The Crystal and Molecular Structure of Scandium(III), Yttrium(III), and Some Lanthanoid(III) *p*-Toluenesulfonates, $[Sc(C_7H_7SO_3)_2(H_2O)_4](C_7H_7SO_3)\cdot 2H_2O$ and $[M(C_7H_7SO_3)_2(H_2O)_6](C_7H_7SO_3)\cdot 3H_2O$ (M=Y, Sm, Gd, Dy, Ho, Er, Yb); and Yttrium(III) and Dysprosium(III) 2-Naphthalenesulfonates, $[M(C_{10}H_7SO_3)_2(H_2O)_6]\text{-}(C_{10}H_7SO_3)\cdot 3H_2O$ (M=Y, Dy)

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Scandium(III) *p*-toluenesulfonate hexahydrate, as well as the isomorphous yttrium(III) and six lanthanoid(III) (Sm, Gd, Dy, Ho, Er, and Yb) *p*-toluenesulfonate enneahydrates, were synthesized and their structures were determined by the single-crystal X-ray diffraction technique. The scandium salt was monoclinic with the space group $P2_1/a$, $Z=4$ (the cell constants were $a=23.672(16)$, $b=15.792(6)$, $c=7.7543(12)$ Å, $\beta=92.86(3)°$, and the final R value was 0.059). The central metal atom is hexa-coordinated, being in an octahedral geometry, in which two unidentate sulfonate oxygen atoms (in cis-configuration) and four water oxygen atoms are ligated. The latter seven salts were also monoclinic with a space group of $P2_1/n$, and $Z=4$ (the cell constants of the holmium salt, for example, were $a=25.058(19)$, $b=7.476(2)$, $c=17.802(10)$ Å, $\beta=98.80(8)°$, and its final R value was 0.039). The central metal atom of these complexes are octa-coordinated, being in a square-antiprism geometry in which two unidentate sulfonate and six water oxygen atoms are ligated. In both types of complexes, no ligand bridgings were found, and one in three sulfonate ions was not coordinated to the metal atom. In the respective lanthanoid(III) complexes, M-O(sulfonato) bonds are shorter than the M-O(water) ones. The corresponding M-O bonds of the respective complexes decrease, almost proportional to the sum of the Shannon's ionic radii of the metal and oxygen, with the metal atomic numbers. Each M-O bond length of the yttrium(III) *p*-toluenesulfonate and 2-naphthalenesulfonate had the value expected from the corresponding bond lengths of the series of the respective isomorphous lanthanoid(III) salts, referring to its metal ionic radius.

Since only a few structural data concerning lanthanoid sulfonates have been published, the coordination behavior of such a hard base to a hard acid metal is very interesting. The structures of the lanthanoid 2-naphthalenesulfonates had already been elucidated,[1] but since the ligand is large, we should also examine the other arenesulfonates in order to reveal the common structure of the group of complexes. In the rare earth ethyl sulfates (La—Yb), all the coordination positions around the metal atom were occupied not by the sulfato but by the water oxygen atoms[2,3] On the other hand, in crystals of the lanthanoid(III) (Pr—Yb) 2-naphthalenesulfonates two in three anions as well as six water molecules act as unidentates. Since no bridging or chelating of the ligand was found, the coordination geometry around the metal atom is not so deformed as the carboxylato complexes.[4-8]

Recently, we could synthesize the scandium(III), yttrium(III), and some lanthanoid(III) (Sm through Yb) *p*-toluenesulfonates approximately by the same synthetic method. It is interesting to compare their structures with each other, especially those of the scandium and yttrium salts with the lanthanoid(III) ones.

We have relatively small numbers of structural data concerning the scandium(III) and yttrium(III) complexes. Regarding the scandium(III) carboxylates studied, the central metal atom was always hexa-coordinated and the high coordination number found in the yttrium or lanthanoid complexes were not recognized.[9,10] However, it was reported that tris(cyclopentadienyl)scandium and -lutetium have the same type chain structure, probably due to their similar atomic radii.[11] Therefore, the hexa-coordination of scandium is thought not to be always assured in all kinds of the complexes.

From the structural data, it was found that yttrium(III) formate,[12] acetate,[13] chloroacetate,[10] hexafluoroacetylacetonate,[14] and some acetylacetonates,[15,16] are isomorphous with the corresponding salts of lanthanoid(III). As the energy levels of the 4f orbitals in the yttrium(III) ion are thought to be too high to make any hybrid orbitals,[17] the orbitals are not likely used in the coordination bonds of its complexes. Although Cotton already wrote that 4f electrons hardly contribute to the formation of hybrid orbitals,[18] this fact can be more clearly proved if any isomorphous yttrium and lanthanoid complexes of the same ligand are found to always have the same geometrical environment around the respective metal atoms.

From this point of view, it is desirable to compare more structural data concerning their same ligand complexes, especially those which are obtained by the same synthetic technique and are isomorphous with each other.

The present study of the series of the rare earth *p*-

toluenesulfonates was aimed at investigating: 1) how the arenesulfonate ions are coordinated with the metal atoms, 2) if the scandium(III) and yttrium(III) salts have the same structures as those of the lanthanoid salts, and 3) how the M-O bond strength (which is related to the bond length observed) changes with the atomic number and with the metal ionic radius.

Therefore, we studied their crystal and molecular structures by the single-crystal X-ray diffraction technique. Their structures, bond lengths and angles were examined comparatively; especially their observed M-O bond lengths were compared with the standard values (the respective sums of the Shannon's ionic radii).[19]

The structures of the series of the rare-earth 2-naphthalenesulfonates,[1] including the newly obtained yttrium(III) and dysprosium(III) salts, have been examined comparatively, in order to clarify whether the relation between the observed M-O bond lengths and the sums of Shannon's ionic radii is the same as the *p*-toluenesulfonates.

Table 1. Analyses of the Rare Earth *p*-Toluenesulfonates and 2-Naphthalenesulfonates[a)]

	Chemical formula	Analysis(n/%)		
		M	C	H
$ScL_3 \cdot 3H_2O$[b,c)]	$ScC_{21}H_{27}O_{12}S_3$	7.20 (7.34)	41.00 (41.17)	4.19 (4.44)
$YL_3 \cdot 9H_2O$	$YC_{21}H_{39}O_{18}S_3$	11.69 (11.63)	32.99 (32.99)	4.98 (5.14)
$SmL_3 \cdot 9H_2O$	$SmC_{21}H_{39}O_{18}S_3$	18.13 (18.20)	30.24 (30.52)	4.57 (4.76)
$GdL_3 \cdot 9H_2O$	$GdC_{21}H_{39}O_{18}S_3$	18.80 (18.88)	30.26 (30.28)	4.42 (4.72)
$DyL_3 \cdot 9H_2O$	$DyC_{21}H_{39}O_{18}S_3$	19.48 (19.51)	30.09 (30.09)	4.55 (4.69)
$HoL_3 \cdot 9H_2O$	$HoC_{21}H_{39}O_{18}S_3$	19.62 (19.62)	29.93 (30.00)	4.52 (4.68)
$ErL_3 \cdot 9H_2O$	$ErC_{21}H_{39}O_{18}S_3$	19.77 (19.84)	29.77 (29.92)	4.48 (4.66)
$YbL_3 \cdot 9H_2O$	$YbC_{21}H_{39}O_{18}S_3$	20.40 (20.39)	29.59 (29.72)	4.41 (4.63)
$YL'_3 \cdot 9H_2O$[d)]	$YC_{30}H_{39}O_{18}S_3$	10.25 (10.19)	41.28 (41.29)	4.46 (4.50)
$DyL'_3 \cdot 9H_2O$[d)]	$DyC_{30}H_{39}O_{18}S_3$	17.05 (17.17)	37.99 (38.08)	4.20 (4.15)

a) The calculated values are shown in parentheses. b) HL=*p*-toluenesulfonic acid. c) Three in six water molecules of the original crystal $ScL_3 \cdot 6H_2O$ were lost by the drying process before the elemental analysis (lost water; Found 8.03%; Calcd 8.11%). d) HL'=2-naphthalenesulfonic acid.

Experimental

Syntheses of [Tetraaquabis(*p*-toluenesulfonato)scandium(III)] *p*-Toluenesulfonate Dihydrate. Into an aqueous solution of scandium(III) cholride (prepared by dissolving Sc_2O_3 (0.14 g, 1.0 mmol) into an excess of hydrochloric acid), excess of sodium hydroxide was added. Precipitated scandium(III) hydroxide was separated and dissolved in 10 cm^3 of water and *p*-toluenesulfonic acid hydrate (1.14 g, 6.0 mmol). The aqueous solution was left standing for several days until about two thirds of the water was evaporated off. Crystals of the title complex were deposited and were used for an X-ray structure analysis. Yield: 0.78 g (59%). Elemental analyses

Table 2. Crystallographic Data and Some Experimental Conditions to Obtain their Intensity Data of Scandium, Yttrium and Lanthanoid *p*-Toluenesulfonates: $[Sc(C_7H_7SO_3)_2(H_2O)_4](C_7H_7SO_3) \cdot 2H_2O$ (Monoclinic, Space Group $P2_1/a$, Z=4); and $[M(C_7H_7SO_3)_2(H_2O)_6](C_7H_7SO_3) \cdot 3H_2O$ (M=Y, Sm, Gd, Dy, Ho, Er, and Yb) (Monoclinic, Space Group $P2_1/n$, Z=4)

