The Crystal and Molecular Structure of Di-μ-hydroxo-bis[pentaaquascandium(III)] Benzenesulfonate Tetrahydrate, $[\{(H_2O)_5Sc\}(OH)_2\{Sc(H_2O)_5\}](C_6H_5SO_3)_4\cdot4H_2O$: A Dimeric Complex in Pentagonal-Bipyramidal Hepta-Coordination

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Synopsis. The crystal and molecular structure of the new title complex has been determined by means of a single-crystal X-ray diffraction method. It is triclinic with the space group $P\bar{1}$, Z=2, a=15.518(5), b=19.827(7), c=7.493(2) Å, α=100.90(3), β=103.94(2), γ=82.85(3)°. Both of the metal atoms have almost the same coordination geometry, pentagonal bipyramidal which coordinates the oxygen atoms of five water molecules (2 axial and 3 equatorial ones) and the two hydroxide ions which bridge the both metal atoms. The Sc(1)···Sc(2) distance is 3.403(2) Å. The average Sc-O(H_2O) bond length is 2.194 Å, which is much longer than that of Sc-O(OH), 2.072 Å. Benzenesulfonate ions and the other water molecules do not coordinate to the metal atoms, though their oxygen atoms as well as those of the coordinated water are connected with each other by a network involving hydrogen bonding.

Although the structures of scandium complexes have not yet been sufficiently clarified, some of them were recently elucidated: most of them are in the octahedral hexa-coordinated geometry,[1–5] and the others are in the octa-coordination.[6–10] Some scandium salts have a layer,[7] a chain[3,4] or a dimeric structure[8] like the lanthanoid complexes.[11–14]

Previously, the authors investigated the structures of several scandium salts,[3–5] and recently were able to obtain the new title complex. Subsequently, its crystal and molecular structure was determined by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Di-μ-hydroxo-bis[pentaaquascandium(III)] Benzenesulfonate Tetrahydrate. Scandium oxide (69 mg, including 1 mmol of Sc) was dissolved into hydrochloric acid (6 mol dm^{-3}, 10 cm^3) after boiling. The solution was dried up on a water bath, and the residue was dissolved into 10 cm^3 of water. To the solution sodium benzenesulfonate hydrate (610 mg, 3.1 mmol) was added, dissolved by warming, and left standing in a desiccator over silica gel at room temperature until one third of the solvent was evaporated; plate-like crystals were deposited. Yield: 92 mg (0.091 mmol as a dimer, 18%) Found: Sc, 9.14; C, 28.67; H, 4.70%. Calcd for $Sc_2C_{24}H_{50}O_{28}S_4$: Sc, 8.95; C, 28.69; H, 5.02%.

X-Ray Structure Analysis. The used crystal was colorless, approximately parallelepiped in shape (0.30×0.25×0.25 mm^3), triclinic, space group $P\bar{1}$, Z=2 (including four Sc atoms in a unit cell), a=15.518(5), b=19.827(7), c=7.493(2) Å, α=100.90(3), β=103.94(2), γ=82.85(3)°, U=2190(1) Å, D_m=1.51(3), D_x=1.52 g cm^{-3}, μ(Mo $K\alpha$)=5.92 cm^{-1}. The intensities were measured with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), a ω-2θ scan technique being employed (the scan speed was 4° min^{-1} (ω), scan width, 1.00+0.5 tanθ (ω), and the scan range was 3—55° (2θ)). Of the 10123 independent reflections measured, 5866 reflections of $|F_o|>3\sigma(|F_o|)$ were used for its structure calculation. The intensities were corrected for both Lorentz and polarization factors, but not for absorption and extinction. The structure was solved by the heavy-atom method. The positional and thermal parameters of the atoms were refined by a block-diagonal least-squares method. The positions of the hydrogen atoms of coordinated water molecules and hydroxide ions were obtained from a difference synthesis map; they were included in the structure factor calculations (without fixing); the other hydrogen atoms were excluded from the calculations. During the final stage (in the map) almost no electron clouds could be recognized around the ligated oxygen atoms. The observed H-O bond lengths of the water molecules and the hydroxide ions are 0.91 and 0.90 Å (on the average), respectively (they were a little too short, which may be due to their large temperature factors). The H-O-H bond angles of water, and Sc-O-H of water and hydroxide ions are 110, 122, and 120° (on the average), respectively. The final R value was found to be 0.070 by applying anisotropic temperature factors for all nonhydrogen atoms.[15]

