by means of successive Fourier syntheses and refined by the block-diagonal least-squares method. The final *R* values obtained by applying the anisotropic temperature factors are shown in Table 2.[14)] As **2** and **3** were found to be isomorphous with **1**, and **4** respectively, from their X-ray crystallographic data, the positional and thermal parameters of the latter complexes were tentatively applied to the former ones as the starting data, and they were then refined as usual.

Other Measurements. The X-ray powder patterns of these complexes were obtained by the use of a diffractometer, Model DX-GO-F JEOL, using Cu *Kα* radiation, in the range from 6° to 50° in 2θ. The infrared absorption spectra of the samples were obtained by means of a JASCO A-202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull. The simultaneous thermogravimetric(TG) and differential thermal analyses(DTA) were carried out with a Rigaku Denki "Thermoflex" M-8075, using a sample of about 10 mg in each run, referring to Al_2O_3, at the heating rate of 2.5 K min^{-1}. The pH of the titrated solution was measured by the use of a Toa-Dempa glass electrode pH meter, model HM-5A.

Table 2. Crystallographic data and X-ray-measurement conditions of the complexes

Ln[a)]	La	Nd	Sm	Er
$a(l/Å)$	12.351(11)	12.287(4)	10.580(1)	10.586(4)
$b(l/Å)$	15.533(10)	15.542(7)	12.006(5)	11.943(6)
$c(l/Å)$	9.250(4)	9.194(3)	10.105(2)	10.027(5)
$\alpha(\phi/°)$	109.86(4)	109.64(3)	111.14(2)	111.11(3)
$\beta(\phi/°)$	101.40(6)	101.46(3)	90.27(1)	90.53(4)
$\gamma(\phi/°)$	62.95(6)	62.83(3)	97.16(2)	97.26(4)
$U(v/Å^3)$	1484.6(20)	1469.0(11)	1186.1(6)	1171.0(10)
$D_m(d/Mg\ m^{-3})$	1.69(3)	1.71(3)	1.78(3)	1.82(3)
$D_x(d/Mg\ m^{-3})$	1.70	1.73	1.78	1.85
Z	4	4	4	4
μ(Mo Kα) (n/mm^{-1})	1.56	1.87	2.57	3.79
F.W.[b)]	760.4	765.8	633.8	650.7
Scanned range(2θ/°)	3—42	3—42	3—44	3—43.5
Measured reflections	3473	3426	3142	3007
Reflections used for calculation[c)]	3087	3022	2958	2925
R	0.039	0.038	0.030	0.039

a) The central metal atom of the complexes. Their formulae are shown in Table 1. b) For the formulae containing one atom of the central metal. c) The reflections of $|F_o|>3\sigma(|F_o|)$ were selected and used.

Results and Discussion

The final atomic parameters of the complexes are listed in Table 3.[15] The perspective drawings of **1** and **4** around each central metal atom, together with their numbering scheme are shown in Figs. 1 and 2. Their crystal packing diagrams are shown in Figs. 3 and 4.

TABLE 3. FINAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B_{eq}/Å^2), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(1) Diaquatris(*m*-hydroxybenzoato)lanthanum(III) *m*-hydroxybenzoic acid dihydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [a]
La	4935.4(4)	4635.0(4)	2143(1)	1.7
O(11)	3575(5)	4129(4)	3074(6)	2.6
O(12)	4003(5)	4753(4)	5522(6)	2.8
O(13)	706(5)	4971(5)	8245(7)	4.3
O(21)	5508(5)	6744(4)	4(6)	3.0
O(22)	5148(5)	5876(4)	1139(6)	2.5
O(23)	4312(6)	8317(4)	6557(7)	4.3
O(31)	3167(5)	6280(4)	3611(6)	2.6
O(32)	2758(4)	5643(4)	1181(6)	2.2
O(33)	-1797(5)	7632(4)	421(7)	3.7
O(41)	8571(5)	1340(5)	2322(7)	4.4
O(42)	9169(5)	2349(5)	1799(8)	4.7
O(43)	13506(5)	188(5)	498(8)	4.7
C(11)	3400(7)	4371(6)	4474(9)	2.3
C(12)	2442(7)	4166(6)	4917(9)	2.4
C(13)	1983(8)	3524(6)	3830(10)	3.1
C(14)	1041(8)	3391(7)	4242(11)	3.8
C(15)	613(8)	3863(7)	5723(10)	3.5
C(16)	1113(7)	4499(6)	6794(9)	2.6
C(17)	2013(7)	4643(6)	6371(9)	2.3
C(21)	5359(7)	6625(6)	1204(9)	2.3
C(22)	5457(7)	7344(6)	2724(9)	2.0
C(23)	6223(8)	7817(7)	2896(10)	3.5
C(24)	6304(9)	8498(8)	4308(11)	4.6
C(25)	5653(9)	8688(7)	5555(10)	4.0
C(26)	4942(8)	8173(6)	5334(10)	3.0
C(27)	4814(7)	7504(6)	3928(9)	2.1
C(31)	2437(7)	6298(6)	2438(9)	2.0
C(32)	1151(7)	7106(6)	2551(9)	2.5
C(33)	858(8)	7965(6)	3857(10)	3.2
C(34)	-344(8)	8708(7)	3884(11)	3.9
C(35)	-1219(8)	8612(7)	2752(10)	3.4
C(36)	-906(7)	7732(7)	1530(10)	2.9
C(37)	281(7)	6988(6)	1395(9)	2.6
C(41)	9391(8)	1540(7)	1937(10)	3.4
C(42)	10624(7)	678(6)	1686(9)	2.6
C(43)	10861(8)	-226(7)	1928(11)	4.0
C(44)	12009(9)	-994(7)	1704(12)	4.6
C(45)	12910(8)	-870(7)	1216(11)	4.2
C(46)	12655(7)	20(6)	973(11)	3.1
C(47)	11521(7)	814(7)	1225(10)	3.0
O(W1)	6993(5)	3676(4)	1028(6)	2.9
O(W2)	6373(5)	3080(4)	3278(6)	2.8
O(W3)	5537(5)	8417(4)	9376(7)	3.3
O(W4)	1580(5)	4289(4)	890(7)	3.6