M=	Sc	Y	Sm	Gd	Dy	Ho	Er	Yb
F. W.	666.14	764.09	825.58	832.43	837.68	840.11	842.44	848.22
a(*l*/Å)	23.672(16)	25.034(12)	25.150(12)	25.122(9)	25.073(7)	25.058(19)	25.031(11)	24.981(13)
b(*l*/Å)	15.792(6)	7.477(2)	7.515(2)	7.499(1)	7.481(1)	7.476(2)	7.473(3)	7.457(2)
c(*l*/Å)	7.7543(12)	17.815(8)	17.898(7)	17.862(5)	17.833(4)	17.802(10)	17.796(8)	17.774(6)
β(ϕ/°)	92.86(3)	98.84(4)	99.00(4)	98.94(3)	98.90(2)	98.80(5)	98.77(4)	98.75(3)
U(v/Å^3)	2895(2)	3295(2)	3340(2)	3324.2(17)	3304.7(13)	3296(3)	3290(2)	3273(2)
D_m(d/Mg m^{-3})	1.51(3)	1.52(3)	1.62(3)	1.65(3)	1.68(3)	1.69(3)	1.69(3)	1.69(3)
D_x(d/Mg m^{-3})	1.53	1.54	1.64	1.66	1.68	1.69	1.70	1.72
μ(Mo $K\alpha$) (n/mm^{-1})	0.53_9	2.09	2.04	2.31	2.61	2.75	2.91	3.27
Number of reflections measured	6262	6311	7528	7496	7454	7433	7423	7186
Reflections used for the calculation[e)]	4153	3839	5038	5010	5587	5402	5235	5250
Measured range (2θ/°)	3—52	3—50	3—53	3—53	3—53	3—53	3—53	3—53
R[f)]	0.059	0.064	0.045	0.049	0.038	0.039	0.047	0.040
Size of crystal used (v/mm^3)	0.50×0.30 ×0.20	0.25×0.25 ×0.25	0.30×0.30 ×0.20	0.20×0.10 ×0.10	0.35×0.35 ×0.30	0.31×0.30 ×0.28	0.30×0.35 ×0.15	0.30×0.30 ×0.32
Slit width (θ/°)	1.02+ 0.5tanθ	1.01	1.00	1.00	1.00	1.01	1.01	1.01

e) Reflections with $|F_o| > 3\sigma(|F_o|)$ were used. f) $R = \sum||F_o| - |F_c|| / \sum|F_o|$

Table 3. Crystallographic Data and Some Experimental Conditions to Obtain Intensity Data of Yttrium and Dysprosium 2-Naphthalenesulfonates: $[M(C_{10}H_7SO_3)_2(H_2O)_6](C_{10}H_7SO_3)\cdot 3H_2O$ (M=Y, Dy) (Monoclinic, Space Group $P2_1$, Z=2)

M=	Y	Dy
F. W.	872.8	976.4
a(l/Å)	18.117(8)	18.111(7)
b(l/Å)	7.446(2)	7.452(3)
c(l/Å)	14.034(3)	14.049(5)
$\beta(\phi/^\circ)$	107.80(2)	107.78(3)
$U(v/Å^3)$	1802.5(10)	1805.4(12)
$D_m(d/Mg\,m^{-3})$	1.61(3)	1.73(3)
$D_x(d/Mg\,m^{-3})$	1.61	1.74
μ(Mo $K\alpha$)(n/mm^{-1})	1.92	2.40
Number of reflections measured	5572	4505
Reflections used for the calculation[e]	4203	3284
Measured range ($2\theta/^\circ$)	3—60	3—55
R[f]	0.057[g]	0.058[g]
Size of crystal used (v/mm^3)	0.15×0.15 ×0.25	0.20×0.10 ×0.15
Slit width ($\theta/^\circ$)	1.08+ 0.5tanθ	1.10+ 0.5tanθ

e, f) See footnotes of Table 2. g) Their R values with inverse chirality were 0.069 and 0.059 respectively.

revealed that a sample dried for 24h in a vacuum desiccator over silica gel lost three water molecules per one metal atom. The results of the elemental analyses are shown in Table 1.

Syntheses of [Hexaaquabis(*p*-toluenesulfonato)yttrium-(III)] *p*-Toluenesulfonate Trihydrate and the Isomorphous. Lanthanoid(III) (Sm, Gd, Dy, Ho, Er, and Yb) Salts. An aqueous solution of the yttrium(III) salt was obtained almost in the same way as for the scandium(III) salt, starting with 0.23 g (1.0 mmol) of yttrium(III) oxide (Y_2O_3) and the acid hydrate (1.14 g, 6 mmol). It was left standing for several days in open air at room temperature until about four fifths of the water was removed. Crystals of the yttrium(III) complex were depositied. Yield: 1.12 g (72%). Isomorphous lanthanoid(III) (Sm, Gd, Dy, Ho, Er, Yb) salts were also obtained by an analogous method; their yields were between 70 and 80%.

All of the obtained salts did not show a mass loss beyond the experimental error after being left standing for two days in a vacuum silica gel desiccator at ambient temperature. However, when they were kept for several months under the conditions, some part of water was lost especially in the case of the samarium(III), and to a smaller extent, in the case of the gadolinium(III) salt. When these crystals were dipped into methanol, ethanol, or 1- or 2-propanol medium, crystals of the samarium salt were destroyed immediately, and those of the gadolinium salt after a few minutes. Althouth the heavier lanthanoid salts did not decompose soon, they also lost water while being kept in the medium longer. When all of these salts, after being kept for a long time in alcohol, were dried in a vacuum silica gel desiccator, dehydrated salts were obtained. The stability of these hydrated crystals probably increases depending on the atomic number of the metal. Analyses of these salts are shown in Table 1.

Attempts to obtain a lighter isomorphous lanthanoid(III) (La—Nd) *p*-toluenesulfonates by the same synthetic method were not successful; their salts in the triclinic system, which effloresce very rapidly, were obtained alternatively.

Syntheses of [Hexaaquabis(2-naphthalenesulfonato)yttrium(III)] 2-Naphthalenesulfonate Trihydrate. The synthetic technique for isomorphous lanthanoid(III) complexes previously reported[1] was used, starting with yttrium(III) chloride ($YCl_3\cdot 6H_2O$) (0.30 g, 1.0 mmol) and 2-naphthalenesulfonic acid (0.70 g, 3.4 mmol). Yield: 0.45 g (52%). Their analyses are shown in Table 1.

Single Crystal X-Ray Structure Analysis. The crystal and molecular structures of the ten titled complex crystals were examined by the single-crystal X-ray diffraction method. Their crystallographic data, experimental conditions for obtaining intensity data, and their final R values calculated after applying anisotropic thermal parameters to all non-hydrogen atoms are shown in Tables 2 and 3.

During the intensity data collection, the crystals of samarium(III) and gadolinium(III) complexes were destroyed through irradiation by X-rays in open air. Consequently, the crystals of the samarium and gadolinium salts used for the X-ray diffraction study were sealed into borosilicate glass capillaries. Since the decomposition rate decreases rapidly, depending on the atomic number of the metal, practically no trouble was found regarding measurements of the heavier lanthanoid complexes.

The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ (λ=0.71073 Å) radiation, with a scan speed of 4° (θ) min^{-1}. The ω-2θ scan technique was used for scandium *p*-toluensulfonate and both of the 2-naphthalenesulfonates, while the ω-scan method was applied for the other *p*-toluenesulfonates. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction.

Structure Determination. The structure of the scandium(III) and yttrium(III) *p*-toluenesulfonates were solved by the heavy-atom method. The positions of the metal and sulfur atoms were, respectively, deduced from three dimensional Patterson maps. The positions of the other atoms were succesively located by Fourier syntheses. Their positional and thermal parameters were repeatedly refined by the block-diagonal least-squares method. In the end, all non-hydrogen atoms were found.

The structures of the isomorphous lanthanoid(III) *p*-toluenesulfonates were refined by starting with the parameters of the isomorphous yttrium complex. The structures of yttrium(III) and dysprosium(III) 2-naphthalenesulfonates were obtained starting with the final parameters of the isomorphous erbium(III) salt, $[Er(C_{10}H_7SO_3)_2(H_2O)_6](C_{10}H_7SO_3)\cdot 3H_2O$, and refined as usual.[1] In these cases, the positions of the naphthalene-ring hydrogen atoms were calculated assuming the C-H bond lengths to be 1.08 Å and their B_{iso}'s to be 6.0 $Å^2$. The parameters of the hydrogen atoms were fixed during the refinement. Since their crystals have no center of symmetry, refinements using the inverse chirality were also carried out; the one giving a lower R value was adopted for each complex. Both of them were found to have the same chirality as the erbium salt. All calculations were carried out on a HITAC M-682H appara-

Table 4. Final Atomic Coordinates ($\times 10^4$) of the Non-Hydrogen Atoms and Their Equivalent Isotropic Temperature Factors of the Complexes (Estimated Standard Deviations in Parentheses)

(4.1) Scandium(III) *p*-Toluenesulfonate Hexahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h)]
Sc	−11.4(4)	1788.9(5)	3301.6(11)	1.9_5
S(1)	694(1)	1505(1)	7204(2)	2.6_3
S(2)	709(1)	3707(1)	2873(2)	3.9_7
S(3)	1338(1)	−867(1)	2471(2)	2.5_7
O(11)	518(2)	1400(2)	5349(4)	3.2_3
O(12)	472(2)	801(2)	8180(4)	3.2_6
O(13)	560(2)	2316(2)	7856(5)	4.5_8
O(21)	386(1)	2907(2)	2993(4)	3.2_1
O(22)	530(2)	4156(3)	1346(8)	7.9_5
O(23)	681(2)	4191(3)	4408(8)	8.2_7
O(31)	1357(2)	−1697(2)	3258(5)	4.2_3
O(32)	1032(2)	−263(2)	3508(4)	3.1_5
O(33)	1117(2)	−869(3)	690(4)	3.9_1
O(W1)	−538(2)	708(2)	3598(4)	3.2_0
O(W2)	490(1)	995(2)	1790(4)	2.8_5
O(W3)	−468(1)	2042(2)	972(4)	3.1_6
O(W4)	−573(1)	2415(2)	4920(4)	3.0_1
O(W5)	−317(2)	3956(3)	6097(6)	5.7_6
O(W6)	−388(2)	3491(3)	−434(7)	6.9_4
C(11)	1432(2)	1387(3)	7278(6)	2.6_3
C(12)	1686(2)	703(3)	8145(6)	2.9_6
C(13)	2274(2)	637(3)	8221(7)	3.2_3
C(14)	2602(2)	1247(4)	7456(6)	3.1_5
C(15)	2341(2)	1925(4)	6594(7)	3.5_2
C(16)	1756(2)	2003(3)	6513(7)	3.2_8
C(17)	3247(2)	1176(4)	7561(8)	4.6_8
C(21)	1416(2)	3397(3)	2676(6)	2.8_0
C(22)	1838(2)	3845(3)	3567(7)	3.4_8
C(23)	2396(3)	3626(4)	3359(7)	3.8_7
C(24)	2533(2)	2959(4)	2285(7)	3.4_2
C(25)	2102(2)	2507(4)	1402(7)	3.4_5
C(26)	1537(2)	2731(3)	1592(7)	3.2_1
C(27)	3151(3)	2740(5)	2051(10)	5.6_1
C(31)	2041(2)	−508(3)	2440(6)	2.4_0
C(32)	2441(2)	−1028(3)	1741(6)	3.0_8
C(33)	2999(2)	−762(4)	1690(7)	3.8_0
C(34)	3158(2)	37(4)	2320(7)	3.4_0
C(35)	2749(2)	548(4)	3023(7)	3.6_7
C(36)	2193(2)	276(3)	3095(7)	3.3_2
C(37)	3766(3)	330(5)	2253(9)	5.3_9

