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Synthesis, and Crystal and Molecular Structure of Heptaaquabis (1-hydroxy-2-naphthoato)lanthanum(III) 1-Hydroxy-2-naphthoate Hydrate and the Isomorphous Neodymium(III) Salt, $[M\{C_{10}H_6(OH)CO_2\}_2(H_2O)_7][C_{10}H_6(OH)CO_2]\cdot H_2O$ (M=La, Nd)

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Synopsis. The light lanthanoid(III) (La or Nd) 1-hydroxy-2-naphthoate crystals indicated in the title were obtained and their structures were determined by the X-ray diffraction method using their single crystals. They are orthorhombic with the space group $P2_12_12_1$, $Z=4$. The unit-cell axis lengths of the lanthanum(III) complex are: $a=11.985(4)$, $b=40.21(5)$, and $c=7.017(1)$ Å. The central metal atom is ennea-coordinated and is in a tricapped trigonal-prism geometry, where two carboxylate ions act as the unidentates, and the other coordinating positions are occupied by water oxygen atoms. The non-coordinated carboxylate ion is hydrogen-bonded to two ligated water oxygen atoms with its respective carboxylato oxygen atoms. The complex molecules are not directly bridged by the carboxylate ions, but the complexes are linked by hydrogen-bondings in the a- and c-axis directions. Such hydrophilic and the hydrophobic layers of the naphthalene rings, both of them being parallel to the ac-plane, are laid alternately in the crystal.

It has been already reported that many lanthanoid carboxylates have high coordination-number metal atoms and are almost always in dimeric or polymeric structures in their crystals.[1–6] We previously reported two types of neodymium(III) 1-hydroxy-2-naphthoates: one in a dimer form including water and ethanol, $[NdL_3(H_2O)(C_2H_5OH)]_2\cdot 2H_2O\cdot 2C_2H_5OH$ (**1**),[7] and the other is a monomeric type one, $[NdL_2(H_2O)_5]L\cdot 2H_2O$ (**2**) (HL=1-hydroxy-2-naphthoic acid).[8] The metal atoms of both complexes are ennea-coordinated and are in a tricapped trigonal-prism geometry. This time we could obtain other types of the salts (isomorphous lanthanum(III) and neodymium(III) salts), which include eight molecules of water per one metal atom. It is interesting to compare their structures with those of **1** and **2**; we examined their crystal and molecular structure by the single-crystal X-ray diffraction method.

Experimental

Synthesis of [Heptaaquabis(1-hydroxy-2-naphthoato)-lanthanum(III)] (1-hydroxy-2-naphthoate) Hydrate. The lanthanum hydroxide was obtained by mixing aqueous solutions of lanthanum(III) chloride heptahydrate (0.38 g, 1.0 mmol) and an excess sodium hydroxide. The precipitate was separated, washed with water, and dissolved into 30 cm^3 of a warmed 2-propanol–water mixed solvent (2:1=v/v), including 1-hydroxy-2-naphthoic acid (0.56 g, 3.0 mmol). The solution was filtered and the filtrate was left standing for several days at room temperature; and the crystals of the title complex were precipitated. Yield: 0.37 g (43%). Anal ($LaC_{33}H_{37}O_{17}$), La, C, H. A pure lanthanum complex was thus obtained; however, when the same process was applied to the neodymium salt, the product also contained some crystals of **2**. Therefore, from the mixture we picked up the title complex crystals, which were spatula-like thin-plate types that could be clearly distinguished from those of **2**.

Single-Crystal X-Ray Analysis. Crystallographic data and various experimental conditions for collecting intensity data are summarized in Table 1. Reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation, by means of a ω-scan technique (scan speed=4° min^{-1} (θ)). Reflections with $|F_o|>3\sigma(|F_o|)$ were used for a structure determination. All calculations were carried out on a HITAC M-680H computer at the Computer Center of the

Table 1. Crystallographic Data and Some Experimental Conditions of the Complexes $MC_{33}H_{37}O_{17}$

M=	La	Nd
F. W.	844.55	849.89
a (l/Å)	11.985(4)	11.928(10)
b (l/Å)	40.21(5)	40.22(4)
c (l/Å)	7.017(1)	6.996(1)
U (v/Å^3)	3382(4)	3356(5)
D_m (d/Mg m^{-3})	1.65(3)	1.68(3)
D_x (d/Mg m^{-3})	1.66	1.68
μ (Mo $K\alpha$) (n/mm^{-1})	1.38	1.65
Final R[9]	0.054	0.085
R of the Reversed Structure	0.059	0.082
Reflections Measured	5627	4398
Reflections Used for Calculation	4036	2454
Used Crystal (v/mm^{-3})	0.40×0.12×0.10	0.30×0.15×0.10
Scan Width (θ/°)	1.04	1.10
Scanned Range (2θ/°)	3—60	3.5—55

Table 2. Selected Bond Lengths and Bond Angles of the Complexes $\mathrm{MC_{33}H_{37}O_{17}}$ (M=La, Nd)

