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The Synthesis and Crystal and Molecular Structures of [Pentaaquabis(1-hydroxy-2-naphthoato)neodymium(III)] (1-Hydroxy-2-naphthoate) Dihydrate, $[Nd\{C_{10}H_6(OH)CO_2\}_2(H_2O)_5][C_{10}H_6(OH)CO_2]\cdot 2H_2O$

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The title complex was synthesized, and its crystal and molecular structures were determined by the single-crystal X-ray-diffraction method. It is triclinic, with the space group of $P\bar{1}$; the cell constants are a=20.621 (4), b=22.288 (5), c=7.724 (1) Å, α=93.30 (2), β=96.78 (2), γ=107.43 (2)°, Z=4, and the final R value is 0.048. Although there are two kinds of crystallographically independent complexes, their structures are almost the same, with only a slight difference in the orientations of the naphthalene rings of the ligands. Both of the central metal atoms are ennea-coordinated and are in the tricapped trigonal-prism geometry: two carboxylato ligands make four-membered chelate rings, and they are also ligated five water oxygen atoms. No carboxylate ions bridge the metal atoms, but the oxygen atoms of the ligands, isolated carboxylate ions, and the crystalline water molecules are linked through hydrogen bondings along the bc-plane. The metal atoms lie on a plane parallel to (100), and the planes are separated by the layers of the naphthalene rings of the naphthoate ions.

The structures of many lanthanoid carboxylates have already been reported, and it has been found that almost all of them are in dimeric or polymeric forms, bridged by carboxylato ligands in various modes.[1-8] The present authors were interested especially in the structure of the lanthanoid carboxylates, whose ligands have some bulky substituents, such as phenyl or naphthyl rings. In crystals of such a type of complex, the large hydrophobic parts and the hydrophilic central metal-core parts are apt to take separate positions. For example, the lanthanoid(III) 2-naphthalenesulfonates, although they are not carboxylates, have been found to have an accumulated layer structure where the naphthalene-ring part and the metal-core part form hydrophobic and hydrophilic layers alternately.[9] We have previously obtained neodymium(III) 1-hydroxy-2-naphthoate from an ethanol-water mixed solution, where the ethanol and the water molecules are both coordinated to the same metal atom, and where the metal cores are surrounded by the naphthyl groups of the carboxylato ligands.[10]

When a 2-propanol-water solvent was used instead of ethanol-water, we could obtain alcohol-free neodymium(III) 1-hydroxy-2-naphthoate. This compound is stable in air, unlike the ethanol-coordinated complex, which effloresced quite rapidly.[10] To clarify this difference, we have determined its crystal structure using the single-crystal X-ray-diffraction method.

Experimental

Synthesis of [Pentaaquabis(1-hydroxy-2-naphthoato)-neodymium(III)] (1-Hydroxy-2-naphthoate) Dihydrate. An aqueous solution of neodymium(III) chloride hexahydrate (0.38 g, 1.0_5 mmol) was mixed with an excess of a solution of sodium hydroxide. The hydroxide thus precipitated was washed with water and then dissolved into 20 cm^3 of a warm 2-propanol-water mixture (2:1=v/v) together with 1-hydroxy-2-naphthoic acid (0.59 g, 3.1 mmol); some residue subsequently filtered off. The filtrate was left standing for several days; the crystalline salt was thus precipitated. Yield: 0.36 g, 0.43 mmol, 41%. Found: Nd, 17.30; C, 47.21; H, 4.13%. Calcd for $NdC_{33}H_{35}O_{16}$: Nd, 17.34; C, 47.65; H, 4.24%.

Single-Crystal X-Ray Analysis. A crystal 0.5×0.32×0.10 mm^3 in size was used as the sample without any shaping. The crystallographic data: $NdC_{33}H_{35}O_{16}$, F.W.=831.87, triclinic, space group $P\bar{1}$, a=20.621 (4), b=22.288 (5), c=7.724 (1) Å, α=93.30 (2), β=96.78 (2), γ=107.43 (2)°, U=3347.2 (12) Å^3, Z=4, D_m=1.63 (3), D_x=1.65 Mg m^{-3}, μ(Mo $K\alpha$)=1.65 mm^{-1}. The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation (0.7107 Å), in the range of $3° < 2\theta < 55°$, the ω scan technique being employed (scan speed: 4° min^{-1} (θ)); scan width: $1.27+0.5 \tan\theta$ (θ/°)). Of the 15417 independent reflections observed, 7579 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the refinement. The intensities were corrected for the Lorentz and polarization factors, as well as for the absorption.