(4.2) Yttrium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h)]
Y	2506.0(3)	−165.3(10)	4707.9(4)	2.2_9
S(1)	1453(1)	−3160(3)	3867(1)	3.4_3
S(2)	3387(1)	3414(3)	4240(1)	2.9_7
S(3)	3439(1)	2235(3)	7721(1)	3.2_3
O(11)	1820(2)	−2229(8)	4467(3)	3.6_2
O(12)	1526(2)	−5076(9)	3921(4)	5.6_8
O(13)	1502(2)	−2520(10)	3127(3)	5.2_2
O(21)	3078(2)	1751(7)	4148(3)	3.0_9
O(22)	3219(2)	4638(7)	3621(3)	3.9_7
O(23)	3377(2)	4219(7)	4979(3)	3.9_9
O(31)	3147(2)	3899(8)	7502(4)	5.2_0
O(32)	3420(2)	1773(8)	8506(3)	4.1_9
O(33)	3218(2)	794(8)	7217(3)	4.7_1
O(W1)	2099(2)	2589(8)	4890(3)	3.9_8
O(W2)	2017(2)	642(7)	3503(3)	3.7_8
O(W3)	2108(2)	−415(7)	5835(3)	3.8_3
O(W4)	2937(2)	−2596(7)	5360(3)	3.4_3
O(W5)	3117(2)	1161(7)	5694(3)	3.2_4
O(W6)	2908(2)	−1871(7)	3826(3)	3.5_8
O(W7)	2192(2)	3832(8)	2730(3)	4.4_0
O(W8)	2160(2)	3460(9)	6386(3)	5.3_5
O(W9)	3216(3)	−2783(9)	6864(3)	7.3_6
C(11)	802(3)	−2695(11)	4046(4)	3.4_2
C(12)	418(4)	−2062(14)	3462(5)	5.3_7
C(13)	−111(4)	−1764(15)	3611(6)	6.3_7
C(14)	−241(4)	−2026(17)	4321(6)	6.7_3
C(15)	145(4)	−2749(25)	4872(7)	10.9_6
C(16)	672(4)	−3026(21)	4741(5)	8.1_3
C(17)	−829(4)	−1688(24)	4462(8)	11.4_8
C(21)	4058(3)	2794(10)	4215(4)	2.8_6
C(22)	4186(4)	2015(15)	3567(5)	5.2_3
C(23)	4730(4)	1469(15)	3563(6)	6.0_9
C(24)	5121(3)	1779(13)	4189(6)	5.3_7
C(25)	4979(4)	2571(17)	4816(6)	7.0_9
C(26)	4448(4)	3116(15)	4845(5)	5.6_3
C(27)	5711(4)	1182(17)	4181(8)	8.4_5
C(31)	4108(3)	2538(11)	7606(4)	3.2_8
C(32)	4236(3)	3626(12)	7030(4)	4.0_1
C(33)	4783(4)	3805(13)	6929(5)	4.6_0
C(34)	5185(4)	2858(13)	7402(5)	5.0_6
C(35)	5050(4)	1801(14)	7973(5)	5.3_7
C(36)	4514(4)	1587(13)	8087(5)	4.8_5
C(37)	5782(4)	3041(17)	7284(7)	7.3_7

tus at the Computer Center of the University of Tokyo using a local version of the UNICS program.[20] The atomic scattering factors were taken from Ref. 21.

Other Measurements. Their infrared spectra were obtained by a JASCO A-202 grating infrared spectrophotometer using liquid paraffin and hexachloro-1,3-butadiene mull. Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were carried out with a Rigaku Denki "Thermoflex" M-8075 using samples weighing about 10 mg each, at a heating rate of 10 °C min^{-1} in air, α-alumina as the reference.

Results and Discussion

The final atomic parameters and the equivalent isotropic temperature factors of the scandium(III), yttrium(III), and lanthanoids(III) (Sm, Gd, Dy, Ho, Er, Yb) *p*-toluenesulfonates, as well as those of the yttrium(III) and dysprosium(III) 2-naphthalenesulfonates are shown in Table 4. Their selected bond lengths and bond angles are tabulated in Tables 5, 6, and 7.[22] A perspective drawings of the scandium(III) and yttrium(III) *p*-toluenesulfonates around their central metals, together with the numbering scheme, are shown in Figs. 1 and 2. The crystal packing diagrams of the scandium(III) and yttrium(III) *p*-toluenesulfonates, together with the nomination of the toluene rings, are shown in Figs. 3 and 4 respectively.

In the scandium(III) *p*-toluenesulfonate, the central metal atom is hexa-coordinated and is in an octahedral geometry, where two unidentate sulfonato oxygen

Table 4. (Continued)

(4.3) Samarium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h]
Sm	2505.1(1)	−179.6(4)	4703.1(2)	2.2_2
S(1)	1432(1)	−3185(3)	3860(1)	3.4_1
S(2)	3401(1)	3414(2)	4227(1)	3.0_3
S(3)	3429(1)	2242(2)	7718(1)	3.1_7
O(11)	1795(2)	−2268(7)	4455(3)	3.7_3
O(12)	1497(2)	−5099(8)	3901(4)	6.3_3
O(13)	1474(2)	−2514(9)	3123(3)	5.3_8
O(21)	3086(2)	1769(6)	4130(3)	3.2_7
O(22)	3232(2)	4620(6)	3602(3)	3.8_8
O(23)	3394(2)	4227(7)	4962(3)	4.3_4
O(31)	3152(2)	3879(7)	7491(4)	5.2_7
O(32)	3422(2)	1798(8)	8497(3)	4.4_9
O(33)	3227(2)	811(7)	7222(3)	4.5_9
O(W1)	2092(2)	2668(7)	4893(3)	4.3_5
O(W2)	2011(2)	636(7)	3469(3)	3.9_8
O(W3)	2102(2)	−405(7)	5858(3)	4.1_7
O(W4)	2943(2)	−2664(6)	5377(3)	3.6_5
O(W5)	3132(2)	1206(6)	5708(3)	3.4_4
O(W6)	2908(2)	−1929(6)	3796(3)	3.8_2
O(W7)	2189(2)	3830(7)	2745(3)	4.3_7
O(W8)	2161(2)	3477(8)	6390(3)	5.2_2
O(W9)	3230(3)	−2805(8)	6875(3)	7.0_1
C(11)	786(3)	−2714(10)	4036(4)	3.3_0
C(12)	401(3)	−2105(13)	3469(5)	5.5_0
C(13)	−125(4)	−1772(14)	3621(6)	6.7_3
C(14)	−259(4)	−2050(16)	4302(6)	6.8_4
C(15)	131(4)	−2733(26)	4859(7)	11.3_6
C(16)	659(4)	−3077(20)	4737(5)	8.7_7
C(17)	−835(4)	−1681(23)	4449(8)	10.8_0
C(21)	4069(3)	2795(8)	4213(4)	2.7_8
C(22)	4196(3)	1969(13)	3578(5)	5.1_3
C(23)	4733(4)	1454(14)	3577(5)	6.1_4
C(24)	5119(3)	1741(12)	4188(5)	5.3_5
C(25)	4981(4)	2564(16)	4802(6)	6.8_1
C(26)	4454(3)	3123(13)	4829(5)	5.5_4
C(27)	5712(4)	1152(16)	4173(7)	8.4_0
C(31)	4104(3)	2544(10)	7607(4)	3.1_8
C(32)	4229(3)	3651(10)	7032(4)	3.7_0
C(33)	4770(3)	3790(11)	6935(5)	4.6_0
C(34)	5176(3)	2893(12)	7406(5)	4.8_2
C(35)	5040(3)	1788(13)	7967(5)	5.5_3
C(36)	4509(3)	1612(12)	8078(5)	4.7_5
C(37)	5769(3)	3071(15)	7286(6)	6.6_8

(4.4) Gadolinium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h]
Gd	2505.8(1)	−174.9(4)	4704.3(2)	2.2_4
S(1)	1441(1)	−3178(3)	3865(1)	3.4_3
S(2)	3396(1)	3409(3)	4232(1)	3.0_4
S(3)	3429(1)	2240(3)	7720(1)	3.1_9
O(11)	1808(2)	−2263(8)	4455(3)	3.7_7
O(12)	1510(3)	−5094(9)	3909(4)	6.1_0
O(13)	1488(2)	−2479(10)	3125(3)	5.1_3
O(21)	3081(2)	1765(7)	4139(3)	3.4_3
O(22)	3231(2)	4623(7)	3611(3)	3.9_9
O(23)	3385(3)	4227(7)	4965(3)	4.3_8
O(31)	3150(3)	3872(8)	7495(4)	5.2_5
O(32)	3427(2)	1772(9)	8501(3)	4.5_6
O(33)	3223(3)	791(8)	7223(3)	4.8_0
O(W1)	2096(2)	2636(8)	4882(3)	4.1_9
O(W2)	2011(2)	634(8)	3488(3)	3.9_8
O(W3)	2102(2)	−416(8)	5846(3)	4.1_7
O(W4)	2940(2)	−2644(7)	5370(3)	3.4_0
O(W5)	3122(2)	1188(7)	5704(3)	3.4_0
O(W6)	2908(2)	−1906(7)	3805(3)	3.6_3
O(W7)	2188(2)	3831(8)	2738(3)	4.2_5
O(W8)	2163(3)	3457(9)	6388(4)	5.2_9
O(W9)	3228(4)	−2792(9)	6872(4)	7.2_6
C(11)	788(3)	−2705(11)	4039(4)	3.2_1
C(12)	411(4)	−2076(15)	3460(6)	5.6_3
C(13)	−111(4)	−1752(16)	3618(7)	6.6_4
C(14)	−259(4)	−2049(18)	4288(7)	6.8_6
C(15)	129(5)	−2707(28)	4855(7)	10.6_4
C(16)	665(4)	−3040(22)	4742(6)	8.3_6
C(17)	−838(4)	−1734(26)	4443(10)	11.1_9
C(21)	4071(3)	2798(10)	4212(4)	3.0_0
C(22)	4193(4)	1937(14)	3573(5)	4.9_2
C(23)	4732(4)	1461(16)	3573(6)	5.9_8
C(24)	5128(4)	1748(13)	4201(6)	5.3_3
C(25)	4976(4)	2588(18)	4809(7)	7.0_6
C(26)	4446(4)	3116(16)	4831(6)	5.9_0
C(27)	5710(4)	1159(19)	4179(9)	8.5_6
C(31)	4107(3)	2543(11)	7610(4)	3.3_2
C(32)	4237(3)	3658(11)	7031(4)	3.7_3
C(33)	4772(4)	3796(13)	6933(5)	4.5_5
C(34)	5185(4)	2882(13)	7405(5)	4.9_7
C(35)	5046(4)	1801(15)	7972(6)	5.6_0
C(36)	4507(4)	1605(13)	8080(5)	4.7_3
C(37)	5777(4)	3043(17)	7287(7)	6.6_8

