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The Structure of Aquatris(*m*-hydroxybenzoato)cerium(III), $[Ce(HOC_6H_4CO_2)_3(H_2O)]_n$

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Synopsis. The crystal and molecular structure of the title complex has been determined by the use of the single-crystal X-ray diffraction method. The crystal of $CeC_{21}H_{17}O_{10}$, F. W. 569.48, was monoclinic; space group $P2_1/c$, a=13.401(2), b=19.173(5), c=8.079(1) Å, β=98.94(1)°, U=2050.6(8) Å^3, Z=4, D_m=1.84(3), D_x=1.84 Mg m^{-3}, and μ(Mo $K\alpha$)=2.31 mm^{-1}. Each cerium(III) atom is ennea-coordinated and is in a tri-capped trigonal-prism geometry. They are in a linear polymer, and each cerium(III) atom is bridged to the next metal atom by three carboxylate ligands.

The structures of lanthanoid(III) carboxylates, are actively being investigated.1–5) The present authors showed in previous paper the structure of the lanthanoid(III) complexes of *m*-hydroxybenzoic acid with the formula of $[LnL_3(H_2O)_2]\cdot HL\cdot 2H_2O$, where Ln= La, Ce, Pr, and Nd, and HL=*m*-hydroxybenzoic acid.6) Although the type of the complex of cerium(III) was obtained from aqueous solution containing an excess of the free acid, the titled complex was crystallized from the aqueous solution containing cerium(III) and the carboxylate ions in a stoichiometric ratio (pH≈5). Therefore, its crystal and molecular structure was determined by the single-crystal X-ray-diffraction method.

Experimental

*Synthesis of [Aquatris(*m*-hydroxybenzoato)cerium(III)] Polymer.* The cerium(III) hydroxide obtained by mixing aqueous solutions of about 1.5 g (4 mmol) of cerium(III) chloride heptahydrate and an excess of sodium hydroxide was dissolved into a hot aqueous solution of *m*-hydroxybenzoic acid (1.7 g (12 mmol) in 20 cm^3 of water). The insoluble matter was filtered off, and the filtrate was kept in a silica-gel desiccator several days, until the volume of the solution was reduced to about 10 cm^3. The precipitated crystals were filtered off and washed with water and acetone, in that order. The yield was about 1.1 g (48%).

Single-crystal X-Ray Analysis. A crystal with dimensions of 0.4×0.4×0.2 mm^3 was used for the measurement. All its edges were ground off. The reflections within the range of $3° < 2\theta < 46°$ were collected on a Rigaku AFC-6A four-circle automated X-ray diffractometer with Mo $K\alpha$ radiation, where the ω-scan (3—30°) or θ-2θ-scan (30—46°) technique was employed. From the 2978 independent reflections observed, 2479 $|F_o| > 3\sigma(|F_o|)$ were selected and used for the refinement. The intensities were corrected for the Lorentz and polarization factors, but no correction was made for the absorption or extinction.

All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using the local version of the UNICS.7) The scattering factors were taken from the tables.8)

Structure Determination. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All non-hydrogen atoms were found, and the final R value was 0.032, with anisotropic temperature factors for all atoms.9)

Results and Discussion

The selected final atomic coordinates and equivalent isotropic temperature factors are shown in Table 1, while the bond lengths and bond angles, in Table 2.10) A perspective drawing of the complex, with the numbering scheme, is shown in Fig. 1; its crystal packing diagram, in Fig. 2, and a schematic presentation of the bonding modes of the ligands, in Fig. 3.

