The Structure of Diaquatris[(methylthio)acetato]-ytterbium(III), $[Yb(CH_3SCH_2CO_2)_3(H_2O)_2]_n$

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(Received October 8, 1984)

Synopsis. The crystal and molecular structure of the title complex has been determined by the use of single-crystal X-ray diffraction. The crystal of $YbC_9H_{19}O_8S_3$, $F.W.$= 524.48, was monoclinic, with a space group of $P2_1/a$; a= 12.501(6), b=25.096(9), c=10.788(2) Å, β=90.25(3)°, U=3384 (2) Å^3, Z=8, D_m=2.07(3), D_x=2.06 Mg m^{-3}, and μ(Mo $K\alpha$)= 6.20 mm^{-1}. Both Yb(1) and Yb(2) are octa-coordinated and are in a dodecagedral geometry. They are in a linear polymer form, parallel to the c axis; Yb(1) and Yb(2) are arrayed in a line alternatively, bridged by one carboxylate ligand.

In a previous paper,[1] the present authors showed the structure of the neodymium(III) complex of (methylthio)acetic acid (Hmesa), $[Nd_2(mesa)_6(H_2O)_3]_n$, which is isostructural to its cerium(III), praseodymium(III), and europium(III) salts.

In that paper, the dysprosium(III) and ytterbium(III) complexes of the same ligand were found to have the $[M(mesa)_3(H_2O)_2]$ formula (where M=Dy or Yb).[1] Therefore the crystal and molecular structures of the ytterbium(III) complex have now been determined by the single-crystal X-ray diffraction technique.

Experimental

Single-crystal X-Ray Analysis. The title complex is obtained as described in the previous paper[1] and is recrystallized from water. However, as the crystals thus obtained were mostly in thin plates and poor in the b-axis direction and as, moreover, many of them were twin crystals, we chose the best one from among the about 30 samples tested.

A 0.3×0.3×0.1 mm^3 crystal was used, without shaping. The reflections whithin the range of $3°<2\theta<55°$ were collected on a Rigaku AFC-6A four-circle automated X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation by means of the ω-scan technique. From the 8019 independent reflections observed, 4046 $|F_o|>3\sigma(|F_o|)$ reflections were 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.[2] The scattering factors were taken from the tables.[3]

The structure was solved by the heavy-atom method. All the non-hydrogen atoms were found; the final R-value was 0.086,[4] with anisotropic temperature factors for all atoms.

Results and Discussion

The selected interatomic distances and bond angles are shown in Table 1.[5] A perspective drawing of the complex with the numbering scheme is given in Fig. 1, and a schematic presentation to show the positions of the ligating atoms around Yb(1) and Yb(2), in Fig. 2.[5]

As is shown in the figures, both the central metal atoms of the complex are octa-coordinated, and they are in a deformed dodecahedral geometry; their coordi-

Table 1. Selected inter-atomic distances and bond angles, with estimated standard deviations in parentheses

Bond length	l/Å	Bond length	l/Å
Yb(1)-O(11W)	2.28(1)	Yb(1)-O(12W)	2.29(2)
Yb(1)-O(13)	2.38(1)	Yb(1)-O(14)	2.40(2)
Yb(1)-O(15)	2.38(1)	Yb(1)-O(16)	2.39(1)
Yb(1)-O(17)	2.24(1)	Yb(1)-O(27^i)	2.22(1)
Yb(2)-O(21W)	2.28(1)	Yb(2)-O(22W)	2.31(1)
Yb(2)-O(23)	2.41(1)	Yb(2)-O(24)	2.34(2)
Yb(2)-O(25)	2.36(1)	Yb(2)-O(26)	2.42(1)
Yb(2)-O(28)	2.25(1)	Yb(2)-O(18)	2.19(2)
Yb(1)···Yb(2)	5.573(2)	Yb(1)···Yb(2^i)	5.777(2)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
Yb(1)-O(13)-C(11)	93.2(15)	Yb(1)-O(14)-C(11)	91.5(15)
Yb(1)-O(15)-C(14)	95.2(15)	Yb(1)-O(16)-C(14)	94.7(15)
Yb(2)-O(23)-C(21)	90.7(16)	Yb(2)-O(24)-C(21)	94.0(17)
Yb(2)-O(25)-C(24)	94.7(15)	Yb(2)-O(26)-C(24)	95.4(16)
Yb(1)-O(17)-C(17)	169.9(16)	Yb(2)-O(18)-C(17)	143.4(17)
Yb(1)-O(27^i)-C(27^i)	140.0(16)	Yb(2)-O(28)-C(27)	168.8(19)
O(13)-C(11)-O(14)	120(2)	O(25)-C(24)-O(26)	117(2)
O(17)-C(17)-O(18)	126(2)	O(27)-C(27)-O(28)	121(2)

Key to the symmetric operations: i, x, y, $-1.0+z$.