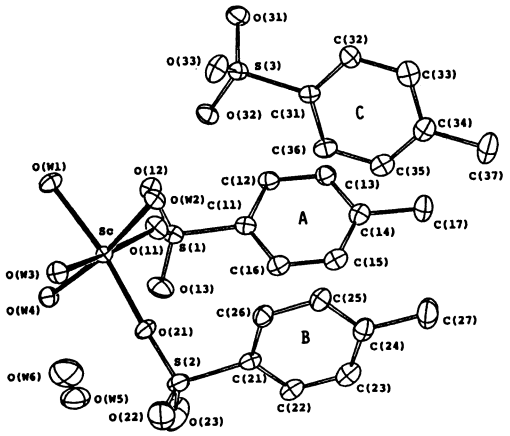

Fig. 1. A perspective drawing of scandium(III) *p*-toluenesulfonate hexahydrate with the numbering scheme.

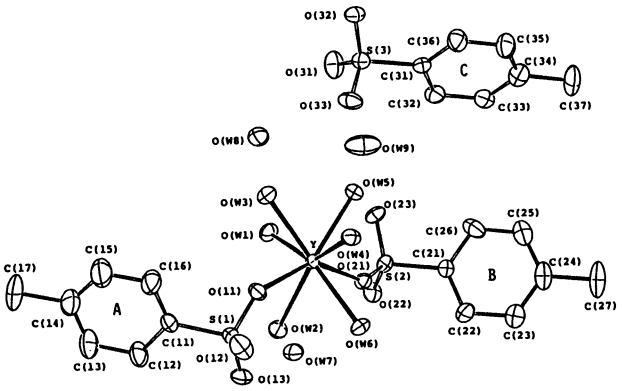

Fig. 2. A perspective drawing of yttrium(III) *p*-toluenesulfonate enneahydrate with the numbering scheme.

Table 4. (Continued)

(4.5) Dysprosium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h]
Dy	2506.4(1)	−167.2(3)	4707.2(1)	2.2_0
S(1)	1449(1)	−3168(2)	3868(1)	3.3_3
S(2)	3392(1)	3415(2)	4236(1)	2.9_2
S(3)	3429(1)	2239(2)	7721(1)	3.1_7
O(11)	1816(2)	−2239(6)	4464(2)	3.5_7
O(12)	1516(2)	−5082(7)	3925(4)	5.7_5
O(13)	1493(2)	−2490(8)	3123(3)	5.1_6
O(21)	3080(2)	1757(6)	4141(2)	3.3_1
O(22)	3227(2)	4638(6)	3612(3)	3.8_1
O(23)	3385(2)	4229(6)	4973(3)	4.0_7
O(31)	3153(2)	3885(7)	7500(3)	5.2_7
O(32)	3425(2)	1776(7)	8503(2)	4.1_2
O(33)	3220(2)	796(7)	7223(3)	4.6_6
O(W1)	2104(2)	2602(6)	4890(3)	4.0_6
O(W2)	2019(2)	654(6)	3505(3)	3.7_5
O(W3)	2106(2)	−417(6)	5835(3)	3.9_3
O(W4)	2933(2)	−2609(6)	5366(2)	3.4_6
O(W5)	3121(2)	1171(6)	5697(2)	3.2_2
O(W6)	2904(2)	−1881(6)	3820(2)	3.6_1
O(W7)	2193(2)	3819(7)	2733(3)	4.3_8
O(W8)	2162(2)	3457(7)	6387(3)	5.2_0
O(W9)	3226(3)	−2782(8)	6865(3)	7.1_8
C(11)	796(3)	−2692(9)	4041(4)	3.2_0
C(12)	414(3)	−2064(12)	3468(5)	5.5_4
C(13)	−108(3)	−1763(14)	3615(6)	6.6_5
C(14)	−249(3)	−2020(14)	4295(6)	6.5_5
C(15)	133(4)	−2734(26)	4861(6)	11.6_5
C(16)	664(3)	−3070(18)	4737(5)	8.0_4
C(17)	−834(4)	−1664(22)	4441(8)	10.9_8
C(21)	4064(2)	2796(8)	4215(3)	2.8_5
C(22)	4186(3)	1976(12)	3580(4)	4.8_5
C(23)	4730(3)	1479(14)	3571(5)	6.1_6
C(24)	5123(3)	1753(11)	4198(5)	4.9_1
C(25)	4979(3)	2567(16)	4806(5)	6.9_8
C(26)	4452(3)	3140(13)	4829(5)	5.4_8
C(27)	5707(3)	1189(16)	4167(7)	8.0_5
C(31)	4105(3)	2532(9)	7603(3)	3.1_4
C(32)	4232(3)	3636(10)	7038(4)	3.8_2
C(33)	4775(3)	3775(11)	6939(4)	4.6_7
C(34)	5184(3)	2858(11)	7408(4)	4.8_1
C(35)	5042(3)	1784(12)	7974(5)	5.2_4
C(36)	4511(3)	1597(11)	8081(4)	4.6_1
C(37)	5779(3)	3034(15)	7289(6)	6.9_8

(4.6) Holmium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h]
Ho	2506.5(1)	−163.1(3)	4708.1(1)	2.1_5
S(1)	1452(1)	−3162(2)	3869(1)	3.2_7
S(2)	3389(1)	3417(2)	4239(1)	2.8_8
S(3)	3428(1)	2237(2)	7722(1)	3.1_0
O(11)	1818(2)	−2225(6)	4467(2)	3.5_8
O(12)	1522(2)	−5071(7)	3920(3)	5.7_1
O(13)	1498(2)	−2502(8)	3125(2)	5.0_5
O(21)	3079(2)	1763(5)	4145(2)	3.3_0
O(22)	3223(2)	4634(6)	3615(3)	3.7_9
O(23)	3381(2)	4224(6)	4978(3)	4.0_7
O(31)	3156(2)	3892(7)	7505(3)	5.3_3
O(32)	3422(2)	1774(7)	8505(2)	4.2_5
O(33)	3219(2)	799(7)	7222(3)	4.6_5
O(W1)	2102(2)	2590(6)	4893(3)	4.0_5
O(W2)	2019(2)	650(6)	3508(2)	3.8_3
O(W3)	2106(2)	−416(6)	5831(2)	3.8_5
O(W4)	2935(2)	−2590(5)	5363(2)	3.3_8
O(W5)	3120(2)	1160(6)	5695(2)	3.2_3
O(W6)	2897(2)	−1868(5)	3819(2)	3.4_6
O(W7)	2194(2)	3825(7)	2729(2)	4.2_7
O(W8)	2161(2)	3454(7)	6385(3)	5.2_3
O(W9)	3222(3)	−2800(7)	6862(3)	7.1_7
C(11)	797(2)	−2686(8)	4044(3)	3.1_3
C(12)	417(3)	−2055(12)	3467(5)	5.5_6
C(13)	−109(3)	−1762(13)	3621(6)	6.4_5
C(14)	−251(3)	−2058(15)	4303(6)	7.2_7
C(15)	143(4)	−2741(24)	4869(6)	11.1_7
C(16)	669(3)	−3064(17)	4738(5)	7.8_1
C(17)	−832(4)	−1699(21)	4442(8)	10.9_3
C(21)	4061(2)	2802(7)	4217(3)	2.6_8
C(22)	4191(3)	1981(12)	3577(4)	5.0_3
C(23)	4731(3)	1488(13)	3568(5)	6.0_2
C(24)	5122(3)	1743(10)	4191(5)	5.0_8
C(25)	4978(3)	2576(15)	4808(5)	7.0_5
C(26)	4448(3)	3118(12)	4835(4)	5.5_1
C(27)	5710(3)	1178(15)	4163(7)	8.2_1
C(31)	4107(2)	2531(8)	7599(3)	3.1_6
C(32)	4234(3)	3623(9)	7036(4)	3.9_3
C(33)	4779(3)	3784(10)	6939(4)	4.5_7
C(34)	5188(3)	2860(11)	7404(4)	4.7_9
C(35)	5047(3)	1804(12)	7968(5)	5.2_6
C(36)	4510(3)	1595(11)	8080(4)	4.7_1
C(37)	5784(3)	3027(14)	7284(6)	7.0_5

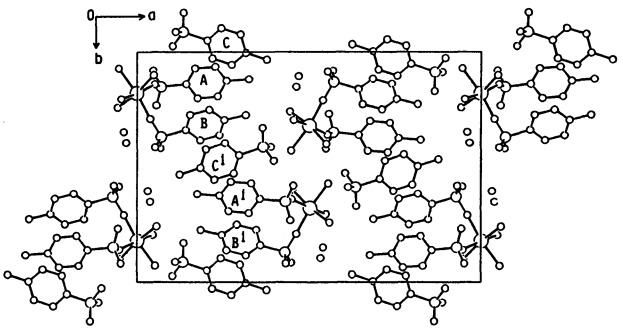

Fig. 3. A projection of the unit cell to the ab plane of scandium(III) *p*-toluenesulfonate hexahydrate. Key to the symmetry operations: i, 0.5−*x*, 0.5+*y*, 1−*z*.