As is shown in the figures, this complex has a structure different from those of the tetracarboxylates $[ML_3(H_2O)_2]\cdot HL\cdot 2H_2O$ (M=La—Nd) or of the tricarboxylates $[ML_3(H_2O)_3]_2\cdot 2H_2O$ (M=Sm—Yb) (HL= *m*-hydroxybenzoic acid), where the complex molecules are lined parallel to the c-axis.6) In this complex, the central cerium(III) atom is ennea-coordinated and is in a deformed tri-capped trigonal-prism geometry. One of the oxygen atoms of each ligand, O(11), O(21), and O(31), takes each cap position, while O(22) or O(32)

TABLE 1 FINAL ATOMIC COORDINATES (×10^4) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2 a)
Ce	2617.0(3)	2207.0(2)	328.3(4)	1.37
O(11)	4164(3)	2661(2)	1816(5)	2.55
O(12)	4016(3)	3310(2)	4034(5)	2.14
O(21)	3071(4)	1035(2)	1469(5)	2.83
O(22)	2951(3)	1769(2)	3526(5)	2.04
O(31)	1110(3)	3020(2)	-219(5)	2.37
O(32)	1879(3)	3097(2)	2375(5)	1.90
C(11)	4542(5)	3012(3)	3062(7)	1.85
C(12)	5670(5)	3085(3)	3388(7)	1.93
C(21)	3143(4)	1164(3)	3019(7)	1.71
C(22)	3414(4)	585(3)	4230(7)	1.66
C(31)	1189(4)	3291(3)	1202(7)	1.78
C(32)	477(4)	3856(3)	1487(7)	1.98
O(W)	1004(3)	1642(3)	1248(6)	3.21

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

TABLE 2. BOND LENGTHS AND BOND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å	Bond length	l/Å
Ce-O(11)	2.392(4)	Ce-O(21)	2.468(5)
Ce-O(22)	2.687(4)	Ce-O(31)	2.535(4)
Ce-O(32)	2.671(4)	Ce-O(W)	2.628(5)
Ce-O(12$^{\text{ii}}$)	2.489(4)	Ce-O(22$^{\text{ii}}$)	2.526(4)
Ce-O(32$^{\text{ii}}$)	2.506(4)	O(11)-C(11)	1.251(7)
O(12)-C(11)	1.270(8)	O(13)-C(16)	1.376(8)
O(21)-C(21)	1.265(7)	O(22)-C(21)	1.269(7)
O(31)-C(31)	1.249(7)	O(32)-C(31)	1.273(7)

Bond angle	Φ/°	Bond angle	Φ/°
O(11)-Ce-O(21)	90.00(14)	O(11)-Ce-O(31)	117.93(14)
O(11)-Ce-O(22)	68.23(13)	O(11)-Ce-O(32)	80.33(13)
O(11)-Ce-O(W)	134.03(14)	O(21)-Ce-O(31)	140.15(14)
O(22)-Ce-O(32)	68.09(12)	O(11)-Ce-O(32$^{\text{ii}}$)	138.28(13)
O(22)-Ce-O(12$^{\text{ii}}$)	104.80(13)	O(11)-Ce-O(12$^{\text{ii}}$)	72.91(14)
O(11)-Ce-O(22$^{\text{ii}}$)	77.85(13)		
O(12$^{\text{ii}}$)-Ce-O(22$^{\text{ii}}$)	81.69(13)		

Key to symmetry operations: i. x, $0.5-y$, $0.5+z$; ii. x, $0.5-y$, $-0.5+z$.

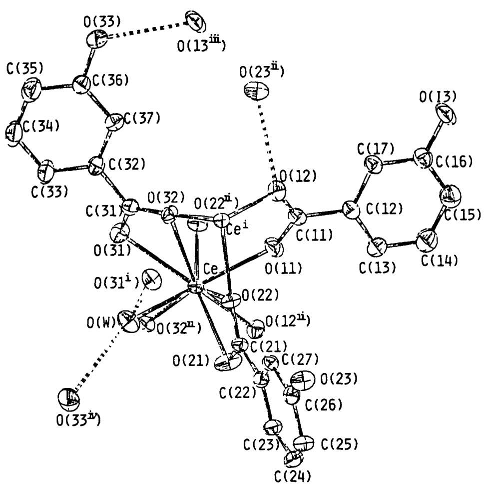

Fig. 1. The perspective drawing of the complex and the numbering scheme.