Structure Determination. The structure was solved by the heavy-atom method. Because all the k-odd reflections were very weak, it was assumed that the crystal is formed by the alternate pile of almost identical structures along the b-axis. At first, the average positions of the metal atoms and some coordinated oxygen atoms were deduced from a Patterson map. The other non-hydrogen atoms were located by means of successive Fourier syntheses. The atomic parameters were refined successively by the block-diagonal least-squares method.

At this stage, the structure of the complex was almost converged, but the naphthalene rings parallel to (010) plane were quite deformed, and the difference Fourier synthesis showed the presence of another orientation of the ring. Therefore, the structure was refined with two independent structures, using all the reflections. At the end of the refinement, all the naphthalene rings were found to be in the normal form. The final R value was 0.048.[11]

All the calculations were carried out on a HITAC M-280H apparatus at the Computer Center of the University of Tokyo, using the local version of the UNICS program.[12] The atomic scattering factors were taken from Ref. 13.

Table 1. Final Atomic Coordinates ($\times 10^4$) of the Complex, together with the Equivalent Isotropic Temperature Factors, with their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^2$ a)	Atom	x	y	z	$B_{eq}/\text{Å}^2$ a)
Nd(1)	4539.9(2)	3669.1(2)	2701.5(6)	2.2_1	Nd(2)	4570.1(2)	8663.3(2)	2695.8(6)	2.4_2
O(1)	3426(3)	3398(3)	3808(8)	3.8_4	O(7)	3352(3)	8388(3)	3542(9)	4.1_1
O(2)	3364(3)	3518(3)	1015(8)	4.1_2	O(8)	3446(4)	8393(4)	762(9)	4.7_3
O(3)	5678(3)	3471(3)	3163(9)	3.9_9	O(9)	5710(3)	8484(3)	3318(9)	3.6_2
O(4)	5758(3)	4472(3)	3601(8)	3.3_4	O(10)	5767(3)	9476(3)	3630(9)	3.7_2
O(5)	3999(4)	393(3)	1097(9)	4.4_9	O(11)	4012(3)	5429(3)	977(8)	3.3_4
O(6)	4282(3)	1432(3)	1850(8)	3.8_3	O(12)	4293(3)	6438(3)	1823(8)	3.3_9
O(W1)	4367(3)	4702(3)	3468(8)	3.5_4	O(W8)	4357(4)	9675(3)	3549(8)	4.0_6
O(W2)	4614(4)	2968(3)	4(8)	3.8_6	O(W9)	4683(4)	7973(3)	125(8)	3.9_1
O(W3)	4744(3)	4313(3)	219(8)	3.3_9	O(W10)	4759(4)	9307(3)	259(8)	3.9_5
O(W4)	4188(4)	2563(3)	3243(9)	4.7_7	O(W11)	4230(4)	7545(3)	3367(9)	4.5_0
O(W5)	4705(3)	3759(3)	5916(8)	3.5_5	O(W12)	4675(3)	8715(3)	5886(8)	3.7_6
O(W6)	6232(5)	707(5)	2403(10)	7.2_3	O(W13)	6201(4)	5645(3)	2485(9)	4.5_4
O(W7)	6488(10)	2004(9)	2379(25)	19.7	O(W14)	6492(4)	7048(3)	2181(9)	4.7_3
O(C1)	2419(3)	3299(3)	5504(8)	3.9_1	O(C31)	2229(4)	8414(4)	4510(11)	6.4_7
O(C11)	6668(4)	3075(3)	4227(10)	4.6_2	O(C41)	6683(3)	8109(3)	4406(8)	3.5_2
