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The Crystal and Molecular Structure of Diaquadihydroxotetrakis-(*m*-nitrobenzenesulfonato)discandium(III) in a Linear Polymeric Form, $[Sc_2(OH)_2(O_2NC_6H_4SO_3)_4(H_2O)_2]_n$

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Synopsis. The crystal and molecular structures of the title complex has been determined by the single-crystal X-ray diffraction method. It is monoclinic, with the space group *Pn*, $Z=2$ (including 4 metal atoms), $a=28.90(2)$, $b=10.251(4)$, $c=5.981(1)$ Å, and $\beta=94.68(3)°$. Both of the metal atoms, Sc(1) and Sc(2), have the hexa-coordinated octahedral geometry, being coordinated to four sulfonato oxygen atoms as well as to two water oxygen (Sc(1)) or to two hydroxide oxygen atoms (Sc(2)). Any pair of the neighboring metal atoms along the b-axis are bridged by two sulfonato ions, forming an infinite chain structure; however, the Sc(2)-O bond lengths (2.307(10)—2.556(19) Å; average, Sc(2)-O (sulfonate), 2.422; Sc(2)-O(OH^-), 2.394 Å) are much longer than the Sc(1)-O lengths (2.031(7)—2.150(8) Å; average, Sc(1)-O(sulfonate), 2.055; Sc(1)-O(H_2O), 2.122 Å).

Many scandium(III) salts are known to have a hexa-coordinated octahedral geometry around their metal atoms;[1-3] they are not in high coordination number like yttrium(III) or lanthanoid(III) complexes.[4,5] However, some scandium(III) salts, especially its carboxylates, have a chain structure like the other rare earth complexes.[6,7]

On the other hand, it was reported that arenesulfonate ions act as a unidentate in many rare earth(III) complexes;[8,9] moreover, alkyl sulfate ligands are not coordinated to the metal atoms in their salts,[10] although both of them are also oxo acidate anions.

Therefore, it is interesting to examine whether such sulfonate ligands can act as multidentates in some rare earth complexes, and whether or not the scandium(III) atom keeps the hexa-coordination geometry in such salts.

This time, since we could synthesize the title complex, its crystal and molecular structure was determined by the single-crystal X-ray diffraction technique.

Experimental

Synthesis of Deaquadihydroxotetrakis(*m*-nitrobenzenesulfonato)discandium(II) Scandium oxide (Sc_2O_3 0.14 g, including 2 mmol of Sc) was dissolved into hydrochloric acid (6 mol dm^{-3}, 20 cm^3), and the solution was evaporated off on a water bath. The residue was dissolved into 15 cm^3 of water together with sodium *m*-nitrobenzenesulfonate (1.36 g, 6.0 mmol). The solution was kept in a silica-gel desiccator until about one third of the solvent was evaporated off. The crystals deposited. Yield: 0.75 g (0.77 mmol (as a dimer), 77%). Found, C, 30.11; H, 2.48; N, 5.86%. Calcd for $Sc_2C_{24}H_{22}O_{24}N_4S_4$ (F.W., 968.62): C, 29.76; H, 2.29; N, 5.78%.

X-Ray Structure Analysis. The used crystal was colorless, approximately parallelepiped in shape (0.35×0.35×0.20 mm^3), monoclinic, space group *Pn*, $Z=2$ (including four Sc atoms in a unit cell), $a=28.90(2)$, $b=10.251(4)$, $c=5.981(1)$ Å, $\beta=94.68(3)°$, $U=1776(1)$ Å^3, $D_m=1.79(3)$, $D_x=1.82$ g cm^{-3}, μ(Mo $K\alpha$)=7.25 cm^{-1}. The intensities were measured on a Rigaku AFC-6A automated 4-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ A), an ω-scan technique being employed (the scanspeed was 4° min^{-1} (θ), scan width 1.03° (θ), and the scanned range was 3—65° (2θ)). Of the 6721 independent reflections measured, 4507 (reflections of $|F_o|>3\sigma(|F_o|)$) were used for a structure determination. The intensities were corrected for the 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 repeatedly by the block-diagonal least-squares method. At the final step, all non-hydrogen atoms were found and included in the refinement with the anisotropic temperature factors: all the hydrogen atoms were excluded from the structure factor calculations. The final *R* value was 0.074 (the *R* value for the structure assuming an inversed chirality was also 0.074).