M=	La	Nd	M=	La	Nd
Bond Lengths (l/Å)			Bond Angles (ϕ/°)		
M-O(1)	2.447(7)	2.415(14)	O(1)-M-O(W2)	78.3(2)	79.1(4)
M-O(3)	2.521(7)	2.473(16)	O(W2)-M-O(W5)	77.54(19)	77.9(4)
M-O(W1)	2.548(7)	2.512(14)	O(W5)-M-O(1)	70.0(2)	70.9(4)
M-O(W2)	2.531(6)	2.475(13)	O(1)-M-O(W1)	71.0(2)	70.0(5)
M-O(W3)	2.589(7)	2.548(14)	O(1)-M-O(3)	131.2(2)	131.5(5)
M-O(W4)	2.575(7)	2.526(15)	O(1)-M-O(W6)	70.4(2)	70.0(5)
M-O(W5)	2.583(6)	2.584(14)	O(W1)-M-O(3)	113.0(2)	112.4(5)
M-O(W6)	2.578(7)	2.562(15)	O(3)-M-O(W6)	128.6(2)	130.9(5)
M-O(W7)	2.637(7)	2.615(16)	O(W6)-M-O(W1)	118.4(2)	116.7(5)
O(1)-C(C1)	1.235(11)	1.20(2)	O(W3)-M-O(W4)	77.3(2)	77.1(5)
O(2)-C(C1)	1.275(12)	1.23(3)	O(W4)-M-O(W7)	68.0(2)	68.8(5)
C(C1)-C(2)	1.497(13)	1.46(3)	O(W7)-M-O(W3)	76.0(2)	77.3(5)
C(1)-O(C1)	1.349(13)	1.40(3)	O(W3)-M-O(3)	67.7(2)	68.4(5)
O(3)-C(C2)	1.282(10)	1.28(2)	O(W3)-M-O(W1)	144.4(2)	143.7(5)
O(4)-C(C2)	1.244(10)	1.28(2)	O(W3)-M-O(W6)	70.1(2)	71.6(5)
C(C2)-C(12)	1.467(11)	1.48(3)	M-O(1)-C(C1)	165.7(6)	166.8(14)
C(11)-O(C11)	1.361(11)	1.37(2)	O(1)-C(C1)-O(2)	122.7(9)	121(2)
O(5)-C(C3)	1.255(11)	1.26(2)	O(1)-C(C1)-C(2)	119.9(9)	121.6(18)
O(6)-C(C3)	1.271(12)	1.22(2)	O(2)-C(C1)-C(2)	117.4(8)	116.8(18)
C(C3)-C(22)	1.492(11)	1.49(3)	M-O(3)-C(C2)	144.6(5)	143.3(14)
C(21)-O(C21)	1.380(10)	1.36(2)	O(3)-C(C2)-O(4)	122.1(7)	122.9(18)
O(W3)···O(6)	2.659(9)	2.65(2)	O(3)-C(C2)-C(12)	117.8(7)	118.7(17)
O(W4)···O(5)	2.784(10)	2.77(2)	O(4)-C(C2)-C(12)	120.1(7)	118.4(17)
O(W6)···O(W8)	2.901(11)	2.91(2)	M-O(W3)···O(6)	120.1(3)	119.7(6)
			M-O(W4)···O(5)	120.1(3)	121.0(6)
			M-O(W6)···O(W8)	109.9(3)	109.5(6)

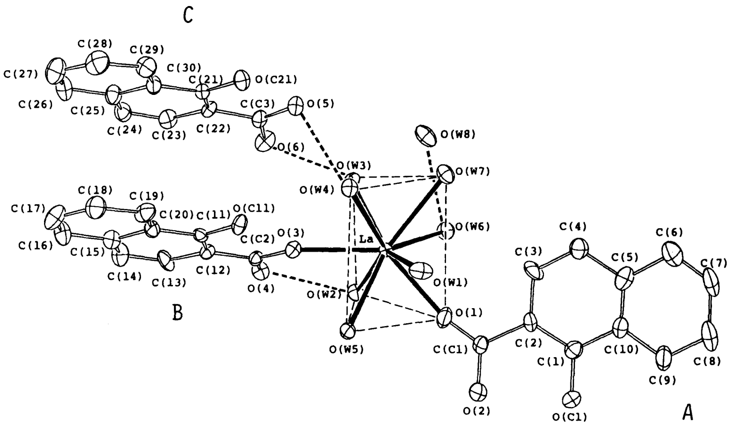

Fig. 1. A perspective drawing around the metal atom with the numbering scheme of the atoms and the notation of the naphthalene rings.

University of Tokyo, using the local version of UNICS.[10] The scattering factors were taken from Ref. 11.

The structure of the lanthanum(III) complex was solved by common heavy-atom method. Refinements of the parameters of the neodymium(III) complex were started from the final parameters of the isomorphous lanthanum(III) salt, and was refined as usual. Their final *R* values are shown in Table 1, together with those of the reversed structures. As the *R* value of the reversed structure was larger in the case of the lanthanum complex, it was rejected; however, that of the neodymium complex was a little smaller and should be adopted for the salt.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 2.[12] A perspective drawing of the complex together with a carboxylate ion and a water molecule near it is shown in Fig. 1; the numbering scheme of the atoms as well as the notation of the naphthalene rings are also given. A projection of the unit cell is shown in Fig. 2.