O(C21)	2822(4)	−213(3)	−436(11)	5.6_8	O(C51)	2829(3)	4830(3)	−623(10)	4.6_6
C(C1)	3083(4)	3428(4)	2392(12)	3.1_4	C(C4)	3095(5)	8369(5)	1969(14)	4.5_6
C(C2)	6030(4)	4018(5)	3766(12)	3.7_6	C(C5)	6051(4)	9065(4)	3844(11)	2.4_9
C(C3)	3867(4)	906(5)	1078(12)	3.5_3	C(C6)	3858(4)	5937(4)	1084(10)	2.5_8
C(1)	2077(4)	3342(4)	3975(11)	2.7_3	C(31)	1970(6)	8324(5)	2824(17)	5.5_4
C(2)	2354(4)	3404(4)	2408(11)	2.7_5	C(32)	2351(5)	8280(5)	1507(14)	4.2_2
C(3)	1942(5)	3446(5)	817(13)	4.2_0	C(33)	2049(6)	8161(6)	−323(16)	5.5_1
C(4)	1260(5)	3421(6)	826(15)	5.0_1	C(34)	1363(7)	8080(7)	−737(20)	7.2_1
C(5)	959(5)	3350(5)	2401(14)	4.1_2	C(35)	972(7)	8170(6)	531(22)	7.6_0
C(6)	263(5)	3331(6)	2449(16)	5.2_5	C(36)	236(8)	8110(8)	136(27)	10.7
C(7)	−34(7)	3209(7)	3966(18)	6.4_9	C(37)	−99(8)	8221(8)	1464(27)	10.9
C(8)	380(6)	3171(6)	5514(16)	5.6_9	C(38)	162(7)	8299(7)	3254(24)	9.1_5
C(9)	1059(5)	3197(6)	5508(14)	4.5_7	C(39)	881(7)	8369(7)	3792(24)	8.7_3
C(10)	1356(4)	3295(4)	3981(12)	3.3_6	C(40)	1237(6)	8276(5)	2385(20)	6.2_1
C(11)	7017(5)	3668(5)	4877(12)	3.6_5	C(41)	7037(4)	8735(4)	5016(11)	2.8_1
C(12)	6724(4)	4151(4)	4688(11)	2.6_0	C(42)	6774(4)	9219(4)	4755(11)	3.0_6
C(13)	7104(5)	4775(5)	5419(13)	4.2_8	C(43)	7144(4)	9837(4)	5438(13)	3.4_8
C(14)	7769(5)	4899(5)	6301(13)	3.7_0	C(44)	7790(5)	9982(6)	6370(16)	5.0_5
C(15)	8059(5)	4398(5)	6511(12)	4.0_0	C(45)	8091(5)	9481(5)	6579(14)	3.8_6
C(16)	8737(5)	4526(5)	7439(14)	4.4_2	C(46)	8776(6)	9632(7)	7550(15)	6.1_1
C(17)	8993(6)	4017(7)	7592(17)	6.4_4	C(47)	9050(6)	9144(6)	7789(15)	5.6_6
C(18)	8634(6)	3413(7)	6853(17)	5.9_9	C(48)	8679(6)	8501(7)	7110(16)	6.3_1
C(19)	7975(6)	3287(7)	5947(16)	6.5_6	C(49)	8015(5)	8342(5)	6178(14)	4.4_9
C(20)	7681(5)	3787(5)	5747(12)	3.5_9	C(50)	7729(4)	8848(5)	5951(12)	3.5_9
C(21)	2690(5)	340(5)	−536(13)	4.0_4	C(51)	2713(4)	5393(4)	−594(11)	2.8_5
C(22)	3167(5)	879(5)	195(12)	3.4_5	C(52)	3209(4)	5959(4)	191(11)	2.3_8
C(23)	3023(5)	1482(4)	6(12)	3.2_7	C(53)	3051(5)	6528(5)	204(14)	4.6_5
C(24)	2391(6)	1463(5)	−856(14)	4.6_5	C(54)	2423(5)	6561(5)	−566(15)	4.5_5
C(25)	1894(5)	893(6)	−1571(12)	4.3_4	C(55)	1925(5)	5988(5)	−1338(13)	4.1_3
C(26)	1215(6)	869(7)	−2434(15)	5.6_7	C(56)	1264(5)	6014(6)	−2128(15)	5.6_2
C(27)	764(6)	287(7)	−3055(17)	6.9_5	C(57)	764(6)	5456(6)	−2869(16)	5.4_0
C(28)	910(7)	−257(8)	−2878(20)	7.8_7	C(58)	906(5)	4875(6)	−2946(15)	5.1_9
C(29)	1547(6)	−289(7)	−2099(20)	7.3_7	C(59)	1550(5)	4844(5)	−2180(13)	3.8_4
C(30)	2036(5)	326(6)	−1433(14)	4.7_3	C(60)	2061(4)	5402(4)	−1378(11)	3.0_2

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: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Results and Discussion