(2) Diaquatris(*m*-hydroxybenzoato)neodymium(III) *m*-hydroxybenzoic acid dihydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [a]
Nd	4934.7(4)	4636.8(3)	2128.9(5)	1.7
O(11)	3621(5)	4160(4)	3107(6)	2.6
O(12)	4019(5)	4780(4)	5603(6)	2.6
O(13)	695(5)	4959(5)	8235(7)	3.9
O(21)	5486(5)	6706(4)	-47(6)	2.6
O(22)	5137(5)	5858(4)	1150(6)	2.3
O(23)	4303(6)	8310(5)	6554(7)	4.1
O(31)	3226(4)	6249(4)	3592(6)	2.2
O(32)	2799(4)	5604(4)	1159(6)	2.1
O(33)	-1784(5)	7610(4)	399(7)	3.4
O(41)	8544(5)	1371(5)	2337(7)	4.2
O(42)	9153(5)	2366(5)	1797(8)	4.5
O(43)	13534(5)	174(5)	492(8)	4.6
C(11)	3429(7)	4387(6)	4522(9)	1.9
C(12)	2459(7)	4180(6)	4924(9)	1.9
C(13)	2022(7)	3519(6)	3804(10)	2.7
C(14)	1086(8)	3377(7)	4200(11)	3.4
C(15)	623(7)	3849(6)	5681(10)	3.1
C(16)	1108(7)	4481(6)	6752(9)	2.5
C(17)	2021(7)	4649(6)	6391(9)	2.5
C(21)	5353(7)	6586(6)	1195(9)	1.9
C(22)	5447(7)	7327(5)	2710(9)	1.8
C(23)	6206(8)	7809(6)	2858(10)	3.1
C(24)	6288(9)	8488(7)	4270(11)	4.4
C(25)	5639(8)	8681(7)	5533(10)	3.3
C(26)	4923(7)	8167(6)	5339(10)	2.8
C(27)	4799(7)	7501(6)	3938(9)	2.1
C(31)	2470(7)	6269(6)	2439(9)	2.0
C(32)	1190(7)	7078(6)	2562(9)	2.2
C(33)	895(8)	7942(6)	3845(10)	2.8
C(34)	-304(8)	8700(7)	3888(11)	3.5
C(35)	-1198(8)	8597(6)	2739(11)	3.2
C(36)	-886(7)	7706(6)	1516(10)	2.7
C(37)	311(7)	6960(6)	1360(9)	2.6
C(41)	9382(8)	1552(7)	1946(10)	3.1
C(42)	10610(7)	698(6)	1702(10)	2.4
C(43)	10826(8)	-209(7)	1940(11)	3.4
C(44)	11999(9)	-993(7)	1708(12)	4.6
C(45)	12923(8)	-884(7)	1218(11)	3.6
C(46)	12654(8)	39(7)	977(10)	3.2
C(47)	11506(8)	845(7)	1228(10)	3.0
O(W1)	6957(5)	3696(4)	1021(6)	2.5
O(W2)	6339(4)	3117(4)	3255(6)	2.4
O(W3)	5546(5)	8397(4)	9376(7)	3.2
O(W4)	1615(5)	4276(4)	880(7)	3.5

Table 3. Continued

(3) Di-μ-(*m*-hydroxybenzoato)bis{triaquabis(*m*-hydroxybenzoato)samarium(III)}·dihydrate.[b)]

Atom	x	y	z	B_{eq}/Å^2[a)]
Sm	4934.5(3)	4297.0(2)	2544.2(3)	1.9
O(11)	2147(4)	3593(4)	-908(5)	3.4
O(12)	3341(4)	3486(4)	819(5)	3.6
O(13)	2329(5)	-687(5)	712(8)	7.4
O(21)	3148(4)	6090(4)	6599(4)	3.3
O(22)	3659(4)	5228(4)	4372(5)	3.2
O(23)	158(4)	6023(5)	1552(5)	4.9
O(31)	6119(4)	6343(3)	3640(4)	2.5
O(32)	4594(4)	6163(4)	2069(4)	2.7
O(33)	4472(5)	10410(4)	2217(6)	5.2
C(11)	2484(5)	3024(5)	-190(6)	2.5
C(12)	1934(5)	1735(5)	-535(7)	2.6
C(13)	1046(7)	1174(6)	-1669(7)	3.7
C(14)	592(8)	-45(7)	-2009(8)	4.7
C(15)	1011(7)	-690(6)	-1240(8)	4.2
C(16)	1884(7)	-101(6)	-106(9)	4.3
C(17)	2339(6)	1111(6)	278(8)	3.7
C(21)	2925(5)	5776(5)	5274(7)	2.5
C(22)	1703(5)	6088(5)	4803(6)	2.1
C(23)	793(6)	6470(5)	5783(7)	2.7
C(24)	-360(6)	6698(6)	5324(7)	3.3
C(25)	-591(6)	6557(6)	3915(7)	3.2
C(26)	346(6)	6180(6)	2959(7)	3.1
C(27)	1501(6)	5936(6)	3378(7)	2.9
C(31)	5478(5)	6828(5)	2978(6)	2.1
C(32)	5735(6)	8125(5)	3257(6)	2.3
C(33)	6774(6)	8817(6)	4173(7)	3.3
C(34)	7000(7)	10046(6)	4423(8)	4.1
C(35)	6233(7)	10567(6)	3754(8)	4.0
C(36)	5221(7)	9855(6)	2854(7)	3.7
C(37)	4943(6)	8633(5)	2581(7)	3.0
O(W1)	3988(4)	2805(4)	3519(4)	2.9
O(W2)	5505(4)	2189(4)	1013(5)	3.7
O(W3)	6335(4)	4406(4)	653(4)	2.6
O(W4)	8425(5)	2999(5)	163(8)	7.1

