The Structure of μ-Aquabis(μ-trichloroacetato)bis[aquabis(trichloroacetato)erbium(III)] Hydrate, $[\{Er(CCl_3CO_2)_2(H_2O)\}_2(CCl_3CO_2)_2(H_2O)]_n\cdot nH_2O$

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Synopsis. The structure of the title complex has been determined by the single-crystal X-ray diffraction method. A crystal of $Er_2C_{12}H_8O_{16}Cl_{18}$, F. W. 1380.86 is triclinic, with the space group of $P\bar{1}$, a=12.787(8), b=15.209(7), c=11.685(7) Å, α=102.24(5), β=114.43(5), γ=70.59(4)°, Z=2 (for the dimer formula), D_x=2.36, D_m=2.34(3) Mg m^{-3}, and μ(Mo $K\alpha$)=5.74 mm^{-1}. All the carboxylate ions act as bidentate bridges, and each pair of the side-by-side metal atoms is bridged by four carboxylate ions, or by two carboxylate ions and one water-oxygen atom, alternately, forming a polymeric chain approximately parallel to the [011] axis. The chains are arrayed in layers parallel to the (100) plane, and the respective layers are separated by the trichloromethyl groups.

We have reported previously about the lanthanoid(III) 2-naphthalenesulfonate enneahydrate, where the crystal is composed of alternate layers of hydrophilic metal cores and hydrophobic naphthalene rings.1) However, such a layer structure was not always found, even when the ligand has a large hydrocarbon group in it; for example, in neodymium(III) 1-hydroxy-2-naphthoate–water–ethanol (1/2/2), the ligand-metal cores are surrounded by naphthalene rings.2)

As the layer structure is very interesting, we have been trying to find another example. Along this line, the title complex was chosen, because the trichloromethyl groups in the ligands were also expected to act as a hydrophobic part.

Moreover, as many lanthanoid(III) carboxylates have a complicated polymeric form in their crystals,3,4) it is interesting to compare the structure of the title complex with them. Therefore, its crystal and molecular structure has been determined by the X-ray-diffraction method using a single crystal.

Experimental

Preparation of μ-Aquabis(μ-trichloroacetato)bis[aquabis(trichloroacetato)erbium(III)] Hydrate. Wet erbium(III) hydroxide, freshly prepared from an hydrochloric acid solution of erbium(III) oxide (0.38 g, containing 2.0 mmol of Er(III)) and an excess of sodium hydroxide, was treated with trichloroacetic acid (0.98 g, 6.0 mmol). The aqueous solution thus obtained (about 8 cm^3) was left standing in a desiccator over silica gel for several days at the ambient temperature; about two-thirds of the water was then removed, and crystals were deposited. They were filtered and washed with a little water. Yield: 0.62 g, 45%. Although the crystals were stable in a sealed bottle for several months, they easily lost a part of the water in the open air.

The dysprosium(III) complex, which is thought to be isomorphous, is also obtained by the same technique. (a=12.818(15), b=15.247(16), c=11.648(12) Å, α=102.01(9), β=114.62(9), γ=70.99(9)°, U=1950(4) Å^3).

Anal. ($M_2C_{12}H_8O_{16}Cl_{18}$) M=Er or Dy, C, H.

Single-crystal X-Ray Analysis. A crystal with dimensions of 0.25×0.25×0.15 mm^3 was used for the measurement after its edges have been ground off. The reflections within the range of $3°<2\theta<50°$ were collected on a Rigaku AFC-6A four-circle automated X-ray diffractometer with Mo $K\alpha$ radiation, employing the ω—2θ scan technique. Of the 6957 independent reflections, 4642 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the refinement. The intensities were corrected for the Lorentz and polarization factors, but no correction was made for the absorption and extinction. All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo, using the local version of UNICS.5) The scattering factors were taken from Ref. 6.

Structure Determination. The structure was solved by the heavy-atom method, and all the non-hydrogen atoms were found. However, as the temperature factors of the five chlorine atoms were found to be large, at the final step of the refinement their positions were fixed assuming their B_{iso} value to be 15.0. The final R value thus obtained, by applying the anisotropic temperature factors for the other atoms, was 0.084.7) Although the thermal parameters of some chlorine atoms of this complex are found to be abnormally large, the same kind of positional ambiguities of some atoms are also found in the structural determination of some lanthanoid(III) complexes,8–11) with regard to some carbon atoms of the hydrocarbon groups, or even some sulfur atoms which are apart from the central metal core and are in the hydrophobic moiety in the crystal.