The final atomic parameters and their equivalent isotropic temperature factors are listed in Table 1, while some bond lengths and bond angles, as well as some interatomic distances which are thought to be the hydrogen-bonding ones, are tabulated in Table 2. The projection of the two unit cells along the c-axis, along with the notation of the naphthalene rings, and the perspective drawings of the complex around the metal atoms, Nd(1) and Nd(2), are shown in Figs. 1, 2, and 3, respectively.[14]

Both the metal complexes have almost the same structure: the central metal atoms are ennea-coordinated and are in the tricapped trigonal-prism geometry, where four oxygen atoms of two chelating

Table 2. Selected Bond Lengths and Bond Angles with Their Standard Deviations in Parentheses[16)]

Bond length	(l/Å)	Bond length	(l/Å)
Nd(1)–O(1)	2.462(7)	Nd(2)–O(7)	2.574(7)
Nd(1)–O(2)	2.532(7)	Nd(2)–O(8)	2.491(7)
Nd(1)–O(3)	2.504(7)	Nd(2)–O(9)	2.497(7)
Nd(1)–O(4)	2.597(5)	Nd(2)–O(10)	2.578(5)
Nd(1)–O(W1)	2.483(7)	Nd(2)–O(W8)	2.490(8)
Nd(1)–O(W2)	2.579(7)	Nd(2)–O(W9)	2.518(7)
Nd(1)–O(W3)	2.461(7)	Nd(2)–O(W10)	2.429(7)
Nd(1)–O(W4)	2.429(7)	Nd(2)–O(W11)	2.483(6)
Nd(1)–O(W5)	2.454(6)	Nd(2)–O(W12)	2.441(6)
C(C1)–O(1)	1.247(12)	C(C4)–O(7)	1.260(13)
C(C1)–O(2)	1.268(12)	C(C4)–O(8)	1.241(14)
C(C2)–O(3)	1.246(11)	C(C5)–O(9)	1.290(9)
C(C2)–O(4)	1.301(14)	C(C5)–O(10)	1.234(12)
C(C3)–O(5)	1.252(14)	C(C6)–O(11)	1.266(12)
C(C3)–O(6)	1.288(10)	C(C6)–O(12)	1.258(9)
O(4)···O(W13)	2.726(10)	O(6)···O(W4)	2.753(11)
O(W1)···O(11)	2.756(10)	O(W6)···O(W7)	2.78(2)
O(W7)···O(C11)	2.61(2)	O(12)···O(W11)	2.722(10)
O(W13)···O(W14)	3.031(10)	O(W14)···O(C41)	2.742(10)
O(4)···O(W1$^{\mathrm{i}}$)	2.919(10)	O(6)···O(W12$^{\mathrm{i}}$)	2.719(10)
O(W4)···O(C41$^{\mathrm{i}}$)	2.870(10)	O(W5)···O(12$^{\mathrm{i}}$)	2.701(9)
O(W5)···O(W13$^{\mathrm{i}}$)	2.936(11)	O(W5)···O(W14$^{\mathrm{i}}$)	3.161(10)
O(W6)···O(W12$^{\mathrm{i}}$)	2.956(14)	O(W7)···O(W12$^{\mathrm{i}}$)	2.97(2)
O(C1)···O(W14$^{\mathrm{i}}$)	3.014(11)	O(C11)···O(W11$^{\mathrm{i}}$)	2.891(11)
O(2)···O(W14$^{\mathrm{iv}}$)	2.795(11)	O(5)···O(W10$^{\mathrm{iv}}$)	2.792(11)
O(6)···O(W9$^{\mathrm{iv}}$)	2.819(10)	O(W2)···O(12$^{\mathrm{iv}}$)	2.829(9)
O(W2)···O(W9$^{\mathrm{iv}}$)	2.888(11)	O(W2)···O(W14$^{\mathrm{iv}}$)	2.662(10)
O(W3)···O(W3$^{\mathrm{iv}}$)	2.980(12)	O(W3)···O(11$^{\mathrm{iv}}$)	2.739(9)
O(W3)···O(W13$^{\mathrm{iv}}$)	2.709(10)	O(W6)···O(W10$^{\mathrm{iv}}$)	2.713(11)
O(W7)···O(8$^{\mathrm{iv}}$)	2.57(2)	O(W7)···O(W9$^{\mathrm{iv}}$)	2.93(2)
O(W13)···O(C51$^{\mathrm{iv}}$)	2.993(12)	O(10)···O(W6$^{\mathrm{v}}$)	2.878(12)
O(W8)···O(5$^{\mathrm{v}}$)	2.725(11)	O(10)···O(W8$^{\mathrm{vi}}$)	2.888(10)
O(W10)···O(W10$^{\mathrm{vii}}$)	3.015(13)	O(W6)···O(C21$^{\mathrm{viii}}$)	3.020(15)