(4) Di-μ-(*m*-hydroxybenzoato)bis{triaquabis(*m*-hydroxybenzoato)erbium(III)}·dihydrate[b)]

Atom	x	y	z	B_{eq}/Å^2[a)]
Er	4941.5(3)	4295.2(2)	2510.5(3)	1.6
O(11)	2194(5)	3590(5)	-927(6)	3.1
O(12)	3411(5)	3490(5)	810(6)	3.1
O(13)	2335(7)	-663(6)	820(9)	6.4
O(21)	3260(5)	6042(5)	6503(6)	2.8
O(22)	3676(5)	5185(4)	4229(6)	2.7
O(23)	115(6)	6033(3)	1553(6)	4.5
O(31)	6105(5)	6284(4)	3641(5)	2.2
O(32)	4606(5)	6132(4)	2032(6)	2.9
O(33)	4531(7)	10421(5)	2218(7)	4.5
C(11)	2545(7)	3029(7)	-193(8)	2.3
C(12)	1968(7)	1735(7)	-518(8)	2.4
C(13)	1086(8)	1153(7)	-1683(9)	3.1
C(14)	618(10)	-60(8)	-1987(10)	4.3
C(15)	1039(9)	-695(8)	-1200(10)	3.9
C(16)	1896(8)	-96(7)	-48(11)	3.9
C(17)	2361(8)	1130(7)	331(10)	3.5
C(21)	2984(7)	5733(6)	5183(8)	2.0
C(22)	1750(7)	6076(6)	4764(8)	2.0
C(23)	890(7)	6467(7)	5801(9)	2.6
C(24)	-289(8)	6702(7)	5382(9)	3.2
C(25)	-569(8)	6562(7)	3956(9)	3.2
C(26)	341(8)	6180(7)	2957(9)	2.8
C(27)	1504(7)	5929(7)	3346(8)	2.5
C(31)	5476(7)	6767(6)	2953(7)	1.6
C(32)	5742(7)	8087(7)	3266(8)	2.5
C(33)	6773(8)	8808(7)	4236(9)	2.9
C(34)	7023(9)	10026(7)	4492(11)	3.8
C(35)	6269(9)	10560(8)	3822(10)	3.8
C(36)	5264(8)	9847(7)	2868(9)	3.3
C(37)	4980(8)	8627(7)	2580(8)	2.6
O(W1)	4027(5)	2851(4)	3490(5)	2.6
O(W2)	5523(6)	2231(5)	1032(6)	3.5
O(W3)	6314(5)	4405(4)	691(5)	2.3
O(W4)	8399(7)	3008(6)	144(9)	6.0

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

The Structure of Lanthanum(III) Complex (1). The central lanthanum(III) atom of **1** is octa-coordinated and is in a square-antiprism geometry, being coordinated to eight oxygen atoms. The La atom is bridged to La^{i} as well as to La^{ii} with a couple of the respective carboxylate ligands, to form a linear polymeric structure (where the keys to the symmetry operations are: i: 1.0−x, 1.0−y, 1.0−z; ii: 1.0−x, 1.0−y, −z). Therefore, the zig-zag chain of the polymeric complex is parallel to z-axis. The center of symmetry of **1** exists at the mid-point of La and La^{i}, as well as of La and La^{ii}. Each oxygen atom of the carboxylate ligand, which bridge La and La^{i} atoms, is coordinated to a respective metal atom, forming a La-O-C-O-La^{i}-type bridge. In the case of the ligand, which bridges La and La^{ii}, O(21) and O(22) are coordinated to La^{ii} and La respectively; moreover, the O(22) takes a position not very far from La^{ii} (3.074(8) Å). Taking this additional weak bonding, La···O(22^{ii}), into consideration, the La atom can be said to be ennea-coordinated and to be in a capped square-antiprism geometry. Another carboxylate ligand forms a four-membered chelate ring, coordinated to the metal atom through both of the carboxylate oxygen atoms, O(31) and O(32). Two water oxygen atoms, O(W1) and O(W2), are also coordinated to the metal atom, and the fourth acid molecule forms hydrogen bondings with the water oxygen atoms O(W1)···O(42), 2.698(8) Å, and O(W2)···O(41), 2.860(7) Å, where the former bonding is

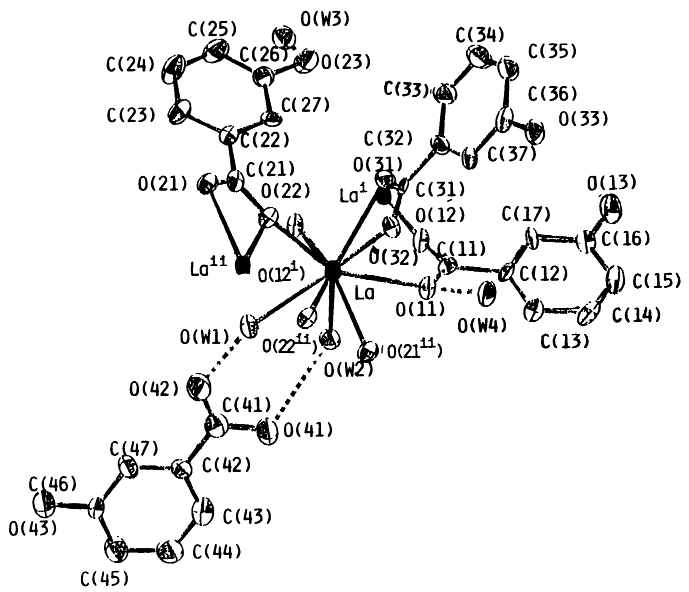


Fig. 1. A perspective drawing of diaquatris(*m*-hydroxybenzoato)lanthanum(III)(*m*-hydroxybenzoic acid)·dihydrate, and the numbering scheme of atoms.

