Syntheses and Crystal and Molecular Structure of [Hexaaquabis-(2-naphthalenesulfonato)lanthanoid(III)] 2-Naphthalenesulfonate Trihydrate, $[Ln(C_{10}H_7SO_3)_2(H_2O)_6](C_{10}H_7SO_3)\cdot 3H_2O$ (Ln=Pr, Nd, Sm, Eu, Gd, Dy, Er, and Yb)

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Eight isomorphous 2-naphthalenesulfonato complexes of lanthanoids(III) (Pr, Nd, Sm, Eu, Gd, Dy, Er, and Yb) were synthesized, and the structures of five of them were determined by the single-crystal X-ray-diffraction method. They are monoclinic, with the space group of $P2_1$; the cell constants of the Pr^{III} complex, for example, were $a=18.228(8)$, $b=7.498(4)$, $c=14.177(9)$ Å, $\beta=107.75(4)°$, $Z=2$, and its final R value was 0.043. The unit-cell size of the complex decreases with the increase in the atomic number of the metal atom. The central metal atom is in a square-antiprism geometry and is octa-coordinated with two unidentate 2-naphthalenesulfonato ligands and six water-oxygen atoms. Nonligated oxygen atoms of the sulfonato ions form hydrogen-bonds with the coordinated and lattice water molecules to form a double-layered network along the ab-plane. All the naphthalene rings stand together to form hydrophobic sheets between the hydrogen-bonding networks.

It has already been reported by several authors that the carboxylato or the oxoacid-anionic ligands are coordinated to the metal atoms in a variety of ways, especially in their lanthanoid complexes. In the cases of carboxylato ligands, they act not only as unidentate, but also as bidentate chelating or bridging ligands.[1-5] In the case of the sulfato complexes, the ligands act as bridging ligands or as the chelating bidentate.[6,7] Therefore, it is very interesting to examine the coordination geometry of some sulfonates of lanthanoid(III). The structure of the lanthanoid(III) ethyl sulfate enneahydrates has already been clarified.[8,9] In their crystals, not the ethyl sulfate ions but nine water molecules are ligated to the central metal atom, and the sulfate anions as well as the water molecules, including the coordinated ones, are linked by the network of hydrogen bonds.

This time, we have succeeded in obtaining the title complexes in the crystalline state. Therefore, we have tried to determine their structures by the single-crystal X-ray-diffraction method: not only the structure of one complex, but also a series of isomorphous ones were investigated comparatively, especially with regard to the changes resulting from the increase in the atomic number of the central metal atom.

Experimental

Synthesis of [Hexaaquabis(2-naphthalenesulfonato)praseodymium(III)] 2-Naphthalenesulfonate Trihydrate. Praseodymium(III) chloride hexahydrate (1.0 g, 2.8 mmol) and sodium 2-naphthalenesulfonate (2.1 g, 9.1 mmol) were dissolved in about 20 cm^3 of a warmed ethanol-water mixed solvent (2:1=v/v), after with the solution was stirred and filtered while it was hot. When the filtrate has cooled, the complex was deposited, and the product was collected and washed by the mixed solvent, ethanol, and diethyl ether, in that order. The yield was 1.5 g on the average (1.6 mmol, 58%). The neodymium, samarium, europium, gadolinium, dysprosium, erbium, and ytterbium complexes were also obtained in almost the same way; the yields were about 60% on the average. The complexes thus obtained could be recrystallized from the ethanol-water (2:1=v/v) mixed solvent. The crystals used for the single-crystal X-ray-diffraction method were those deposited from the 2-propanol-water (2:1=v/v) mixed solvent solution, which had been left standing in open vessels over a silica-gel desiccator at the ambient temperature. Attempts to obtain the lanthanum(III) and cerium(III) complexes using the same operation were not successful, probably because the stable forms of their complexes are different from those of the heavier lanthanoids. The europium(III) complex is colorless, implying that there is no charge-transfer band such as is observed in some *O,O'*-dialkyl dithiophosphates of the metal.[10] Anal. ($MC_{30}H_{39}O_{48}S_3$) M, C, H. (M=Pr, Nd, Sm, Eu, Gd, Dy, Er, and Yb).