Bond angle	(ϕ/°)	Bond angle	(ϕ/°)
O(2)–Nd(1)–O(W1)	78.5(2)	O(8)–Nd(2)–O(W8)	85.6(2)
O(2)–Nd(1)–O(W3)	74.5(2)	O(8)–Nd(2)–O(W10)	73.4(2)
O(W1)–Nd(1)–O(W3)	71.1(2)	O(W8)–Nd(2)–O(W10)	72.6(2)
O(W4)–Nd(1)–O(W5)	79.0(2)	O(W11)–Nd(2)–O(W12)	75.0(2)
O(W4)–Nd(1)–O(3)	79.1(2)	O(W11)–Nd(2)–O(9)	78.5(2)
O(W5)–Nd(1)–O(3)	82.0(2)	O(W12)–Nd(2)–O(9)	81.0(2)
O(1)–Nd(1)–O(W2)	116.3(2)	O(7)–Nd(2)–O(W9)	114.4(2)
O(1)–Nd(1)–O(4)	137.3(2)	O(7)–Nd(2)–O(10)	139.5(2)
O(4)–Nd(1)–O(W2)	106.3(2)	O(10)–Nd(2)–O(W9)	106.1(2)
O(2)–Nd(1)–O(W4)	89.9(2)	O(8)–Nd(2)–O(W11)	87.1(2)
O(W1)–Nd(1)–O(W5)	77.3(2)	O(W8)–Nd(2)–O(W12)	76.3(2)
O(W3)–Nd(1)–O(3)	97.9(2)	O(W10)–Nd(2)–O(9)	100.5(2)
O(1)–Nd(1)–O(2)	51.8(2)	O(7)–Nd(2)–O(8)	50.9(2)
O(1)–Nd(1)–O(W1)	75.2(2)	O(7)–Nd(2)–O(W8)	72.4(2)
O(1)–Nd(1)–O(W5)	69.3(2)	O(7)–Nd(2)–O(W12)	72.2(2)
O(1)–Nd(1)–O(W4)	70.4(2)	O(7)–Nd(2)–O(W11)	72.3(2)
O(W2)–Nd(1)–O(2)	81.0(2)	O(W9)–Nd(2)–O(8)	75.0(2)
O(W2)–Nd(1)–O(W3)	70.8(2)	O(W9)–Nd(2)–O(W10)	72.5(2)
O(W2)–Nd(1)–O(3)	72.2(2)	O(W9)–Nd(2)–O(9)	72.9(2)
O(W2)–Nd(1)–O(W4)	69.4(2)	O(W9)–Nd(2)–O(W11)	70.6(2)
O(4)–Nd(1)–O(W1)	73.9(2)	O(10)–Nd(2)–O(W8)	74.4(2)
O(4)–Nd(1)–O(W3)	75.0(2)	O(10)–Nd(2)–O(W10)	75.4(2)
O(4)–Nd(1)–O(3)	50.8(2)	O(10)–Nd(2)–O(9)	50.7(2)
O(4)–Nd(1)–O(W5)	75.7(2)	O(10)–Nd(2)–O(W12)	77.9(2)
C(C1)–O(1)–Nd(1)	95.7(6)	C(C4)–O(7)–Nd(2)	91.3(6)
C(C1)–O(2)–Nd(1)	91.8(6)	C(C4)–O(8)–Nd(2)	95.7(7)
O(1)–C(C1)–O(2)	120.4(9)	O(7)–C(C4)–O(8)	121.3(10)
C(C2)–O(3)–Nd(1)	97.3(6)	C(C5)–O(9)–Nd(2)	95.8(5)
C(C2)–O(4)–Nd(1)	91.6(6)	C(C5)–O(10)–Nd(2)	93.4(5)
O(3)–C(C2)–O(4)	118.5(8)	O(9)–C(C5)–O(10)	119.1(7)
O(5)–C(C3)–O(6)	123.2(9)	O(11)–C(C6)–O(12)	120.2(8)