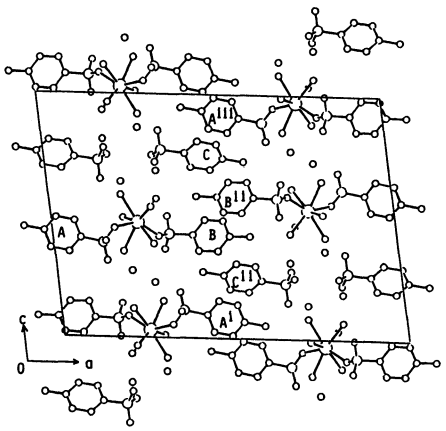

Fig. 4. A projection of the unit cell to the ac-plane of yttrium(III) *p*-toluenesulfonate enneahydrate. Key to the symmetry operations: i, 0.5−*x*, 0.5+*y*, 0.5−*z*; ii, 1−*x*, 1−*y*, 1−*z*; iii, 0.5+*x*, 0.5−*y*, 0.5+*z*.

Table 4. (Continued)

(4.7) Erbium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h)]
Er	2506.9(1)	−162.3(4)	4708.9(2)	2.2_2
S(1)	1456(1)	−3159(3)	3872(1)	3.3_0
S(2)	3387(1)	3417(3)	4241(1)	2.9_6
S(3)	3427(1)	2235(3)	7723(1)	3.2_6
O(11)	1820(2)	−2215(8)	4463(3)	3.6_4
O(12)	1526(3)	−5070(8)	3923(4)	5.7_0
O(13)	1498(2)	−2501(10)	3126(3)	4.9_7
O(21)	3075(2)	1768(7)	4145(3)	3.1_8
O(22)	3222(2)	4639(7)	3618(3)	3.8_6
O(23)	3377(2)	4218(8)	4979(3)	4.2_0
O(31)	3153(2)	3887(8)	7505(4)	5.1_7
O(32)	3421(2)	1771(8)	8506(3)	4.2_1
O(33)	3219(3)	789(8)	7218(3)	4.5_7
O(W1)	2107(2)	2601(8)	4898(3)	4.2_3
O(W2)	2021(2)	643(8)	3518(3)	3.8_8
O(W3)	2107(2)	−403(7)	5823(3)	3.6_1
O(W4)	2932(2)	−2591(7)	5363(3)	3.5_1
O(W5)	3120(2)	1157(7)	5693(3)	3.2_4
O(W6)	2900(2)	−1859(7)	3826(3)	3.6_0
O(W7)	2198(2)	3813(9)	2732(3)	4.4_7
O(W8)	2164(2)	3454(9)	6390(4)	5.0_9
O(W9)	3220(4)	−2807(9)	6856(4)	7.4_4
C(11)	801(3)	−2686(11)	4049(5)	3.3_8
C(12)	423(4)	−2041(14)	3457(6)	5.3_2
C(13)	−107(4)	−1757(16)	3612(7)	6.6_2
C(14)	−250(4)	−2029(17)	4305(6)	6.3_7
C(15)	129(5)	−2757(28)	4856(7)	10.7_0
C(16)	669(4)	−3075(21)	4747(6)	7.7_9
C(17)	−836(4)	−1688(24)	4433(9)	10.1_3
C(21)	4063(3)	2794(10)	4218(4)	2.7_3
C(22)	4187(4)	2008(15)	3576(5)	5.1_3
C(23)	4731(4)	1506(16)	3565(6)	6.1_6
C(24)	5117(4)	1780(13)	4193(6)	5.2_0
C(25)	4972(4)	2559(18)	4817(7)	7.0_9
C(26)	4443(4)	3124(15)	4838(6)	5.5_5
C(27)	5711(4)	1180(18)	4157(9)	8.3_0
C(31)	4103(3)	2545(11)	7602(4)	3.3_6
C(32)	4234(3)	3620(12)	7033(5)	3.9_7
C(33)	4781(4)	3769(13)	6936(5)	4.6_5
C(34)	5185(4)	2854(13)	7403(5)	4.5_5
C(35)	5050(4)	1795(15)	7969(6)	5.4_7
C(36)	4513(4)	1586(13)	8082(5)	4.8_0
C(37)	5784(4)	3016(17)	7277(7)	6.7_7

(4.8) Ytterbium(III) *p*-Toluenesulfonate Enneahydrate

Atom	*x*	*y*	*z*	B_{eq}/Å^{2} [h)]
Yb	2507.0(1)	−158.9(3)	4710.2(1)	2.1_0
S(1)	1463(1)	−3160(3)	3874(1)	3.1_7
S(2)	3383(1)	3420(2)	4244(1)	2.8_2
S(3)	3426(1)	2234(2)	7723(1)	3.0_6
O(11)	1826(2)	−2213(7)	4469(3)	3.4_1
O(12)	1533(2)	−5072(7)	3928(4)	5.5_3
O(13)	1509(2)	−2490(9)	3128(3)	4.8_1
O(21)	3066(2)	1764(6)	4146(3)	3.2_0
O(22)	3218(2)	4646(6)	3619(3)	3.5_8
O(23)	3375(2)	4230(6)	4984(3)	4.0_3
O(31)	3152(2)	3894(7)	7510(4)	5.1_8
O(32)	3418(2)	1753(7)	8504(3)	4.0_8
O(33)	3218(2)	796(7)	7216(3)	4.4_6
O(W1)	2103(2)	2562(7)	4896(3)	4.0_2
O(W2)	2028(2)	660(7)	3528(3)	3.5_2
O(W3)	2104(2)	−426(7)	5820(3)	3.7_9
O(W4)	2930(2)	−2563(6)	5351(3)	3.3_1
O(W5)	3112(2)	1138(6)	5686(2)	3.0_4
O(W6)	2896(2)	−1833(6)	3832(2)	3.3_0
O(W7)	2198(2)	3826(7)	2726(3)	4.2_2
O(W8)	2162(2)	3443(8)	6381(3)	4.8_6
O(W9)	3219(3)	−2793(8)	6859(3)	6.8_9
C(11)	807(3)	−2670(9)	4048(4)	3.1_5
C(12)	429(3)	−2049(13)	3460(5)	5.2_0
C(13)	−103(4)	−1733(14)	3618(6)	6.6_1
C(14)	−248(3)	−2055(16)	4308(6)	6.4_4
C(15)	140(4)	−2731(27)	4864(6)	11.2_7
C(16)	674(4)	−3036(19)	4751(5)	7.8_5
C(17)	−832(4)	−1699(21)	4452(8)	10.0_3
C(21)	4058(3)	2806(8)	4220(4)	2.8_2
C(22)	4182(3)	2011(12)	3566(4)	4.6_6
C(23)	4731(3)	1503(14)	3561(6)	5.9_8
C(24)	5120(3)	1773(11)	4200(5)	5.1_5
C(25)	4974(4)	2561(17)	4817(5)	6.7_0
C(26)	4440(3)	3116(14)	4847(5)	5.5_0
C(27)	5711(4)	1206(16)	4171(7)	7.9_7
C(31)	4105(3)	2519(9)	7605(4)	3.0_8
C(32)	4232(3)	3629(10)	7028(4)	3.8_6
C(33)	4783(3)	3765(11)	6930(4)	4.2_7
C(34)	5191(3)	2852(11)	7407(5)	4.6_0
C(35)	5055(3)	1778(13)	7979(5)	5.2_9
C(36)	4513(3)	1582(12)	8090(4)	4.5_7
C(37)	5787(3)	3022(15)	7282(6)	6.8_1

atoms are ligated in the cis-configuration; the other four coordinating positions are occupied by water oxygen atoms.

Both of the Sc-O (sulfonato) (2.044 Å, on the average (hereafter, shown by av.)) are shorter than the Sc-O (water) (2.117 Å av.), and the average of all the Sc-O bond lengths is 2.092 Å; this is approximately the same as the sum of the Shannon's ionic radii of Sc (Valence (Val)=3+, Coordination number (CN)=6) and O (Val=2−, CN=2), 2.10 Å.[19] The angle of Sc-O(11)-S(1) (147.2(2)°) is about the same as any M-O-S angles of lanthanoid *p*-toluenesulfonates and 2-naphthalenesulfonates,[1] but the other angle Sc-O(21)-S(2) (175.6(2)°) is much larger. This is probably due to a steric hindrance of the ligand coordinated at the cis-position. The third sulfonate ion is not coordinated to the metal atom, although it is bridged by hydrogen bondings to the coordinated water oxygen atoms. All three S-O bond lengths of the non-coordinated anion are not much different from each other (1.445, 1.452, and 1.462 Å). While in the coordinated anions, the S-O bond lengths of the ligated oxygen atoms (1.485 Å av.) are longer than the other two to the non-ligated oxygen atoms (1.431 Å av.). However, the average of all three S-O bond lengths of the coordinated and non-coordinated ions are not much different from each other (1.453 and 1.449 Å, respectively).