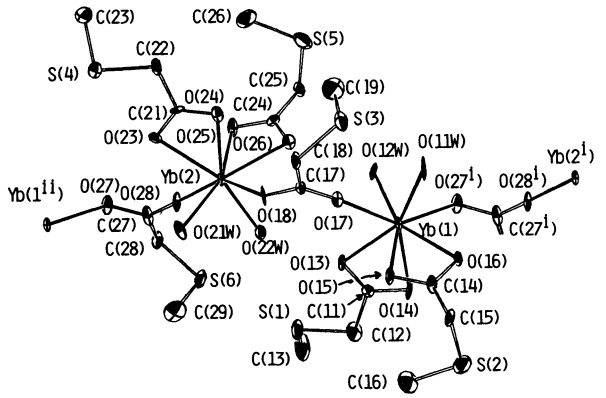

Fig. 1. The perspective drawing of the complex and the numbering scheme of atoms. (Key to the symmetry operations; i, x, y, $-1.0+z$; ii, x, y, $1.0+z$)

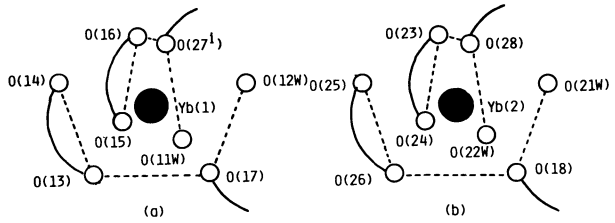

Fig. 2. Schematic presentation of the bonding modes of the ligands around (a) Yb(1) and (b) Yb(2) atoms (●, ytterbium ; and ○, oxygen atoms).

nation number is smaller than that of the neodymium(III) complex of the same ligand, where both types of metal atoms are ennea-coordinated.[1] Although lanthanoid(III) carboxylates, such as *m*-hydroxybenzoates[6] and nicotinates,[7] are also in octa-coordination, they are rather in a square-antiprism geometry. The deviations of the atomic positions of the four oxygen atoms and the central metal atom from each average trapezium plane are relatively large: 0.316 Å at the maximum (O(17)) and 0.124 Å on the average. The dihedral angles between the two trapezia around the same metal atom are 83.9 and 87.2° respectively.

The arrangements of the ligated atoms around both metal atoms are about the same; as is shown in Fig. 2, two oxygen atoms of one carboxylate occupy both the apexes of an oblique edge of each trapezium, forming a four-membered chelate ring. On the other oblique edge of each trapezium, the oxygen atom of the coordinated water takes the bottom-end position, and the oxygen atom of the bridging ligand, the other-end one.

The Yb–O bond lengths of the complex are classified into three groups. The shortest ones are those of the bridging ligand oxygen atoms (2.223 Å on the average), the second ones are those of the water oxygen atoms (2.293 Å on the average), and the longest ones are those of the chelating oxygen atoms (2.383 Å on the average). As the ionic radii of Yb^{III} and of O^{2-} are 0.985 and 1.38 Å respectively,[8] the bridging oxygen atoms bond to the metal atoms strongly, consequently, the bridges are likely to be stable. As shown in Table 1, Yb(1)···Yb(2), and Yb(1)···Yb(2^i) are 5.573(2) and 5.777(2) Å respectively, not much different from one another. Both of the bridges are of the *Z–E* type,[9] where the Yb–O–C angles of the *Z*-side (O(17) and O(28) sides) are 169.9(16) and 168.8(19)°, while those of the *E*-side (O(18) and O(27) sides) are 143.4(17) and 140.0(16)° respectively. None of the sulfide sulfur atoms are coordinated to any metal atoms, as in the case of the neodymium(III) complex.

Thus, the complex chains in a zig-zag form lie nearly parallel to the c-axis, and there is almost no interaction between the chains.

The authors are greatly obliged to the Shin-Etsu Chemical Ind. Co., Ltd., for aiding this study by presenting the highly pure ytterbium(III) oxide. The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 57430011) from the Ministry of Education, Sciences, and Culture.

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4) $R=\Sigma||F_o|-|F_o||/\Sigma|F_o|$.
5) The crystal packing diagram, the final atomic coordinates, and their thermal parameters, the final F_o-F_c values, and some additional data about the bond lengths and bond angles are deposited as Document No. 8512 at the Office of the Editor of Bull. Chem. Soc. Jpn.
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