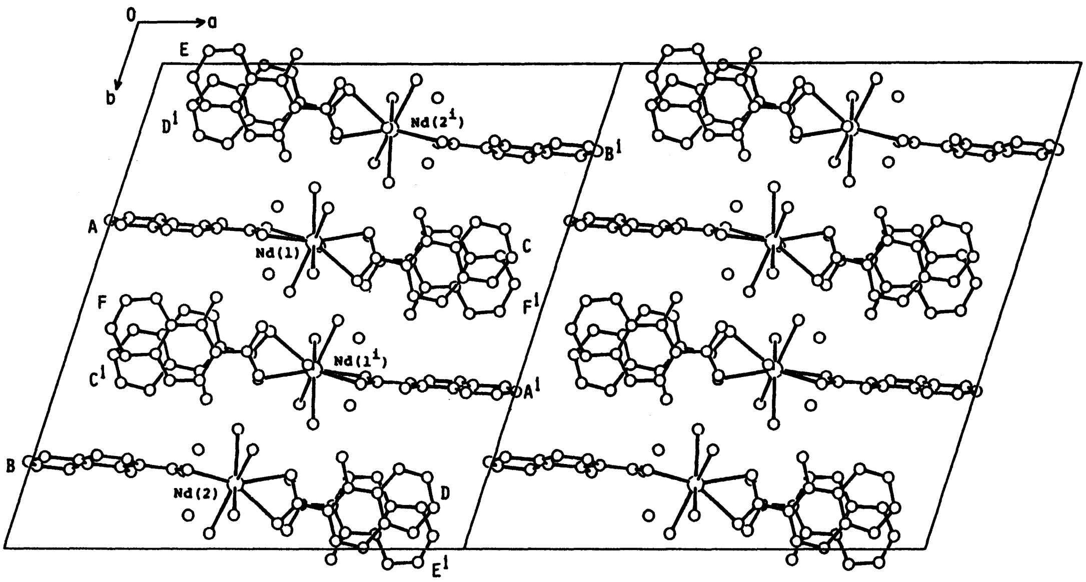

Fig. 1. Projection along the c-axis of the two unit cells with the notations of the naphthalene rings.[16)]

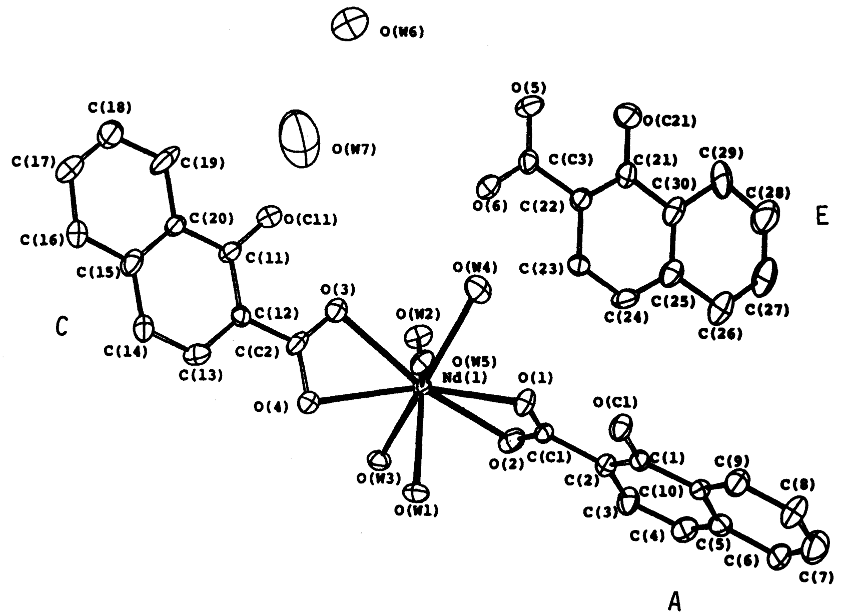

Fig. 2. Perspective drawing of the complex around Nd(1) atom and a non-coordinated naphthoate ion (**E**) with the numbering scheme.

ligands (forming four-membered rings) and five water oxygen atoms are coordinated. The main distinction between the geometries around the two metal atoms lies in the orientations of the A and B naphthoato ligands. As is shown by the schematic presentation in Fig. 4, around Nd(1) and Nd(2) both chelating ligands span the apexes of the trigonal prism and the cap positions respectively; such chelating positions are usual with this type of complex, because the distance between an apex and its nearest cap point is shorter than the edge between two apexes of the prism.[10)]