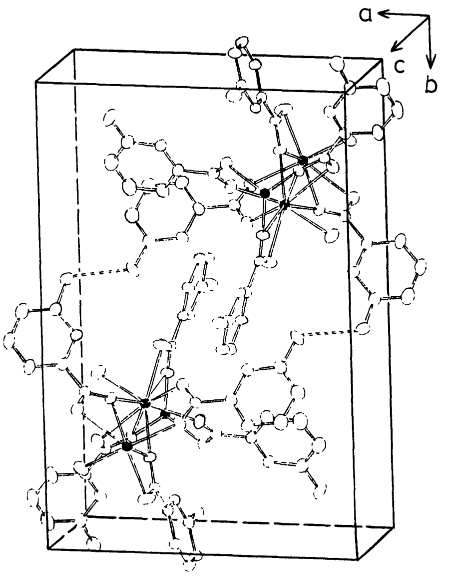

Fig. 2. The crystal packing diagram of the title complex.

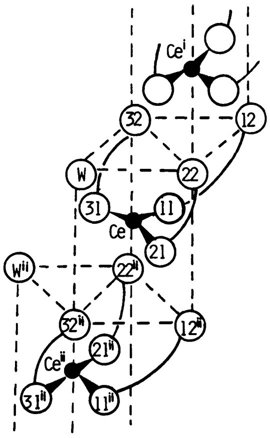

Fig. 3. Schematic presentation of the bonding modes of ligands.
(●: cerium(III), O: oxygen atoms)

take the tips of the upper triangle of the prism. The water oxygen atom, O(W), occupies the other tip of the triangle. All of the three ligands form bridges to the next cerium(III) atom, Ce^{i},11) and O(12), O(22), and O(32) atoms are at the three tips of the bottom triangle of the prism around the Ce^{i} atom. Thus, the O(22)–O(32) edge is common to both of the triangles, as is shown in Fig. 3. The three oxygen atoms at the bottom triangle of the prism around the Ce atom are O(12^{ii}), O(22^{ii}), and O(32^{ii}),11) which are parts of the bridging ligands between Ce and Ce^{ii} atoms.11) Thus, Ce and Ce^{i}, as well as Ce and Ce^{ii}, are each bridged with three carboxylate ligands. One of the three ligands bond to each cerium(III) atom with one each oxygen atom of its carboxyl group. Each one of the other two ligands bridges two metal atoms by one carboxyl oxygen atom, and, at the same time, the other carboxyl oxygen atom of the ligand is coordinated to one of the bridged metal atoms. One of the Ce–O bondings of each latter type of ligand, Ce–O(22) or Ce–O(32), is a little longer than the other Ce–O bondings, as is shown in Table 2. The bond length of Ce–O(W) is also a little longer than the others. The difference in the C–O bond lengths of each carboxyl group of the ligands is not large: 0.019, 0.004, and 0.024 Å respectively, and the oxygen atom of the shorter C–O bond occupies the cap position.

It is found that some O···O interatomic distances are shorter than about 2.9 Å, and hydrogen bondings between the phenol oxygen atoms and the oxygen atoms of the other ligands are expected to exist; the O(33)···O(13^{iii}), O(12)···O(23^{ii}), O(W)···O(33^{iv}), and O(W)···O(31^{i}), shown in Fig. 2, are examples (2.723(7), 2.820(7), and 2.910(6) Å respectively).11) Thus, the linear complex chains weakly bond with other chains.

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9) $R=\sum||F_o|-|F_c||/\sum|F_o|$
10) The final atomic parameters, the final F_o-F_c values, and some additional data about bond lengths and bond angles are deposited as Document No. 8418 at the Office of the Editor of Bull. Chem. Soc. Jpn.
11) Key to symmetric operations: i. x, $0.5-y$, $0.5+z$; ii. x, $0.5-y$, $-0.5+z$; iii. $1.0-x$, $1.0-y$, $1.0-z$; iv. $-x$, $-0.5+y$, $0.5-z$.