All of the 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.[11] The atomic scattering factors were taken from Ref. 12.

Table 1. Bond Lengths and Bond Angles of the Complex with the Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)
Sc(1)-O(1)	2.150(8)	Sc(1)-O(2)	2.094(7)
Sc(1)-O(11)	2.035(7)	Sc(1)-O(21)	2.059(8)
Sc(1)-O(32^{ii})	2.031(7)	Sc(1)-O(42^{ii})	2.095(8)
Sc(2)-O(3)	2.367(12)	Sc(2)-O(4)	2.420(11)
Sc(2)-O(12)	2.460(11)	Sc(2)-O(22)	2.364(9)
Sc(2)-O(31)	2.307(10)	Sc(2)-O(41)	2.556(10)
S(1)-O(11)	1.517(8)	S(1)-O(12)	1.390(8)
S(1)-O(13)	1.467(10)	S(2)-O(21)	1.484(8)
S(2)-O(22)	1.409(7)	S(2)-O(23)	1.436(9)
S(3)-O(31)	1.434(8)	S(3)-O(32)	1.484(8)
S(3)-O(33)	1.448(9)	S(4)-O(41)	1.427(8)
S(4)-O(42)	1.438(8)	S(4)-O(43)	1.414(9)
Sc(1)···Sc(2)	5.102(6)	Sc(2)···Sc(1^{i})	5.149(6)
O(1)···O(23^{iii})	2.670(11)	O(1)···O(43^{iv})	2.656(11)
O(2)···O(13^{v})	2.736(11)	O(2)···O(33^{vi})	2.652(10)
O(3)···O(12^{v})	3.086(15)	O(4)···O(41^{iii})	3.064(13)
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
Sc(1)-O(11)-S(1)	142.8(4)	Sc(2)-O(12)-S(1)	141.1(6)
Sc(1)-O(21)-S(2)	164.2(5)	Sc(2)-O(22)-S(2)	135.6(5)
Sc(2)-O(31)-S(3)	139.4(6)	Sc(1^{i})-O(32)-S(3)	160.5(5)
Sc(2)-O(41)-S(4)	140.7(5)	Sc(1^{i})-O(42)-S(4)	143.6(5)

Key to the symmetry operations: i, x, $1+y$, z; ii, x, $-1+y$, z; iii, x, y, $-1+z$; iv, x, $1+y$, $-1+z$; v, x, y, $1+z$; vi, x, $1+y$, $1+z$.

Results and Discussion

The selected bond lengths and bond angles are shown in Table 1. The perspective drawing of the complex, together with the numbering scheme of the atoms is shown in Fig. 1, and the projection of the unit cell to the ab-plane in Fig. 2.[13]

Both of the scandium(III) atoms, Sc(1) and Sc(2), are in an octahedral geometry, being coordinated with six oxygen atoms: in addition to four sulfonate oxygen atoms, two water oxygen (Sc(1)), or two hydroxide oxygen atoms (Sc(2)), are ligated to the respective metal atoms in a trans-configuration.

Each pair of the neighboring metal atoms along the b-axis are apparently bridged with two sulfonate ions, where the anions act as a bidentate being coordinated to the both side metal atoms with their sulfonato oxygen atoms.

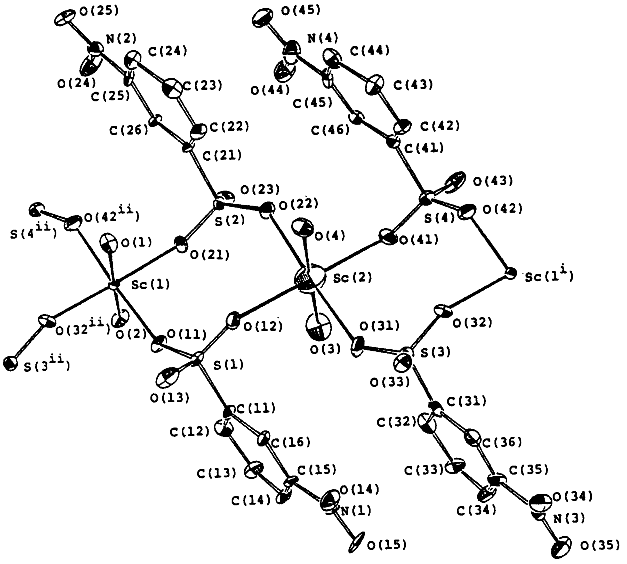

Fig. 1. A perspective drawing of the structure of the complex in a chain form, with the numbering scheme of the atoms. Key to the symmetry operations: i, x, $1+y$, z; ii, x, $-1+y$, z.