All calculations were carried out on a HITAC M-682H computer at the Computer Center of the University of Tokyo using a local version of the UNICS program system.[16] The atomic scattering factors were taken from Ref. 17.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1. A perspective drawing of the dimeric complex together with the numbering scheme of the atoms is shown in Fig. 1, and a projection of the unit cell along b-axis, together with the numbering of some metal and other atoms, in Fig. 2.[18]

Both of the scandium(III) atoms, Sc(1) and Sc(2) are approximately in the same coordination geometry, deformed pentagonal bipyramidal. The seven ligating oxygen atoms are five water oxygen atoms (two are axial and three equatorial) and two oxygen atoms of hydroxide ions (equatorial). The two hydroxide ions make bridges between the two metal atoms. The axial Sc-O(H_2O) bonds are shorter than the equatorial ones (the axial bonds are 2.146 Å on the average, and the average equatorial bond length is 2.227 Å), while the Sc-O (hydroxide) bonds are the shortest (2.072 Å on the average). The bond angles of O(hydroxide)-

Table 1. Selected Interatomic Distances and Bond Angles with Their Standard Deviations in Parentheses

Interatomic distance	(l/Å)	Interatomic distance	(l/Å)
Sc(1)···Sc(2)	3.403(2)	O(A6)···O(A7)	2.353(6)
Sc(1)-O(A1)	2.143(6)	Sc(2)-O(B1)	2.152(4)
Sc(1)-O(A2)	2.152(6)	Sc(2)-O(B2)	2.138(4)
Sc(1)-O(A3)	2.230(4)	Sc(2)-O(B3)	2.228(5)
Sc(1)-O(A4)	2.256(4)	Sc(2)-O(B4)	2.249(4)
Sc(1)-O(A5)	2.200(4)	Sc(2)-O(B5)	2.196(5)
Sc(1)-O(A6)	2.071(4)	Sc(2)-O(A6)	2.076(4)
Sc(1)-O(A7)	2.069(4)	Sc(2)-O(A7)	2.072(4)
Bond angle	(ϕ/°)	Bond angle	(ϕ/°)
Sc(1)-O(A6)-Sc(2)	110.3(2)	Sc(1)-O(A7)-Sc(2)	110.5(2)
O(A1)-Sc(1)-O(A2)	160.2(2)	O(B1)-Sc(2)-O(B2)	160.4(2)
O(A1)-Sc(1)-O(A3)	91.3(2)	O(B1)-Sc(2)-O(B3)	82.6(2)
O(A1)-Sc(1)-O(A4)	80.6(2)	O(B1)-Sc(2)-O(B4)	79.8(2)
O(A1)-Sc(1)-O(A5)	81.8(2)	O(B1)-Sc(2)-O(B5)	93.3(2)
O(A1)-Sc(1)-O(A6)	115.3(2)	O(B1)-Sc(2)-O(A6)	112.4(2)
O(A1)-Sc(1)-O(A7)	84.2(2)	O(B1)-Sc(2)-O(A7)	81.8(2)
O(A2)-Sc(1)-O(A6)	81.8(2)	O(B2)-Sc(2)-O(A6)	84.1(2)
O(A2)-Sc(1)-O(A7)	112.5(2)	O(B2)-Sc(2)-O(A7)	115.1(2)
O(A3)-Sc(1)-O(A4)	73.3(1)	O(B3)-Sc(2)-O(B4)	73.2(2)
O(A4)-Sc(1)-O(A5)	74.4(2)	O(B4)-Sc(2)-O(B5)	74.3(2)
O(A5)-Sc(1)-O(A6)	77.2(2)	O(B3)-Sc(2)-O(A6)	76.6(2)
O(A6)-Sc(1)-O(A7)	69.3(2)	O(A6)-Sc(2)-O(A7)	69.1(2)
O(A7)-Sc(1)-O(A3)	76.6(2)	O(A7)-Sc(2)-O(B5)	77.6(2)