In the crystal, the metal atoms are approximately on the (200) planes. The hydrophobic layers of the tolyl groups of the ligands intercalate between respective pairs of hydrophilic metal complex planes. No ligand bridgings have been found between any neighboring

Table 4. (Continued)

(4.9) Yttrium(III) 2-Naphthalenesulfonate Enneahydrate

Atom	x	y	z	B_{eq}/Å^{2} h)
Y	7225.9(4)	7500	5032.8(5)	1.7_0
S(1)	6088(1)	4487(3)	3199(1)	2.2_3
S(2)	7000(1)	10993(3)	6760(1)	2.2_4
S(3)	9581(1)	5023(3)	3341(1)	2.5_2
O(1)	6785(3)	5559(8)	3717(4)	2.6_6
O(2)	6138(3)	2674(10)	3594(4)	3.4_7
O(3)	5381(3)	5371(8)	3186(4)	2.9_5
O(4)	6824(3)	9419(8)	6104(4)	2.6_7
O(5)	6367(3)	12271(9)	6489(4)	3.3_7
O(6)	7738(3)	11807(8)	6801(4)	3.1_1
O(7)	8809(3)	4476(9)	3321(4)	3.4_6
O(8)	9851(4)	6578(9)	3965(4)	4.4_6
O(9)	10141(3)	3564(9)	3607(4)	4.1_0
O(W1)	8230(3)	7194(9)	4272(4)	3.5_3
O(W2)	8350(3)	8890(8)	6119(4)	2.6_6
O(W3)	7969(3)	5056(8)	5875(4)	3.1_2
O(W4)	5930(3)	8401(7)	4180(4)	2.7_9
O(W5)	7314(3)	10225(8)	4226(4)	3.7_1
O(W6)	6422(3)	5740(8)	5723(4)	3.1_2
O(W7)	4837(3)	6352(9)	5350(4)	3.5_1
O(W8)	9477(3)	4911(9)	6176(6)	5.4_8
O(W9)	8783(3)	11072(10)	4260(4)	4.3_6
C(1)	5491(4)	4887(11)	1200(5)	2.1_7
C(2)	6110(4)	4317(10)	1960(5)	2.2_2
C(3)	6765(4)	3537(11)	1788(6)	2.7_2
C(4)	6781(4)	3303(11)	830(5)	2.5_8
C(5)	6142(4)	3874(11)	2(5)	2.4_3
C(6)	6141(4)	3606(12)	−993(5)	3.0_2
C(7)	5509(5)	4114(13)	−1769(6)	3.5_5
C(8)	4855(5)	4831(13)	−1586(6)	3.2_2
C(9)	4836(5)	5113(11)	−646(6)	2.9_4
C(10)	5505(4)	4627(11)	199(5)	2.3_1
C(11)	7734(4)	10557(11)	8739(5)	2.5_5
C(12)	7080(4)	10173(11)	7962(5)	2.4_1
C(13)	6459(4)	9153(12)	8083(6)	2.8_3
C(14)	6502(4)	8556(12)	9023(6)	3.0_4
C(15)	7142(5)	8959(11)	9859(5)	3.0_1
C(16)	7166(5)	8404(13)	10841(6)	4.0_1
C(17)	7808(6)	8880(14)	11629(6)	4.6_5
C(18)	8426(5)	9834(14)	11479(6)	4.0_4
C(19)	8426(5)	10366(13)	10571(6)	3.6_5
C(20)	7771(4)	9937(12)	9712(5)	2.6_6
C(21)	8906(4)	5203(12)	1329(6)	2.9_0
C(22)	9538(4)	5691(11)	2126(5)	2.4_8
C(23)	10157(4)	6663(11)	1979(6)	2.7_9
C(24)	10131(4)	7174(12)	1030(6)	3.2_6
C(25)	9496(4)	6710(11)	194(6)	2.7_0
C(26)	9457(5)	7192(13)	−806(6)	3.7_3
C(27)	8829(6)	6689(14)	−1570(6)	4.6_7
C(28)	8207(5)	5763(14)	−1426(6)	3.6_9
C(29)	8221(5)	5264(13)	−496(6)	3.6_9
C(30)	8869(4)	5715(12)	345(5)	2.8_1

(4.10) Dysprosium(III) 2-Naphthalenesulfonate Enneahydrate

Atom	x	y	z	B_{eq}/Å^{2} h)
Dy	7226.6(4)	7500	5036.8(5)	1.7_1
S(1)	6088(2)	4509(6)	3194(3)	2.2_6
S(2)	7000(2)	11020(6)	6772(3)	2.3_1
S(3)	9582(2)	5049(6)	3339(3)	2.5_1
O(1)	6779(6)	5596(16)	3731(8)	2.9_5
O(2)	6127(6)	2730(25)	3586(7)	3.1_8
O(3)	5382(6)	5388(16)	3177(8)	2.9_7
O(4)	6841(6)	9523(17)	6105(7)	2.9_4
O(5)	6367(6)	12244(18)	6503(7)	2.8_9
O(6)	7733(6)	11823(14)	6811(7)	2.5_9
O(7)	8807(6)	4486(17)	3315(8)	3.0_9
O(8)	9874(8)	6573(18)	3987(9)	4.6_3
O(9)	10138(6)	3604(18)	3604(9)	4.1_5
O(W1)	8248(6)	7200(21)	4274(7)	3.3_7
O(W2)	8339(6)	8913(16)	6128(8)	3.2_3
O(W3)	7986(6)	5123(15)	5911(8)	2.9_8
O(W4)	5930(6)	8446(14)	4166(7)	2.5_6
O(W5)	7318(6)	10252(16)	4225(9)	3.4_4
O(W6)	6424(6)	5757(14)	5754(8)	2.9_0
O(W7)	4839(6)	6376(18)	5345(8)	3.3_4
O(W8)	9474(7)	4922(18)	6167(13)	6.3_4
O(W9)	8787(7)	11112(19)	4273(9)	4.5_6
C(1)	5484(8)	4900(23)	1201(11)	2.3_8
C(2)	6090(8)	4313(18)	1956(10)	1.8_1
C(3)	6781(9)	3545(21)	1803(12)	2.8_1
C(4)	6782(8)	3335(23)	834(11)	2.5_9
C(5)	6143(9)	3865(23)	−5(12)	2.8_4
C(6)	6133(9)	3642(24)	−1004(12)	3.0_0
C(7)	5531(10)	4069(25)	−1757(12)	3.2_0
C(8)	4859(11)	4830(27)	−1579(13)	3.8_5
C(9)	4838(9)	5113(21)	−664(11)	2.4_7
C(10)	5489(8)	4671(20)	207(12)	2.4_1
C(11)	7730(10)	10552(23)	8740(12)	2.8_0
C(12)	7088(9)	10226(23)	7964(10)	2.3_8
C(13)	6450(8)	9217(24)	8092(12)	2.6_4
C(14)	6506(8)	8602(24)	9025(12)	2.8_0
C(15)	7124(10)	8996(24)	9864(12)	3.5_1
C(16)	7198(11)	8462(24)	10856(13)	3.8_1
C(17)	7787(11)	8887(26)	11651(12)	3.7_8
C(18)	8444(11)	9907(27)	11492(11)	3.5_0
C(19)	8425(11)	10381(26)	10562(12)	3.7_2
C(20)	7785(9)	9980(23)	9713(11)	2.9_8
C(21)	8896(9)	5260(22)	1328(12)	2.7_2
C(22)	9519(8)	5691(21)	2126(11)	2.2_4
C(23)	10159(10)	6724(25)	1981(12)	3.2_1
C(24)	10130(9)	7161(22)	1039(12)	2.8_5
C(25)	9512(10)	6789(22)	180(12)	2.9_8
C(26)	9445(10)	7159(23)	−805(11)	3.1_8
C(27)	8831(12)	6724(27)	−1579(13)	4.5_0
C(28)	8213(11)	5764(30)	−1419(15)	4.3_7
C(29)	8229(10)	5259(24)	−472(13)	3.4_2
C(30)	8866(9)	5740(21)	361(11)	2.3_9

h) 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 $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hkB_{12}+2hlB_{13}]$.

metal complexes, though they are bridged by hydrogen bondings via interposed crystalline water molecules and free anions. In the c-axis direction, hydrogen bond bridgings are found between any pairs of side-by-side metal complexes; however, in the b-axis direction, the respective pairs of the neighboring metal complexes are bridged or non-bridged alternately. Therefore, the hydrogen bond network in the crystal is extended like a belt in the c-axis direction.

As shown in Fig. 3, both tolyl groups of the ligands coordinated to the same metal atom are in the same side hydrophobic layer: Their methyl groups are

extended toward the same direction.

All toluene rings of the ligands are laid approximately perpendicular to the bc-plane, and A^i, B, C, as well as A, C^i, B^i, planes (i=0.5−*x*, 0.5+*y*, 1−*z*) are accumulated approximately in parallel, respectively: The dihedral angles between the ab-plane and the both group planes are about −30° and +30°, respectively.[22]

In yttrium(III) *p*-toluenesulfonate and, accordingly, in the isomorphous lanthanoid(III) salts as well the central metal atom is octa-coordinated, being in a square-antiprism geometry in which the oxygen atoms of the unidentate *p*-toluenesulfonate ions take positions on the different squares while keeping the maximum separation from each other. The general feature of the coordination geometry around the metal atom resembles that of the lanthanoid(III) 2-naphthalenesulfonates.[1]

Table 5. Selected Bond Lengths and Bond Angles of Scandium(III) *p*-Toluenesulfonate Hexahydrate

Bond length (*l*/Å)			
Sc-O(11)	2.067(4)	Sc-O(21)	2.021(4)
Sc-O(W1)	2.132(4)	Sc-O(W2)	2.119(4)
Sc-O(W3)	2.097(4)	Sc-O(W4)	2.118(4)
S(1)-O(11)	1.487(4)	S(1)-O(12)	1.457(4)
S(1)-O(13)	1.419(4)	S(2)-O(21)	1.482(4)
S(2)-O(22)	1.427(6)	S(2)-O(23)	1.419(6)
S(3)-O(31)	1.445(4)	S(3)-O(32)	1.462(4)
S(3)-O(33)	1.452(4)		
Bond angle (ϕ/°)			
Sc-O(11)-S(1)	147.2(2)	Sc-O(21)-S(2)	175.6(2)

The Y-O (sulfonato) bond lengths (2.326 Å av.) are shorter than the Y-O (water) (2.361 Å). The average of the all Y-O bond lengths is 2.352 Å, which is a little shorter than the sum of the Shannon's ionic radii, 2.369 Å.[19] The Y-O-S angles are 144.8 and 144.9°. These values are not much different from the corresponding ones of the yttrium and lanthanoid(III) 2-naphthalenesulfonates. As in the case of the scandium salt, the bond from the sulfur to the ligating oxygen atoms (1.467 Å av.) are longer than the bonds to the non-ligating oxygen atoms (1.442 Å av.), while three S-O bonds of the non-coordinated sulfonate ion are not much different from each other (1.453, 1.445, and 1.449 Å). As shown in Table 6, the same bond length relations are also found in the respective lanthanoid(III) salts.

The metal complex cores are located approximately on the planes parallel to (100), which cross the a-axis at 1/4 and 3/4. The metal complexes are connected with each other by two-dimensional hydrogen bonds, as shown schematically in Fig. 5. Each pair of the neighboring hydrophilic layers of the complex cores is intercalated by the hydrophobic layer of the tolyl groups of the anions. As shown in Fig. 4, the arrangement of the tolyl groups in the crystal is different from that in the scandium complex. Both of the toluene rings of the coordinating ligands are in the hydrophobic layers on both sides of the metal atoms; their methyl groups are extended toward the opposite directions from each other.