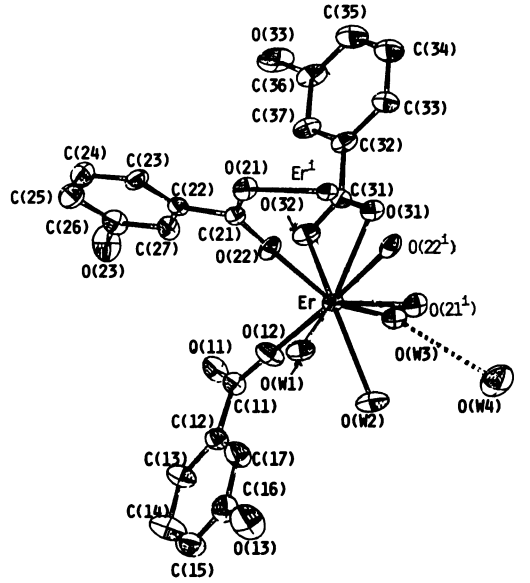


Fig. 2. A perspective drawing of di-μ-(*m*-hydroxybenzoato) bis{triaquabis (*m*-hydroxybenzoato) erbium(III)}·dihydrate, and the numbering scheme of atoms.

through the water hydrogen and the latter one through the acid hydrogen atom. The other water oxygen atoms, O(W3) and O(W4), are not coordinated to the lanthanoid atom. The phenol hydroxyl oxygen atoms of the ligands are not coordinated to the metal atom, either. Possible hydrogen bondings between the oxygen atoms are summarized in Table 4 (less than 2.95 Å). Thus, a polymer chain of the complex is weakly bonded to other chains.

The two C–O bond lengths of each carboxyl group which acts as a ligand are not very different from each other; the differences are O(11), O(12)–C(11), 0.056; O(21), O(22)–C(21), 0.043; and O(31), O(32)–C(31), 0.013 Å. However, that of the fourth acid molecule is a little large, 0.130 Å, like that of a free acid molecule.

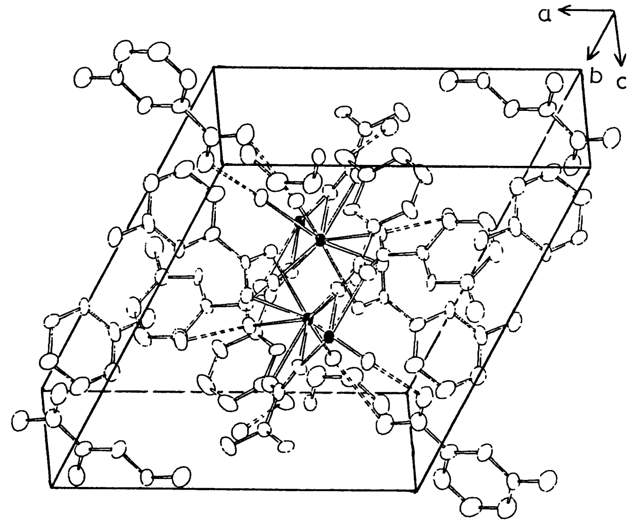


Fig. 3. Crystal packing diagram of the lanthanum(III) complex.

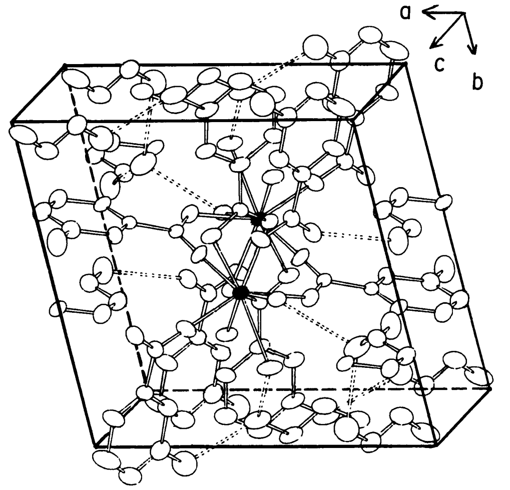


Fig. 4. Crystal packing diagram of the erbium(III) complex.

*The Structure of the Neodymium(III) Complex (**2**).* The **2** complex is isomorphous with **1**, and both structures resemble each other. Every Nd–O length in **2** (2.491 Å in average) is shorter than the corresponding La–O ones in **1** (2.606 Å in average) by about 0.11 Å, and among them, M–O(12$^{\rm i}$), M–O(22$^{\rm ii}$), and M–O(21$^{\rm ii}$) are especially shortened; the reductions of the above-mentioned distances are much larger than those to be expected from the decrease in the central-metal-atom radius (the atomic radii are: La, 1.877; Nd, 1.821 Å[16a]). They are all bridging ligand ones, and the inter-metal-atom distances, M···M$^{\rm i}$ as well as M···M$^{\rm ii}$, also decrease, as is shown in Table 4. The hydrogen bond lengths, O(W1)···O(42) and O(W2)···O(41), of **2** are slightly shorter than the respective ones of **1**.