Results and Discussion

Some selected bond lengths and bond angles are tabulated in Table 1.12) The respective perspective drawings of the complex around Er(1) and Er(2) atoms are shown in Figs. 1 and 2; a schematic presentation to show the coordination geometries around the metal atoms as well as the bridging modes, in Fig. 3, and the crystal packing diagram, in Fig. 4.

All the metal atoms are octa-coordinated and are in the square-antiprism geometry. The Er–O bond lengths of the carboxylato oxygen atoms are 2.28 Å on the average (maximum, Er(1)–O(16^i)=2.387(13) and minimum, Er(2)–O(21)=2.227(17) Å),13) while the Er–O(water) bond lengths are longer than they (2.45 Å on the average, except the Er(2)–O(W2)). The Er(2)–O(W2) is the longest one (3.10(2) Å), and this bond is thought to be very weak.

All the carboxylato ligands act as *Z,Z*-type bidentate bridges.3) Their COM angles of the carboxyl groups are about 140—147°, except for some abnormal ones in **15** and **25**.14)

One oxygen atom, O(W4) is not ligated with any

Table 1. Selected Bond Lengths and Bond Angles of the Complex[13]

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Er(1)-O(12)	2.28(2)	Er(1)-O(13)	2.268(16)	Er(1)-O(15)	2.26(2)
Er(1)-O(22)	2.288(15)	Er(1)-O(W1)	2.43(3)	Er(1)-O(W2)	2.537(17)
Er(1)-O(16$^{\mathrm{i}}$)	2.387(13)	Er(1)-O(11$^{\mathrm{i}}$)	2.277(17)	Er(2)-O(14)	2.244(14)
Er(2)-O(21)	2.227(17)	Er(2)-O(23)	2.29(3)	Er(2)-O(25)	2.233(18)
Er(2)-O(W2)	3.10(2)	Er(2)-O(W3)	2.36(3)	Er(2)-O(24$^{\mathrm{ii}}$)	2.304(17)
Er(2)-O(26$^{\mathrm{ii}}$)	2.300(19)	O(11)-C(11)	1.23(3)	O(12)-C(11)	1.26(4)
O(13)-C(13)	1.24(3)	O(14)-C(13)	1.23(3)	O(15)-C(15)	1.22(3)
O(16)-C(15)	1.23(3)	O(21)-C(21)	1.24(3)	O(22)-C(21)	1.25(3)
O(23)-C(23)	1.26(4)	O(24)-C(23)	1.23(3)	O(25)-C(25)	1.22(3)
O(26)-C(25)	1.24(3)				
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**	**Bond angle**	**ϕ/°**
O(12)-Er(1)-O(16$^{\mathrm{i}}$)	74.6(6)	O(16$^{\mathrm{i}}$)-Er(1)-O(11$^{\mathrm{i}}$)	75.4(5)	O(W2)-Er(1)-O(13)	73.5(5)
O(13)-Er(1)-O(W1)	71.5(7)	O(12)-Er(1)-O(15)	77.5(8)	O(15)-Er(1)-O(11$^{\mathrm{i}}$)	74.6(7)
O(W2)-Er(1)-O(22)	71.8(5)	O(22)-Er(1)-O(W1)	69.7(7)	O(14)-Er(2)-O(W3)	74.6(8)
O(W3)-Er(2)-O(21)	73.9(8)	O(21)-Er-(2)-O(W2)	65.7(6)	O(W2)-Er(2)-O(14)	67.3(5)
O(23)-Er(2)-O(25)	76.7(8)	O(25)-Er(2)-O(26$^{\mathrm{ii}}$)	122.3(7)	O(24$^{\mathrm{ii}}$)-Er(2)-O(23)	125.5(8)
O(26$^{\mathrm{ii}}$)-Er(2)-O(24$^{\mathrm{ii}}$)	78.7(6)				

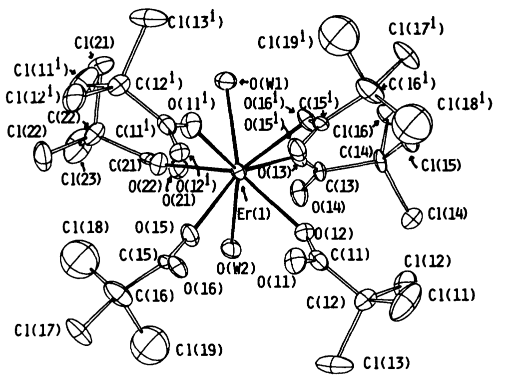

Fig. 1. A perspective drawing of the complex around Er(1) atom, with the numbering scheme of the atoms.[13]