Table 6. Selected Bond Lengths and Bond Angles of Yttrium(III) and Lanthanoid(III) (Sm, Gd, Dy, Ho, Er, and Yb) *p*-Toluenesulfonate Enneahydrates

Bond length (*l*/Å) M=	Y	Sm	Gd	Dy	Ho	Er	Yb
M-O(11)	2.300(5)	2.366(5)	2.341(6)	2.305(4)	2.305(4)	2.297(5)	2.281(5)
M-O(21)	2.352(8)	2.409(7)	2.383(9)	2.362(7)	2.362(7)	2.354(8)	2.333(7)
M-O(W1)	2.342(6)	2.426(6)	2.388(7)	2.349(5)	2.340(5)	2.341(7)	2.312(6)
M-O(W2)	2.380(12)	2.438(11)	2.408(13)	2.378(10)	2.372(10)	2.355(13)	2.336(11)
M-O(W3)	2.382(13)	2.446(13)	2.422(14)	2.390(11)	2.378(11)	2.361(13)	2.355(12)
M-O(W4)	2.331(7)	2.396(7)	2.373(7)	2.340(6)	2.329(6)	2.324(8)	2.294(7)
M-O(W5)	2.363(10)	2.432(9)	2.402(10)	2.376(8)	2.367(8)	2.360(9)	2.330(8)
M-O(W6)	2.365(11)	2.429(10)	2.406(11)	2.373(9)	2.358(9)	2.348(11)	2.324(9)
$M\text{-}O(S)_{av.}$[j]	2.326	2.388	2.362	2.341	2.334	2.326	2.307
$M\text{-}O(W)_{av.}$[k]	2.361	2.428	2.400	2.368	2.357	2.348	2.325
$M\text{-}(all)_{av.}$[l]	2.352	2.418	2.390	2.368	2.357	2.348	2.325
S(1)-O(11)	1.472(11)	1.463(10)	1.460(11)	1.469(9)	1.470(9)	1.463(11)	1.465(9)
S(1)-O(12)	1.445(7)	1.448(6)	1.448(7)	1.444(6)	1.439(5)	1.440(7)	1.437(6)
S(1)-O(13)	1.426(13)	1.431(17)	1.444(18)	1.443(16)	1.435(15)	1.435(18)	1.437(16)
S(2)-O(21)	1.461(5)	1.464(5)	1.460(6)	1.462(4)	1.456(4)	1.456(5)	1.462(5)
S(2)-O(22)	1.445(12)	1.451(10)	1.445(12)	1.450(9)	1.447(9)	1.448(11)	1.449(10)
S(2)-O(23)	1.451(14)	1.453(13)	1.451(14)	1.451(12)	1.450(11)	1.446(14)	1.450(12)
S(3)-O(31)	1.453(7)	1.441(6)	1.436(7)	1.437(6)	1.437(6)	1.436(7)	1.436(6)
S(3)-O(32)	1.445(16)	1.437(15)	1.441(17)	1.438(13)	1.439(13)	1.438(16)	1.436(14)
S(3)-O(33)	1.449(11)	1.437(9)	1.446(10)	1.443(9)	1.442(9)	1.450(11)	1.446(9)
Bond angle (ϕ/°)							
M-O(11)-S(1)	144.8(6)	144.7(5)	145.4(6)	145.0(5)	145.0(5)	145.6(6)	145.2(5)
M-O(21)-S(2)	144.9(7)	144.7(7)	145.1(8)	144.6(6)	144.8(6)	144.8(7)	144.7(7)

j) Average of the M-O lengths of the ligated sulfonato oxygen atoms. k) Average of the M-O lengths of the ligated water oxygen atoms. l) Average of the M-O length of the all ligated oxygen atoms.

Table 7. Selected Bond Lengths and Bond Angles of Yttrium(III) and Dysprosium(III) 2-Naphthalenesulfonate Enneahydrates

Bond length (l/Å) M=	Y	Dy
M-O(1)	2.287(9)	2.27(2)
M-O(4)	2.344(10)	2.38(2)
M-O(W1)	2.383(10)	2.42(2)
M-O(W2)	2.374(6)	2.373(14)
M-O(W3)	2.354(6)	2.347(13)
M-O(W4)	2.381(5)	2.399(10)
M-O(W5)	2.351(9)	2.377(17)
M-O(W6)	2.373(9)	2.389(17)
M-O(S)$_{av.}$[j]	2.316	2.321
M-O(W)$_{av.}$[k]	2.369	2.383
M-O(all)$_{av.}$[l]	2.356	2.368
S(1)-O(1)	1.483(6)	1.488(13)
S(1)-O(2)	1.451(9)	1.43(2)
S(1)-O(3)	1.435(7)	1.432(13)
S(2)-O(4)	1.464(9)	1.429(19)
S(2)-O(5)	1.448(6)	1.423(13)
S(2)-O(6)	1.452(7)	1.441(13)
S(3)-O(7)	1.446(7)	1.456(14)
S(3)-O(8)	1.443(9)	1.451(19)
S(3)-O(9)	1.455(6)	1.444(13)
Bond angle (ϕ/°)		
M-O(1)-S(1)	140.4(7)	142.2(14)
M-O(4)-S(2)	147.1(6)	150.5(12)

j, k, l) See footnotes of Table 6.

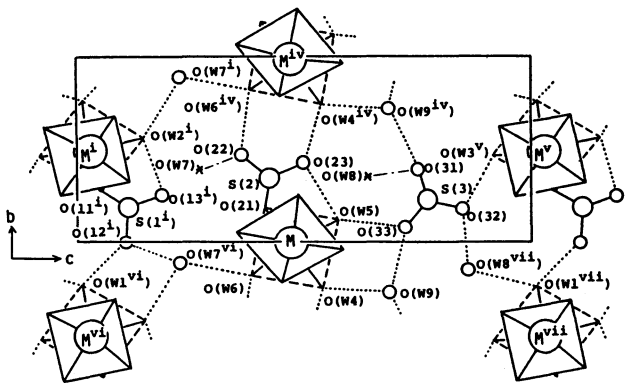

Fig. 5. Schematic presentation of the bridgings between the metal(III) complex molecules of yttrium(III) or lanthanoid(III) (Sm, Gd, Dy, Ho, Er, Yb) p-toluenesulfonate enneahydrates. As four two-fold screw axes are perpendicular to the ac-plane (crossing the plane at; 1/4, 0, 1/4; 1/4, 0, 3/4; 3/4, 0, 1/4; and 3/4, 0, 3/4), the same type of the linkage network exists also in the upper plane. Key to the symmetry operations: i, 0.5−x, 0.5+y, 0.5−z; ii, 1−x, 1−y, 1−z; iv, x, 1+y, z; v, 0.5−x, 0.5+y, 1.5−z; vi, 0.5−x, −0.5+y, 0.5−z; vii, 0.5−x, −0.5+y, 1.5−z.

The toluene rings of the anions are not perpendicular to the bc-plane, nor parallel with each other, and the dihedral angles between the bc-plane, and the A^{i}, B, C, planes are about 75, 79, and 84°, respectively.[22]

Generally, in the complexes of 3d-metals, the hard-base ligands such as the sulfonates cannot make strong coordination bonds, and the M-O bonds are usually longer than those by the common ligands.[23]

Table 8. Dihedral Angles between the Planes in the Square-Antiprism Geometry around Metal Atoms of Yttrium(III) and Lanthanoid(III) (Sm, Gd, Dy, Ho, Er, Yb) p-Toluenesulfonate Enneahydrates (θ/°)

M=	a—b[m]	c—d[m]
Y	1.78	44.34
Sm	1.74	44.64
Gd	1.87	44.29
Dy	1.70	44.53
Ho	1.42	44.51
Er	1.62	44.70
Yb	1.50	44.59

m) Respective least squares planes, a, b, c, and d, include atoms written as follows: a, O(11), O(W3), O(W1), O(W2); b, O(21), O(W5), O(W4), O(W6); c, O(11), M, O(W1); d, O(21), M, O(W4). The numbering of the atoms is the same as Fig. 3.

On the other hand, in these rare earth p-toluenesulfonates as well as in the 2-naphthalenesulfonates, the M-O (sulfonato) bond lengths are shorter than the standard M-O bond longths, the sum of the Shannon's ionic radii.[19] In cases of the other lanthanoid(III) complexes, their carboxylates, for example, have the M-O (carboxylato) bond lengths, which are almost the same as the respective sums of the Shannon's ionic radii.[4–10,12,13,24] Although in some lanthanoid(III) β-diketonates, the M-O (ligand) bond lengths are shorter than the respective sums,[25–27] it is rather due to the chelating effect of the ligand.

Since the title complexes have only unidentate ligands, sulfonato ions and water molecules, the square-antiprism geometry around the central metal atom is not much deformed from the ideal shape, as shown in Table 8. On the contrary, in carboxylato complexes, which have many chelating and bridging ligands, the geometry is much deformed. This is an expected result from the structural consideration by Kepert.[28,29]

As shown in Table 2, in the series of the isomorphous lanthanoid(III) p-toluenesulfonates, the cell-dimensions as well as the cell volume decrease, and the crystal density increases with the atomic number of the central metal atom. However, the size and shapes of the hydrocarbon part of the ligands stay approximately the same.

From a comparison of the atomic parameters of the corresponding atoms of the respective isomorphous complexes, those of the oxygen atom (sulfonato and water) and, to a smaller extent, those of the sulfur atoms change with the metal atomic number. However, the arene-carbon atoms also move to some extent, which may be caused by the larger standard deviations of their parameters. The largest observed deviations of

atomic parameters in the series of complexes are: the *x*-coordinate of O(12) (from 0.1497(2) (Sm) to 0.1533(2) (Yb)); the *y*-coordinate of O(W4) (from −0.2664(6) (Sm) to −0.2563(6) (Yb)); the *z*-coordinate of O(W2) (from 0.3469(3) (Sm) to 0.3528(3) (Yb)). All of these values change with the atomic number of the central metal atom.