*The Structure of the Samarium(III) Complex (**3**).* The central samarium(III) atom of **3** is octa-coordinated and is in a square-antiprism geometry, being coordi-

TABLE 4. INTERATOMIC DISTANCES AND BOND ANGLES OF THE COMPLEXES

M[a]	La(l/Å)	Nd(l/Å)	M[a]	Sm(l/Å)	Er(l/Å)
M-O(22)	2.580(8)	2.479(7)	M-O(22)	2.322(4)	2.231(5)
M-O(32)	2.601(5)	2.512(5)	M-O(31)	2.467(4)	2.396(5)
M-O(21^{ii})	2.634(6)	2.488(6)	M-O(21^{i})	2.364(5)	2.283(6)
M-O(W1)	2.541(6)	2.457(5)	M-O(W1)	2.452(5)	2.386(6)
M-O(12^{i})	2.536(6)	2.356(5)	M-O(12)	2.273(4)	2.198(5)
M-O(31)	2.660(5)	2.559(4)	M-O(32)	2.521(5)	2.474(6)
M-O(11)	2.570(8)	2.466(8)	M-O(W3)	2.455(4)	2.372(6)
M-O(W2)	2.723(6)	2.615(6)	M-O(W2)	2.594(4)	2.534(5)
M-O(22^{ii})	3.074(6)	2.843(6)	M···O(22^{i})	3.273(5)	3.382(6)
O(11)-C(11)	1.346(11)	1.268(10)	O(11)-C(11)	1.239(9)	1.241(11)
O(12)-C(11)	1.290(10)	1.263(10)	O(12)-C(11)	1.276(7)	1.269(9)
O(13)-C(16)	1.450(11)	1.385(10)	O(13)-C(16)	1.378(12)	1.389(15)
C(11)-C(12)	1.530(16)	1.506(15)	C(11)-C(12)	1.496(9)	1.503(11)
C(12)-C(13)	1.422(13)	1.405(12)	C(12)-C(13)	1.388(9)	1.396(11)
C(13)-C(14)	1.432(17)	1.400(17)	C(13)-C(14)	1.397(10)	1.391(13)
C(14)-C(15)	1.483(14)	1.404(13)	C(14)-C(15)	1.384(13)	1.381(16)
C(15)-C(16)	1.439(12)	1.393(13)	C(15)-C(16)	1.381(10)	1.375(12)
C(16)-C(17)	1.392(16)	1.383(15)	C(16)-C(17)	1.384(9)	1.395(12)
C(17)-C(12)	1.460(12)	1.382(11)	C(17)-C(12)	1.393(12)	1.390(15)
O(21)-C(21)	1.325(13)	1.269(12)	O(21)-C(21)	1.266(8)	1.260(9)
O(22)-C(21)	1.282(13)	1.261(13)	O(22)-C(21)	1.252(7)	1.250(9)
O(23)-C(26)	1.469(13)	1.376(13)	O(23)-C(26)	1.376(9)	1.369(11)
O(31)-C(31)	1.324(10)	1.262(9)	O(31)-C(31)	1.274(8)	1.275(10)
O(32)-C(31)	1.311(9)	1.267(8)	O(32)-C(31)	1.278(6)	1.257(8)
O(33)-C(36)	1.417(10)	1.375(10)	O(33)-C(36)	1.386(10)	1.395(13)
O(41)-C(41)	1.338(15)	1.322(15)			
O(42)-C(41)	1.208(14)	1.214(13)			
O(43)-C(46)	1.387(15)	1.369(15)			
M···M^{ii}	4.811(3)	4.473(2)	M···M^{i}	4.625(2)	4.654(3)
M···M^{i}	5.379(3)	4.999(2)	M···M^{ii}	5.959(2)	5.853(3)
O(W1)···O(42)	2.698(8)	2.682(7)			
O(W2)···O(41)	2.860(7)	2.841(7)	O(W2)···O(W3)	2.847(7)	2.767(8)
O(W1)···O(W2)	3.027(11)	2.844(10)	O(W1)···O(W2)	2.919(6)	2.860(8)
O(W1)···O(32^{ii})	2.858(10)	2.700(10)	O(W1)···O(31^{i})	2.686(6)	2.696(7)
O(W2)···O(23^{i})	2.723(12)	2.738(11)	O(W2)···O(21^{i})	2.786(5)	2.760(7)
O(W3)···O(23)	2.898(9)	2.732(8)	O(W2)···O(33^{iii})	2.923(8)	2.913(10)
O(W3)···O(21^{iii})	2.887(11)	2.886(11)	O(W4)···O(13^{iv})	2.606(8)	2.621(9)
O(W4)···O(11)	2.921(8)	2.853(8)	O(33)···O(13^{v})	2.640(8)	2.630(9)
O(W4)···O(13^{iv})	2.713(10)	2.706(9)	O(23)···O(11^{vi})	2.658(7)	2.650(9)
O(33)···O(W4^{v})	2.727(9)	2.692(9)	O(W3)···O(W4)	2.884(7)	2.872(9)
O(43)···O(W3^{vi})	2.863(12)	2.878(12)			

Bond Angles

M	La(ϕ/°)	Nd(ϕ/°)	M	Sm(ϕ/°)	Er(ϕ/°)
O(22)-M-O(32)	74.71(19)	76.06(20)	O(22)-M-O(31)	77.39(13)	77.56(17)
O(32)-M-O(21^{ii})	76.59(16)	77.78(16)	O(31)-M-O(21^{i})	77.96(14)	76.37(18)
O(21^{ii})-M-O(W1)	80.34(17)	81.72(17)	O(21^{i})-M-O(W1)	82.40(16)	80.05(20)
O(W1)-M-O(22)	74.69(21)	76.24(21)	O(W1)-M-O(22)	71.39(15)	71.20(19)
O(31)-M-O(11)	70.29(19)	71.62(20)	O(32)-M-O(W3)	72.75(15)	73.01(19)
O(11)-M-O(W2)	71.01(21)	71.49(21)	O(W3)-M-O(W2)	68.59(13)	68.56(17)
O(W2)-M-O(12^{i})	69.65(17)	71.78(17)	O(W2)-M-O(12)	74.84(14)	75.10(18)
O(12^{i})-M-O(31)	75.73(16)	77.15(16)	O(12)-M-O(32)	80.72(16)	80.93(20)
O(32)-M-O(31)	52.44(14)	51.14(14)	O(31)-M-O(32)	52.17(14)	53.57(17)
O(W1)-M-O(W2)	70.12(17)	68.12(17)	O(W1)-M-O(W2)	70.61(14)	71.02(18)
M-O(11)-C(11)	123.2(5)	124.8(5)	M-O(12)-C(11)	177.5(3)	178.7(4)
M^{i}-O(12)-C(11)	169.2(5)	170.0(5)			