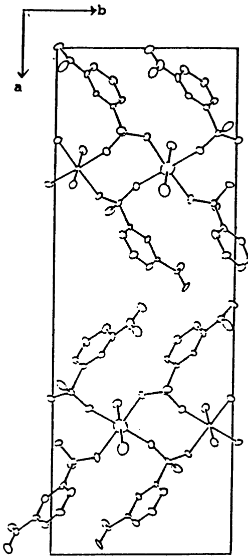

Fig. 2. A projection of the unit cell to the ab-plane.

However, it is an interesting fact that the Sc–O bond lengths around the Sc(1) and Sc(2) atoms are much different from each other.

The Sc(1)–O(1,2) bond lengths (2.150(8) and 2.094(7) Å) are shorter than the Sc(2)–O(3,4) lengths (2.367(12) and 2.420(11) Å). From the spectrochemical study, it was proposed that a hydroxide ion is coordinated to a metal atom more weakly than a water molecule.[14] Therefore, the O(1) and O(2) atoms are assigned to be the water oxygen atoms, while the O(3) and O(4) atoms the hydroxide ones. This is also supported by the fact that, as shown in Table 1, the former two oxygen atoms have two hydrogen bondings to the sulfonate oxygen atoms of the neighboring complexes, while the latter two oxygen atoms have only one such hydrogen bonding, respectively.

Moreover, not only the Sc–O (H_2O, or OH^-) bond lengths, but also the Sc–O (sulfonato) bond lengths around the Sc(1) and Sc(2) atoms are different from each other: the average bond lengths around the Sc(1) atom is 2.055 Å (2.031(7)—2.095(8) Å), while that around the Sc(2) atom is 2.422 Å (2.307(10)—2.556(10) Å). The average of the all six Sc–O coordination bond lengths around the Sc(1) atom is 2.077 Å, while that around the Sc(2) atom is 2.412 Å: the former is approximately the same as the sum of the Shannon's ionic radii, 2.10 Å,[15] while the latter is much longer than the value.

Therefore, the circumstances around the Sc(1) and Sc(2) atoms are much different from each other. The Sc(1) atom is normally coordinated with the ligands, while the Sc(2) atoms is apparently only trapped in a cage of the negatively charged six oxygen atoms around it, because not only all the Sc(2)–O bond lengths are abnormally long, but also the thermal parameter of the latter metal atom is very large ($B_{eq}=8.1_9$ Å^2). Along the linear polymeric chain, which is formed parallel to the b-axis, these two types of the metal atoms are arranged alternately.

The inter-metal-atomic distances of Sc(1)$\cdots$Sc(2) and Sc(2)$\cdots$Sc(1^{i}) (key to the symmetry operation; i, x, $1+y$, z) are 5.102(6) and 5.149(6) A, respectively. Each linear complex chain along the b-axis is connected with the neighboring complex chains on both sides along the c-axis with some hydrogen bondings, but no such bondings are found in the a-axis direction. The nitro-group oxygen and nitrogen atoms are not ligated to any metal atoms.

Of the bridging ligands, the couples of the Sc–O–S angles on both sides of the S(1) and S(4) atoms are not much different from each other: the four angles are in the range of 140.7(5)—143.6(5)°. On the other hand, couples of the bond angles on both sides of the S(2) and S(3) atoms are much different from each other: 135.6(5)° and 164.2(5)° for the couple around the S(2), and 139.4(6)° and 160.5(5)° for those around the S(3) atoms, respectively. Therefore, the latter two bridgings are found to be deformed; however, no clear relation has yet been obtained between the angles and the corresponding Sc–O bond lengths.

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