Thus, the change of the packing in the unit cell due to a decrease in the metal ionic size occurs mainly around the coordination sphere. Consequently, it is important to clarify the relation between the observed M-O lengths and the respective standard value (now the sum of the Shannon's ionic radii[19] was adopted for the purpose) of the series of the isomorphous lanthanoid(III) complexes, which are shown graphically in Fig. 6.

In this figure, lines 1 and 2 show the average M-O (sulfonato) and M-O (water) bond-lengths of the complexes, respectively, while lines 3 to 6 are examples of the M-O bond lengths to the individual oxygen atoms. Line 7 is a reference line which shows the sum of the Shannon's ionic radii.

All of the observed M-O values do not deviate much from the respective lines (1—6), although the points of lines 3—6 are distributed over the wider range than those of lines 1 and 2.

All M-O bond lengths of the yttrium complex were found to be situated not far from the respective corresponding lines if the sum of its Shannon's ionic radii (2.37 Å) was taken as their abscissa value.

Although the same relation was found between the observed M-O bond lengths and the sums of the Shannon's ionic radii in the series of the yttrium and lanthanoid 2-naphthalenesulfonates, more detailed results were not obtained owing to the larger standard deviations of their final atomic parameters.

From these results, not only the carboxylates or β-diketonates, but also the arenesulfonates of yttrium were found to have the same coordination geometry and coordination number of the central metal atom as the corresponding salts of lanthanoids, especially which have approximately the same ionic radii.

Although scandium is also a member of the same group element of the periodic table, since its tervalent ionic radius is much smaller than those of yttrium or lanthanoids, it takes a different coordination number.

As shown in the former section, at ambient temperature, enneahydrated *p*-toluenesulfonates of samarium and gadolinium lost their water more easily. To clarify this dehydration process, we have examined simultaneous TG and DTA measurements of all the synthesized *p*-toluenesulfonates. Curves of the scandium and the gadolinium salts are shown in Fig. 7, as the examples, and the results of all the salts are tabu-

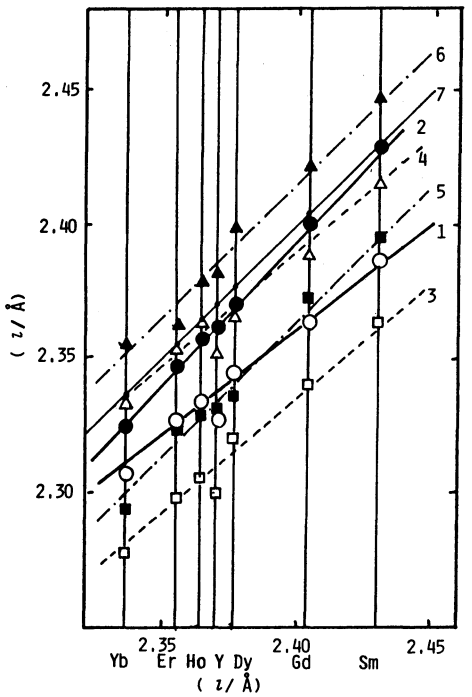

Fig. 6. The relation between the calculated (abscissa) and the observed (ordinate) M-O bond lengths of the yttrium and lanthanoids (Sm—Yb) *p*-toluenesulfonate enneahydrates. 1, —○—, the average of the M-O(sulfonato); 2, —●—, the average of the M-O(water); 3, –□–, M-O(11); 4, –△–, M-O(21); 5, –■–, M-O(W4), 6, –▲–, M-O-(W3), 7, —●—, sum of the Shannon's ionic radii (calculated value).[22]

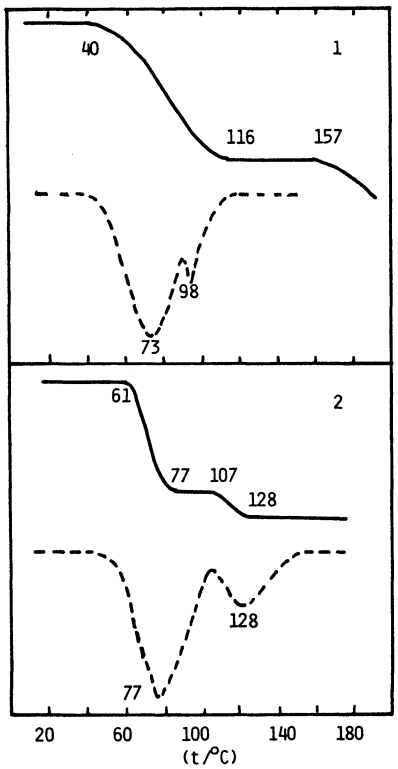

Fig. 7. TG(——) and DTA(----) curves of the *p*-toluenesulfonates; 1, $ScL_3 \cdot 6H_2O$, 2, $GdL_3 \cdot 9H_2O$ (HL=*p*-toluenesulfonic acid). Mass loss of TG was taken downward, and the exothermal change of DTA was taken upward.

Table 9. Thermal Analytical Data of Rare Earth *p*-Toluenesulfonates, $ScL_3 \cdot 6H_2O$ and $ML_3 \cdot 9H_2O$ (HL=*p*-Toluenesulfonic Acid, M=Y, Sm, Gd, Dy, Ho, Er, and Yb)

M=	Sc	Sm	Gd	Dy	Y	Ho	Er	Yb
First mass loss of TG (t/°C)[n]	40	53	61	57	58	57	58	56
Second mass loss (t/°C)[n]		105	107	109	108	104	110	103
Lost water at first step (n/mol)[o]	6.0	7.3	7.4	7.5	7.6	7.6	7.7	7.8
Lost water at second step (n/mol)[o]		1.7	1.6	1.5	1.4	1.4	1.3	1.2
First peak of DTA (t/°C)[p]	73	70	77	84	85	85	86	86
Second peak of DTA (t/°C)[p]	(98)	127	128	127	126	128	128	126

n) The temperature where each TG curve is going down was read (the starting point of each mass loss). o) The mol numbers of the lost water at respective steps were calculated from the TG curves. p) The temperatures of respective endothermic peaks of the DTA curves.

lated in Table 9.

From the TG curves, it was found that the water molecules of the scandium salt were removed in one step, while those of the gadolinium through ytterbium as well as the yttrium complexes in two steps. On their DTA curves, all complexes show two endothermic peaks, the first big one and the second small one; both of them seem to correspond to the respective two steps of the mass loss of the TG curve, except for the scandium salt, which also shows a small second peak at a much lower temperature. The general feature of the respective TG and DTA curves of the isomorphous lanthanoid (Sm—Yb) complexes are approximately the same, though there are some continuous variations depending on the increase of the central metal atomic number:

i) All the hydrated water molecules in the crystals were lost in two steps: the ratio of the first step mass loss to the second one increases. (from 7.3(Sm) to 7.8(Yb) molecules of water).

ii) The temperature of the first endothermic peak of the DTA curve is elevated (from 70 (Sm) to 86 (Yb) (t/°C).

iii) The observed corresponding values of the yttrium complex took positions approximately between those of the dysprosium and holmium salts, while the metal ionic radius of yttrium was between those of the latter two metals.

Although we could clearly recognize that water in the crystals could be removed more easily from complexes of the lighter lanthanoid(III) complexes than those of the heavier ones at ambient temperature, the respective TG and DTA curves were not much different from each other.

As the coordination number of lanthanoid(III) is always high (commonly 8 or 9 except when the ligand is very large[30]) it does not decreased even when the hydrated water molecules are removed from the crystal. The sulfonate anions must move and act as multidentates forming more M-O bonds in place of the removed water oxygen atoms. From their unit cell size, as well as from their density, we can imagine that the anion can move more easily in samarium and gadolinium complexes, since there is more free space in the unit cell. Moreover, since we could not obtain isomorphous members of neodymium or lighter lanthanoid salts when the same synthetic process was applied, the crystal structures of the light lanthanoid elements may not be so stable as the heavier metal salts. However, the energy barrier to keep the hydrated water molecules in the respective positions is probably not high in all of these crystals, although they are effective in the heavier metal complexes at ambient temperature.

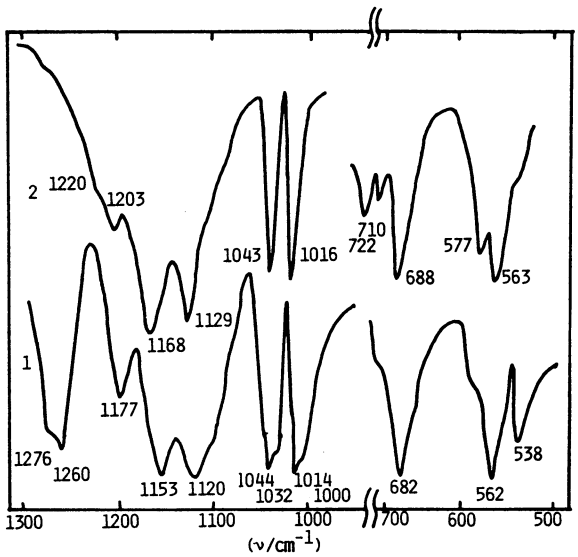

Fig. 8. Infrared spectra of 1, scandium(III) and 2, yttrium(III) *p*-toluenesulfonates, $ScL_3 \cdot 6H_2O$, and $YL_3 \cdot 9H_2O$ (HL=*p*-toluenesulfonic acid).

From their thermal analyses, it was shown that, when the temperature is elevated, all water molecules of even the heavier metal salts obtain sufficient kinetic energy to jump over the barrier and to move in the crystal easily. The dehydration rates of all the member salts are much more accerelated than those at room temperature, and are not much different from each other.

The infrared spectra of the scandium, yttrium, and lanthanoid (Sm, Gd, Dy, Ho, Er, Yb) *p*-toluenesulfonates were examined; the spectra of the former two in the 1100—1300 cm^{-1} as well as 500—700 cm^{-1} regions are shown in Fig. 8, where the characteristic bands of the sulfonato group are expected to appear.

The scandium salt, which is in a hexa-coordination geometry, gave an infrared spectrum that is a little different from those of the other salts, while the isomorphous lanthanoid as well as yttrium salts almost gave the same pattern spectra in these regions. Therefore, there are almost no differences between the bonding character of the sulfonato ions in the series of the latter complexes.

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