Table 4. Continued

M	La(ϕ/°)	Nd(ϕ/°)	M	Sm(ϕ/°)	Er(ϕ/°)
O(11)-C(11)-O(12)	125.4(9)	122.6(9)	O(11)-C(11)-O(12)	122.0(5)	122.6(7)
O(11)-C(11)-C(12)	119.5(7)	118.5(7)	O(11)-C(11)-C(12)	120.3(5)	119.7(6)
O(12)-C(11)-C(12)	115.1(8)	118.9(8)	O(12)-C(11)-C(12)	117.6(6)	117.6(7)
C(11)-C(12)-C(13)	116.3(8)	119.5(7)	C(11)-C(12)-C(13)	119.8(6)	119.9(7)
C(11)-C(12)-C(17)	123.3(9)	121.8(8)	C(11)-C(12)-C(17)	119.3(5)	118.8(7)
M^{ii}-O(21)-C(21)	107.3(5)	104.3(5)	M^{i}-O(21)-C(21)	119.5(4)	125.7(4)
M-O(22)-C(21)	155.7(6)	157.9(6)	M-O(22)-C(21)	174.1(4)	177.1(4)
O(21)-C(21)-O(22)	119.3(7)	120.1(7)	O(21)-C(21)-O(22)	123.0(5)	123.6(7)
M-O(31)-C(31)	90.4(4)	93.4(4)	M-O(31)-C(31)	95.9(3)	94.7(4)
M-O(32)-C(31)	93.3(4)	95.5(4)	M-O(32)-C(31)	93.3(3)	91.5(4)
O(31)-C(31)-O(32)	123.9(5)	119.9(5)	O(31)-C(31)-O(32)	118.6(5)	120.2(6)
O(W2)···O(41)-C(41)	114.0(6)	113.8(6)			
O(W1)···O(42)-C(41)	126.7(6)	126.4(6)			
O(41)-C(41)-O(42)	123.4(8)	121.9(8)			

a) The central metal atom of each complex is shown. The chemical formulae of the first two differ from those of the latter two (see Table 1, footnoot).

Keys to the symmetry operations: For the lanthanum(III) and neodymium(III) complexes: i: 1.0−*x*, 1.0−*y*, 1.0−*z*; ii: 1.0−*x*, 1.0−*y*, −*z*; iii: *x*, *y*, 1.0+*z*; iv: −*x*, 1.0−*y*, 1.0−*z*; v: −*x*, 1.0−*y*, −*z*; vi: 2.0−*x*, 1.0−*y*, 1.0−*z*. For the samarium(III) and erbium(III) complexes: i: 1.0−*x*, 1.0−*y*, 1.0−*z*; ii: 1.0−*x*, 1.0−*y*, −*z*; iii: *x*, −1.0+*y*, *z*; iv: 1.0−*x*, −*y*, −*z*; v: *x*, 1.0+*y*, *z*; vi: −*x*, 1.0−*y*, −*z*.

nated to eight oxygen atoms, as is shown in Fig. 2 (Er(III) analogue). The metal atom Sm is bridged to Sm^{i} with a couple of the carboxylato ligands (where the keys to the symmetry operations are: i: 1.0−*x*, 1.0−*y*, and 1.0−*z*, and Sm···Sm^{i} is 4.625 Å). As the shortest interatomic distance from an oxygen atom of the complex around Sm to Sm^{ii} is O(II)···Sm^{ii}=4.451(5) Å, there is no bridging between Sm and Sm^{ii} (where the keys to the symmetry operations are: ii: 1.0−*x*, 1.0−*y*, −*z*, and Sm···Sm^{ii} is 5.959 Å). Therefore, **3** should be regarded as having a dimeric structure, but the complex molecules are approximately lined to the *z*-axis, as in the case of **1**. Between Sm and Sm^{i}, there are two Sm-O-C-O-Sm^{i}-type bridges, where O(21)-Sm^{i} and O(22)-Sm are 2.364(5) and 2.322(4) Å respectively. As O(22)···Sm^{i} is 3.273(5) Å, it is too far to be considered as a bonding. The eight Sm-O coordination bond distances are in the range of 2.273(4) and 2.594(4) Å (2.431 Å on the average). The difference between a pair of C-O bond lengths of each carboxyl group of the ligands are: O(11), O(12)-C(11), 0.037; O(21), O(22)-C(21), 0.014; O(31), O(32)-C(31), 0.004 Å. They are not large, not even the first one, where the ligand is in a unidentate form. As in the case of **1**, the short O···O distances around O(W4), and the phenyl hydroxyl oxygen atoms are summarized in Table 4; some of them are expected to form the hydrogen bonds.

The Structure of the Erbium(III) Complex (4). The **4** complex is isomorphous with **3**, although the bond distances around the central metal atom are a little different. As the Er-O bond lengths are in the range of 2.198(5) and 2.534(5) Å (2.359 Å on the average), the difference in the average M-O lengths of **3** and **4** is a little longer than that in the metal atomic radii (the atomic radii are: Sm, 1.802; Er, 1.757 Å [16a)]). The interatomic distance, Er···O(22^{i}), is 3.382(6) Å, which is longer than the corresponding Sm···O(22^{i}) distance, 3.273(5) Å, in spite of the fact that the former metal atomic radius is smaller than the latter. The interatomic distances, Er···Er^{i} or Er^{ii}, are not much different from those of the corresponding distances of **3**; the differences are smaller than those between **1** and **2**.