No carboxylato bridgings were found between the metal atoms, although some hydrogen bondings link those complexes in a- and c-axis directions.

The metal atom is ennea-coordinated and is in a tricapped trigonal-prism geometry. Two carboxylate ions are coordinated as unidentates with each carboxyl oxygen atom at one apex of the prism and one cap position; the other seven positions are occupied by the water oxygen atoms. Compared with **2**, where both of

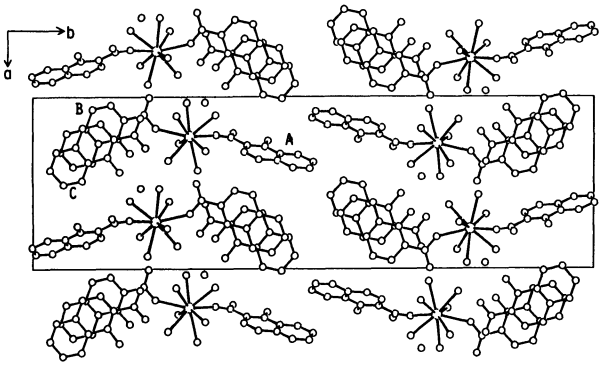

Fig. 2. Crystal packing diagram.

the carboxylate ions form four-membered chelate rings, this compound is regarded as being one in which each carboxyl oxygen atom of the ligands of the former complex is substituted by a water oxygen atom.

The non-coordinated carboxylato oxygen atoms of the coordinated ligands, O(4) and O(2), are hydrogen-bonded with O(W2) and O(W7$^{\text{iii}}$) (Key to the symmetry operation: iii, x, y, $-1+z$). The carboxylato oxygen atoms of the non-coordinated carboxylate ion, O(5) and O(6), atoms are hydrogen bonded with O(W4) and O(W3) atoms, respectively. These water oxygen atoms, O(W2,) O(W7$^{\text{iii}}$), O(W4), and O(W3) atoms are all ligated to respective metal atoms. The crystalline water oxygen, O(W8), and the hydroxyl oxygen atoms of the carboxylate ions also join the hydrogen-bonding network formation, which is spread approximately parallel to the ac-plane.

In this type complex, the M-O(carboxylate) lengths are shorter than those of M-O(water), though in **2**, on the contrary, the average of the former bond lengths is slightly longer than that of the latter ones. Probably the chelate-ring formation in **2** gives some steric effect to lengthen the former bond lengths.

The lanthanum and neodymium complexes are isomorphous with each other, and the respective La-O bond lengths are longer than the corresponding Nd-O ones, except M-O(W5), which are about the same in length in both complexes. Except for these discrepancies, there are no fundamental differences between the corresponding bond lengths and angles of both complexes, respectively.

The arrangement of naphthalene rings of the ligands and the metal core parts resembles that of **2**. The naphthalene ring parts are intercalated between the hydrophilic sheets of the hydrogen bonded metal core layers. As shown in Fig. 3, **B** and **C** naphthalene rings are almost parallel (dihedral angle=0.8°) and, as written in the figure, the inter-layer distances are approximately the thickness of an aromatic ring. The overlapping area[13] of **B** and **C**, and **C** and **B**$^{\text{ii}}$ rings are about 26 and 58%, respectively. The respective dihedral angles between **B** and **A**$^{\text{i}}$, and **C** and **A**$^{\text{i}}$ rings are 81.7° and 81.0°.

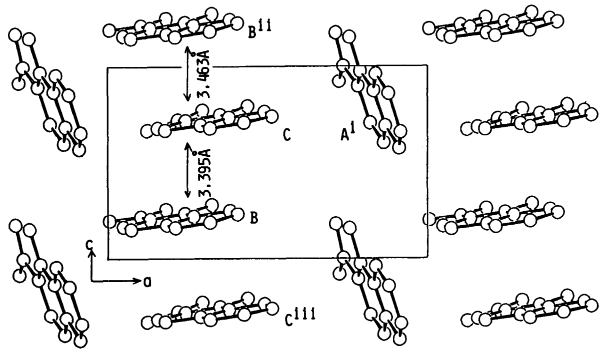

Fig. 3. A projection of the naphthalene rings to the ac-plane. Key to the symmetry operations; i, $0.5+x$, $0.5-y$, $1-z$; ii, x, y, $1+z$; iii, x, y, $-1+z$.

The hydroxyl groups of the parallel **B** and **C** naphthalene rings direct themselves to the same side in these complexes, while those of **2** to opposite sides from each other.

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9) $R=\Sigma||F_{\mathrm{o}}|-|F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}|$

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

11) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp.72, 149.

12) The final atomic and thermal parameters, the final F_{o}—F_{c} table, and some additional data about the bond lengths and bond angles are deposited as Document No. 8729 at the Office of the Editor of Bull. Chem. Soc. Jpn.

13) The former ring is projected to the latter ring plane, and the percentage of the overlapping area of the both rings to the whole ring area was calculated.