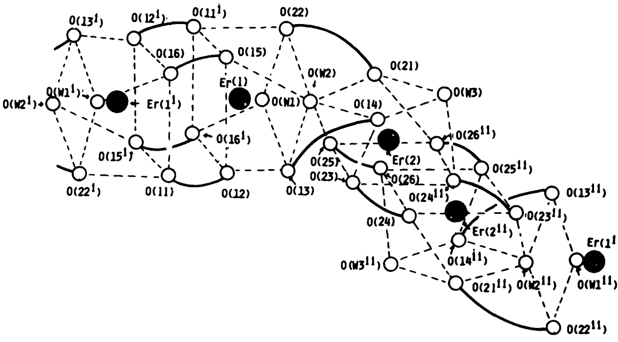

Fig. 3. Schematic presentation to show the coordination geometries around the metal atoms, as well as the bridgings between them.[13]

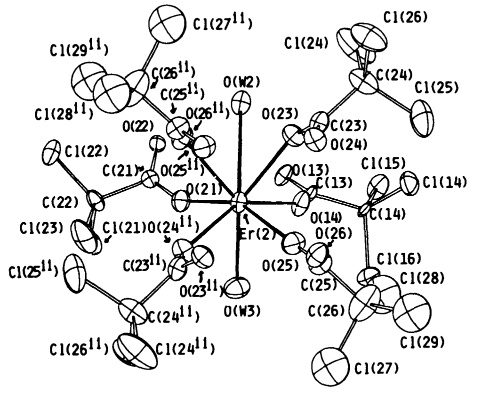

Fig. 2. A perspective drawing of the complex around Er(2) atom, with the numbering scheme of the atoms.[13]

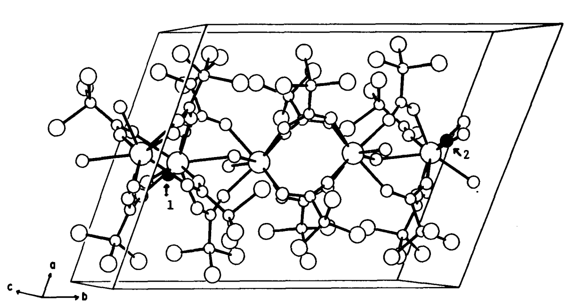

Fig. 4. Crystal packing diagram of the complex. ● atoms are: 1, O(W4); 2, O(W4$^{\mathrm{ii}}$).[13]

metal atom, but it is hydrogen-bonded with O(W1), O(W3), and O(W1^{iii}) atoms.[13]

As is shown in Fig. 3, Er(1^{i})···Er(1), and Er(2)···Er(2^{ii}) are bridged by four carboxylate ions, while Er(1)···Er(2) is bridged by two carboxylate ions and one water oxygen atom O(W2), although Er(2)–O(W2) is a little too long. The dihedral angles of the respective pairs of the square planes above and below the Er(1) and Er(2) atom are 2.8 and 4.8° respectively, while that of the two squares joined by O(W2) is 62.3°. The intermetallic distances of Er(1^{i})···Er(1), Er(1)···Er(2), and Er(2)···Er(2^{ii}) are 4.430(4), 4.823(3), and 4.267(3) Å respectively, and they are aligned approximately along the [011] axis.

As is shown in Fig. 4, the polymeric chains are arrayed in a layer parallel to the (100) plane, and the chlorine atoms of the ligands take positions in the parallel layes on both sides of it. Thus, the layer structure of this complex resemble that of lanthanoid(III) 2-naphthalenesulfonate;[1] the hydrophobic-trichloromethyl group layers act as those of the naphthalene-ring layers of the latter complex.

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12) The final positional and anisotropic thermal parameters, the F_o—F_c table, and some additional bond-length and bond-angle data are deposited as Document No. 8702 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

13) Key to the symmetry operation: i, $1-x$, $-y$, $-z$; ii, $1-x$, $1-y$, $1-z$; iii, $1-x$, $-y$, $1-z$.

14) In this paper, the numbering of the respective carboxylate ions is shown by the number of the carboxyl-carbon atoms of the respective ions. Therefore, the ***n*1**, ***n*3**, and ***n*5** ions (where n=1, 2, or 3) include O(n1) and O(n2); O(n3) and O(n4); and O(n5) and O(n6) atoms, respectively.