The comparison of 1,2-Type and 3,4-Type Complexes. The respective interatomic distances and the bond angles of **1**, **2**, **3**, and **4** are shown in Table 4, while their atomic coordination geometries are shown in Fig. 5.

There are some similarities between **1** and **3**-type complexes. They are triclinic, with the space group P$\bar{1}$; the central metal atom is octa-coordinatated and is in a square-antiprism geometry. Both types of complexes are lined almost parallel to the *z*-axis, although the **3**-type is discrete between M and M^{ii} and is dimer. In the **1**-type, the M···M^{i} distance is about 0.5 Å longer than that of the M···M^{ii}; and therefore, the long and short M···M′ distances appear alternatively in the polymeric chain of the **1**-type complexes. In the **3**-type complexes, an additional water oxygen atom, O(W3), is coordinated to the metal atom in place of one bridging oxygen atom, O(11), of the **1**-type complexes. The positions of the other ligating atoms are almost the same as in both types of complexes.

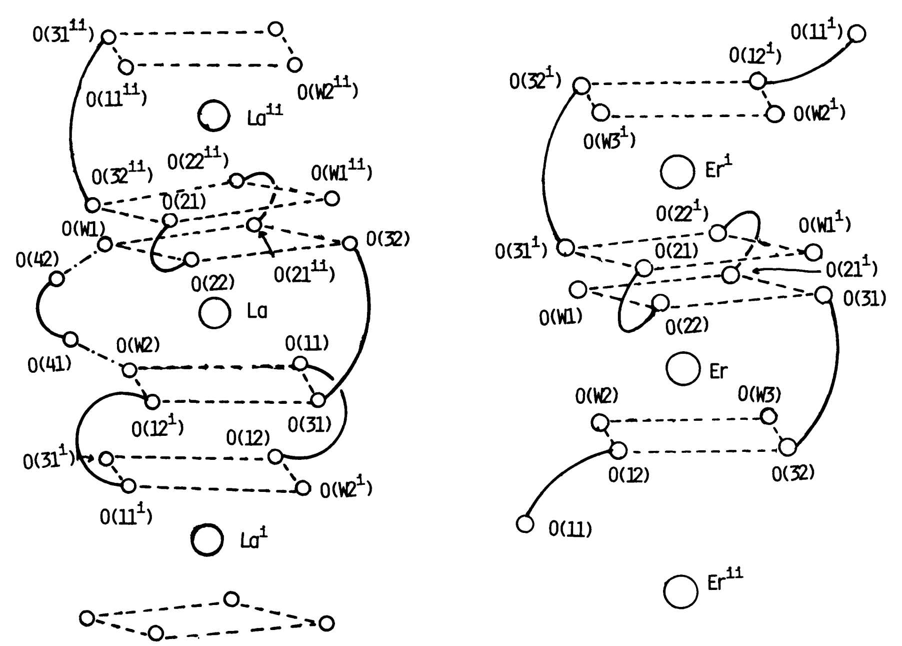
The differences between **1** and **3** may be summarized as follows:

1) The **3**-type complexes do not have the free acid molecule in the crystal.

2) The **3**-type complexes are in the dimeric structure.

3) The interatomic distances, M···O(22^{i}), of **3** is much longer than the corresponding one of **2**, M···O(22^{ii}), and the former complex can not be considered as having the ennea-coordination.

4) When are compared **3** and **2**, the Sm-O(22) and Sm-O(21^{i}) (2.322(4) and 2.364(5) Å) distances are much



(1) (2)

Fig. 5. Arrangement of the coordinating atoms around the central metal atoms of (1) the lanthanum(III) and (2) the erbium(III) complexes. (Key to the symmetric operations: i: 1.0−*x*, 1.0−*y*, 1.0−*z*; ii: 1.0−*x*, 1.0−*y*, −*z*.)

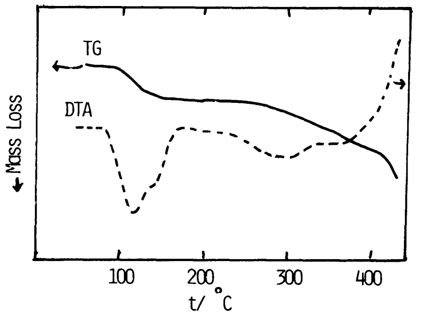


Fig. 6. TG(——) and DTA (----) curves of the lanthanum (III) complex. Mass loss of TG was taken downwards, and the exothermal change of DTA was taken upwards.

shorter than the corresponding Nd-O(22) and Nd-O(21^{ii}) (2.479(7) and 2.488(6) Å) distances of **2**, even the difference of their metal atomic radii is considered (Sm, 1.802 and Nd, 1.821 Å). Nevertheless, the interatomic distance, Sm···Sm^{i} of **3** is longer than the Nd···Nd^{ii} distance of **2** by 0.15 Å.

Although it was already known that the complexes of light and heavy lanthanoid(III) with the same ligand are sometimes different from each other in their chemical compositions,[16b,17,18] only a few comparisons of their structures have been published.[18]

The radii of lanthanoid atoms decrease with the increase in their atomic number. When the reduction of the radius is not large, only the bond lengths between the central metal and the coordinated atoms decrease, and the crystal is kept in an isomorphous state. However, when the radius decreases more, the ligand molecules must approach too near each other if the same configuration in the crystal is kept. Then they are rearranged to another structure, as in the present case.