No bridging by the carboxylate ions is found between metal atoms, and this type of the isolated complex is rather rare among lanthanoid carboxylates. The Nd-O bond lengths of the two carboxyl oxygen atoms of the same chelating ligand are not equal. The average lengths of the long and short bonds are 2.57 (2) and 2.49 (2) Å, respectively. However, there is no tendency for either the longer Nd-O bond to join the shorter C-O bond, or the reverse; that is, all the C-O bond lengths are not much different from the delocalized carboxyl C-O bond length. The Nd-O bond lengths in this compound are rather affected by the respective coordinating positions; generally, the Nd-O bonds at the cap positions are longer than those at the apexes of the trigonal prism. The average Nd-O bond

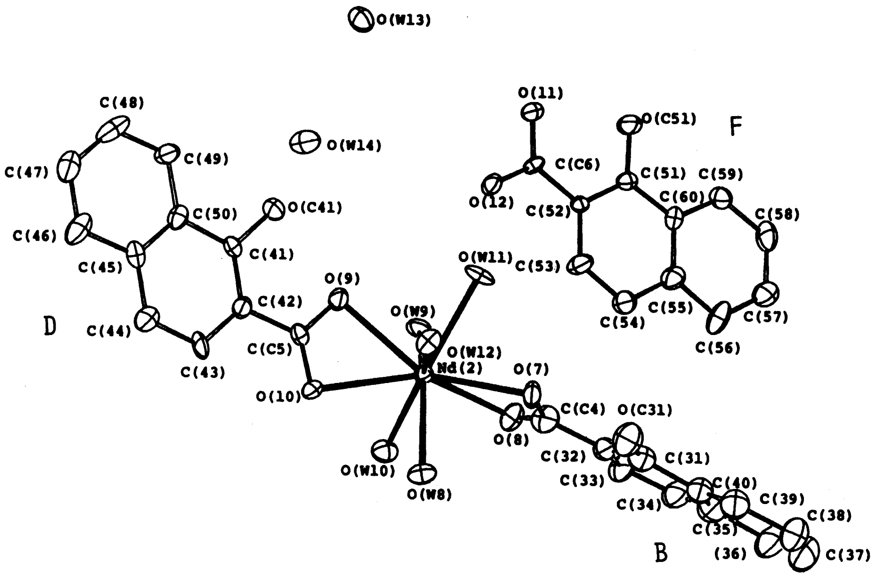

Fig. 3. Perspective drawing of the complex around Nd(2) atom and a non-coordinated naphthoate ion (**F**) with the numbering scheme.

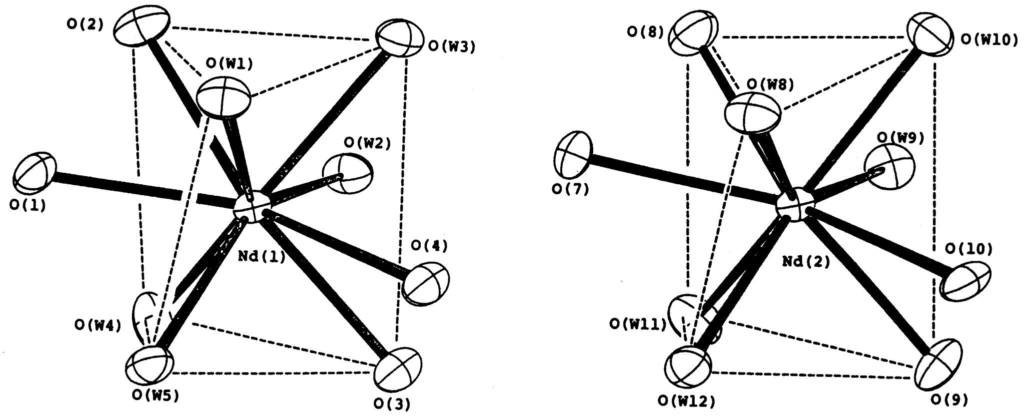

Fig. 4. Schematic presentation to show the coordination geometries around Nd(1) and Nd(2) atoms.

lengths of the water ligands are 2.48 (4) Å, which is a little shorter than that of the carboxylate oxygen atoms, 2.53 (5) Å.