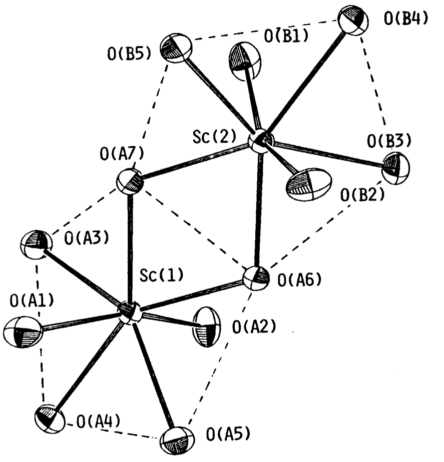

Fig. 1. The perspective drawing of the dimeric complex with the numbering scheme of the atoms: 30% probability thermal ellipsoids are shown for the nonhydrogen atoms of the complex.

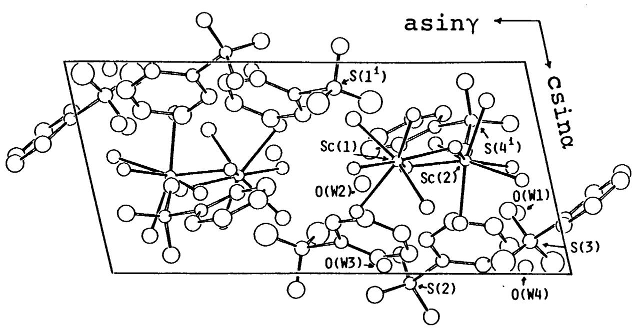

Fig. 2. Projection of the unit cell along b-axis: the numbering scheme of some atoms are also shown (i, x, y, $-1+z$).

Sc-O(hydroxide) and Sc(1)-O(hydroxide)-Sc(2) are, 69.2 and 110.4° (on the average), while the separations of Sc(1)···Sc(2) and O(A6)···O(A7) are 3.403(2) Å and 2.353(6) Å, respectively.

The size and the form of this Sc_2O_2 quadrilateral resemble the corresponding ones of the di-μ-hydroxo bridging found in the dimeric basic nitrate.[8] Moreover, from the difference synthesis map, only one hydrogen atom was found around each O(A6) and O(A7) atom, while two hydrogen atoms were found to exist around the other ligating oxygen atom, respectively. This is further support of our inference that the two bridging oxygen atoms are hydroxide ions.

Three mean-square planes are defined as **A**, **B**, and **C**, including following atoms, respectively: (**A**) Sc(1) and O(A3—A7); (**B**) Sc(1, 2) and O(A6, A7) ; and (**C**), Sc(2) and O(A6, A7, B3—B5). The average positional deviations of the atoms from the respective planes are: **A**, 0.239; **B**, 0.061; and **C**, 0.260 Å. The dihedral angles between them are: **A**-**B**, 147.1; **A**-**C**, 117.8; **B**-**C**, 29.4°, respectively.

The benzenesulfonate ions, as well as crystalline water molecules, are not directly bonded to the metal atoms. Many interatomic distances of 2.6—2.9 Å are observed between the water and sulfonato group oxygen atoms; almost all of them are expected to be hydrogen bondings.[18] Thus, in the crystal the cations, anions, and crystalline water molecules are hydrogen bonded with each other to form a network. However, the O(A6) and O(A7) atoms do not participate in the hydrogen network.

From studies of the solution chemistry of the scandium(III) ion, the existence of a dimeric ion, $[Sc_2(OH)_2]^{4+}$, has already been reported.[19—21] The structure of the present complex may be the same as the species in the above-mentioned solution.

It is an interesting fact that the crystals of scandium benzenesulfonate (**1**), *p*-toluenesulfonate (**2**), and *m*-nitrobenzenesulfonate (**3**), obtained from their aqueous solution under almost the same synthetic conditions, have structures which are much different from each other.[4,5] The very rare coordination number for scandium, 7, was only found in **1**. Moreover, the acid anion does not coordinate only in **1**, in spite of the fact that the acid ion of **1** is the smallest of the three: a minimum mutual steric hindrance is expected for the anion of **1**, even if it coordinates. This fact is also in contradiction to the consideration connecting the inductive effect of the substituents of the benzene rings of their acid anions. Since the methyl group in **2** (in *p*-position) increases, and the nitro group in **3** (in *m*-position) decreases the electron density of the sulfonato group compared with that of **1**, it is unreasonable that only the acid anion of **1** does not coordinate to the scandium atom.

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