Results of Other Measurements. As the four water molecules in **1** are divided into two groups, the coordinated ones and the crystalline ones, they can be expected to be distinguished by the thermal analysis. However, as is shown in Fig. 6, even when a relatively slow temperature-raising speed was applied (2.5 K min^{-1}), the dehydration peak of the DTA curve did not show any clear separation. Only a shoulder was found on the higher-temperature side of the peak, which means that there are two different types of water molecules and that they are removed at slightly different temperatures.

The fourth acid molecule in **1** is bonded only indirectly to the lanthanoid atom in the solid. This molecule can be expected to be liberated in its aqueous solution; this was ascertained by the measurement of the pH variation in the solution during titration with sodium hydroxide. The concentration of the complex used was $[La^{III}]=3.01\times10^{-3}$ mol dm^{-3}, and that of NaOH was 0.1 mol dm^{-3}. The results are shown in Fig. 7. An inflection point was observed when an equimol of NaOH was added, and the metal hydroxide began to precipitate after that point.

The infrared absorption spectra of the free acid, **1**, and of **4** are shown in Fig. 8. The spectra of the other lanthanoid complexes are almost the same as those of the two representative complexes. Although the free acid has two peaks in the ν_{as}(COO) region, at 1675 and 1598 cm^{-1}, the latter one is likely to be mixed with those of the phenyl group or of the hydroxyl group vibration. As the spectra of **1** has a peak at 1690 cm^{-1}, the fourth acid molecule in the complex is expected to act almost as a free acid. Although they may be overlapped, or mixed with other vibrations, the peaks at 1590 and 1502 cm^{-1} are expected to contain the ν_{as}(COO) mode of the coordinated ligand. In the spectra of **4**, one strong

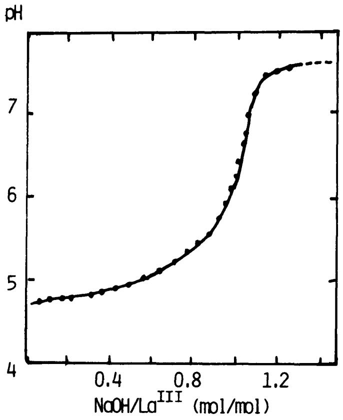


Fig. 7. The titration curve of the lanthanum(III) complex, using sodium hydroxide. ([La^{III}]=3.01×10^{-3} mol dm^{-3}; [NaOH]=0.1 mol dm^{-3}, in aqueous solution).

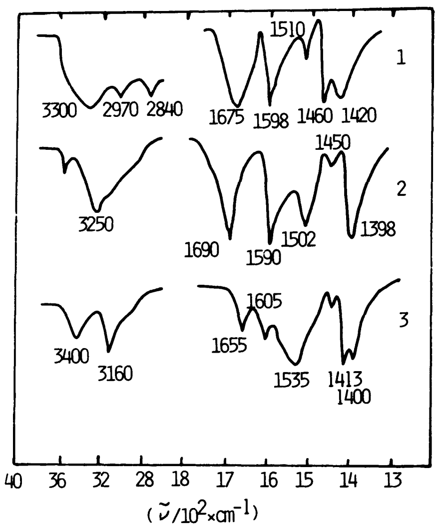


Fig. 8. Infrared absorption spectra of 1) *m*-hydroxybenzoic acid, 2) the lanthanum(III) complex (**1**), and 3) the erbium(III) copmlex (**4**).

peak is found at 1535 cm^{-1}, which is thought to be the ν_{as}(COO) mode of the coordinated ligand. The other peaks in the region, 1655 and 1605 cm^{-1}, may correspond with some modes of the other coordinated ligands in the complex; however, the exact assignment is difficult.

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References

1) G. C. Sadikov, G. A. Kukina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **12**, 859 (1971).

2) G. C. Sadikov, G. A. Kukina, M. A. Porai-Koshits, and L. A. Pospelova, *Zh. Strukt. Khim.*, **9**, 145 (1968).

3) L. A. Aslanov, I. K. Abdul'minev, M. A. Porai-Koshits, and V. I. Ivanov, *Dokl. Akad. Nauk SSSR*, **205**, 343 (1972).

4) M. C. Favas, D. L. Kepert, B. W. Skelton, and A. H. White, *J. Chem. Soc. Dalton Trans.*, **1980**, 454.

5) M. S. Khiyalov, I. R. Amiraslanov, Kh. S. Mamedov, and E. M. Movsumov, *Koord. Khim.*, **7**, 445 (1981).

6) H. R. Wenk, *Z. Krystallogr.*, **154**, 137 (1981).

7) L. A. Aslanov, V. M. Ionov, and I. D. Kiekaev, *Koord. Khim.*, **2**, 1674 (1976).

8) Y. Koizumi, H. Sawase, Y. Suzuki, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 1677 (1984).

9) L. A. Aslanov, I. K. Abdul'minev, and M. A. Porai-Koshits, *Zh. Fiz. Khim.*, **47**, 1055 (1973).

10) H. B. Kerfoot, G. R. Choppin, and T. J. Kistenmacher, *Inorg. Chem.*, **18**, 787 (1979).

11) K. Kimura, "Muki-Kagaku-Zensho IX-2," Maruzen, Tokyo (1949), p. 535.

12) "The Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

13) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

14) $R=\sum||F_o|-|F_c||/\sum|F_o|$

15) The final thermal parameters and the F_o—F_c tables are deposited as Document No.8422 at the office of the Editor of the Bull. Chem. Soc. Jpn.

16) T. Moeller, "The Lanthanides," in "Comprehensive Inorganic Chemistry," ed by J. C. Bailer and others, Pergamon Press, New York, N. Y. (1973), Vol. 4, a) p. 7, b) p. 94.

17) S. Kondo, M. Shimoi, A. Ouchi, and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **55**, 2840 (1982).

18) A. A. Pinkerton, and D. Schwarzenbach, *J. Chem. Soc. Dalton Trans.*, **1976**, 2466.