The sum of the Shannon's ionic radii is 2.51 Å for the Nd-O bond (r_{Nd}(Valence(Val)=3+, Coordination Number (CN)=9)=1.163, and r_{O}(Val=2−, CN=2)=1.35 Å),[15] and both types of Nd-O bond lengths of this complex are not much different.

The other carboxylate anions (**E** and **F**) are not coordinated to the metal atom, and there are two more water molecules per metal atom which are not coordinated. Judging from the interatomic distances, it seems that there are some hydrogen bondings between the carboxyl and hydroxyl-group-oxygen atoms of the carboxylate ions, as well as between the coordinated and non-coordinated water oxygen atoms; many such bondings form a kind of network. Such interatomic distances are shown in Table 2.

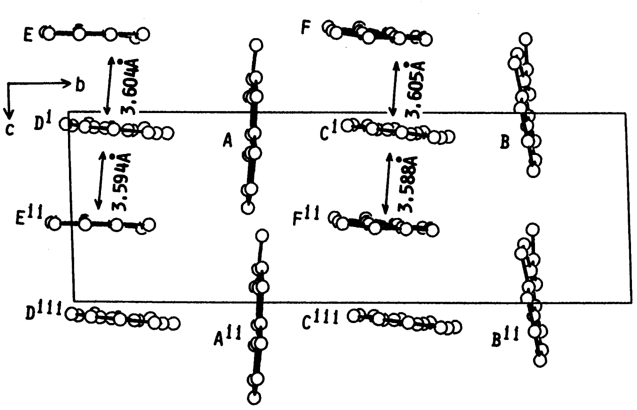

Fig. 5. Packing projection of the naphthalene rings on the plane perpendicular to the **D**^{i} ring plane, which is also approximately perpendicular to all the other naphthalene rings.[16]

As is shown in Fig. 1, the central metal atoms are arrayed almost entirely on (200). Both of the naphthalene rings of the chelate ligands extend to the direction approximately perpendicular to this plane. The naphthalene-ring planes of the ligands on both sides of one metal atom, **A** and **C**, or **B** and **D**, are approximately orthogonal to each other, while those of the non-coordinated naphthoate ions are almost parallel to one of them, **F** and **C**$^{\rm i}$, or **E** and **D**$^{\rm i}$, with their hydroxyl groups directed in opposite directions. Thus, as is shown in Fig. 5, the series of naphthalene-ring planes, **E**, **D**$^{\rm i}$, **E**$^{\rm ii}$, ⋯ and **F**, **C**$^{\rm i}$, **F**$^{\rm ii}$, ⋯ are almost paralle:[16] the maximum dihedral angle between them is 4.7°. They are accumulated approximately in the c-direction. Their inter-planar distances are slightly longer than the thickness of an aromatic ring: **C**$^{\rm i}$-**F**, 3.605; **C**$^{\rm i}$-**F**$^{\rm ii}$, 3.588; **E**-**D**$^{\rm i}$, 3.604; and **D**$^{\rm i}$-**E**$^{\rm ii}$, 3.594 Å.[16] The overlappings of the naphthalene rings of **E**-**D**$^{\rm i}$, **D**$^{\rm i}$-**E**$^{\rm ii}$, **F**-**C**$^{\rm i}$, and **C**$^{\rm i}$-**F**$^{\rm ii}$ are 43, 50, 44, and 51% respectively.[b]

It is of interest to compare this structure with that of lanthanoid(III) 2-naphthalenesulfonate.[9] The latter is also two-dimensional network formed of hydrogen bonds between the coordinated and non-coordinated water molecules and sulfonato group, and the naphthalene rings are intercalated between the hydrophilic layers to form hydrophobic sheets. Naphthalene rings dangling from both sides of the hydrophilic sheets interlock with each other to form only one layer of naphthalene rings, and they are packed very closely, as is shown by the distances between the naphthalene rings, which are almost the thickness of the aromatic rings. In the case of the title complex, the naphthalene rings protruding from the hydrophilic layers do not interlock with each other, but form two sheets of naphthalene layers back to back. These differences may be due to the difference in the bulkiness of the sulfonato group and the carboxylato groups, and also to the participation of hydroxyl groups in the hydrogen bondings of the title complex.

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[b] When a naphthalene ring is projected on another naphthalene ring which is approximately parallel, the percentage of the overlapping area to the ring area is adopted.