Single-crystal X-Ray Analyses. All of these complexes were found to be isostructural from their X-ray powder patterns; the structures of five complexes (M=Pr, Eu, Gd, Er, and Yb) were determined by the single-crystal X-ray-diffraction method. They are monoclinic, space group $P2_1$, $Z=2$; their other crystallographic data are shown in Table 1, together with some experimental conditions and the final R values, obtained by applying the anisotropic thermal parameters to all the non-hydrogen atoms.[11]

The reflections in the ranges shown in Table 1 were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite-monochromated Mo$K\alpha$ radiation (the scan speed was 4°min^{-1}), the ω—2θ scan technique being employed; the scan widths were $(1.03+0.5\tan\theta)°$ for the praseodymium, europium, and ytterbium complexes, $(1.05+0.5\tan\theta)°$ for the samarium complex, and $(1.37+0.5\tan\theta)°$ for the erbium complex. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction. Reflections with $|F_o|>3\sigma(|F_o|)$ were used for refinements.

Structure Determination. The structure of the praseodymium(III) complex was solved by the heavy-atom

TABLE 1. CRYSTALLOGRAPHIC DATA OF THE $[M(C_{10}H_7SO_3)_2(H_2O)_6](C_{10}H_7SO_3)\cdot 3H_2O$ COMPLEXES

M=	Pr	Eu	Gd	Er	Yb
F.W.	924.7	935.7	941.1	951.1	956.9
$a(l/Å)$	18.228(8)	18.148(9)	18.150(13)	18.095(4)	18.069(7)
$b(l/Å)$	7.498(4)	7.467(3)	7.465(3)	7.439(2)	7.427(3)
$c(l/Å)$	14.177(10)	14.096(8)	14.084(9)	14.033(7)	13.993(14)
$\beta(\phi/°)$	107.75(4)	107.73(5)	107.82(7)	107.78(3)	107.83(5)
$V(v/Å^3)$	1845.5(19)	1819.4(17)	1816.8(20)	1798.6(11)	1787.8(21)
$D_m(d/Mg\,m^{-3})$	1.65(3)	1.73(3)	1.71(3)	1.75(3)	1.77(3)
$D_x(d/Mg\,m^{-3})$	1.66	1.71	1.72	1.76	1.78
μ(Mo $K\alpha$)(n/mm^{-1})	1.57	1.98	2.13	2.67	3.01
Number of reflections measured	5811	4537	5712	5662	5626
Reflection used for the calculation	4993	3823	5413	5011	4887
Measured range ($\phi/°$)	3—60	3—55	3—60	3—60	3—60
R	0.043	0.054	0.033	0.043	0.043
R value with inverse chirality	0.045	0.055	0.037	0.047	0.045
Size of the crystal used (v/mm^3)	0.25×0.20×0.08	0.21×0.23×0.10	0.28×0.25×0.15	0.25×0.25×0.12	0.25×0.25×0.10

method. The positions of the metal and some sulfur atoms were deduced from the three-dimensional Patterson map. The positional and thermal parameters were refined successively by the repeated block-diagonal least-squares method and by the Fourier syntheses.

At the end, all the non-hydrogen atoms were found. The positions of the naphthalene hydrogen atoms were calculated by assuming the C–H bond-length to be 1.08 Å; their B_{iso}'s were assumed to be 6.0. The parameters of the hydrogen atoms were fixed in the refinement.

The structures of the other isomorphous complexes were solved by starting with the parameters of the praseodymium(III) complex. As the crystals have no center of symmetry, refinements using inverse chirality were also carried out. For each complex, we adopted the chirality which gave a lower R-value; the respective final R-values for the alternate chirality are also shown in Table 1. According to our selection, europium and gadolinium complexes can be expected to have the structure opposite to that of the other three.

All the calculations were carried out on a HITAC M-280H apparatus at the Computer Center of The University of Tokyo, using the local version of the UNICS program.[12] The atomic-scattering factors were taken from Ref. 13.

Other Measurements. The X-ray powder patterns of these complexes were obtained by the use of a diffractometer, Model DX-GO-F JEOL, using Cu $K\alpha$ radiation in the range from 4° to 30° in 2θ. Their infrared absorption spectra were obtained by means of a JASCO A-202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters of the complexes are listed in Table 2 (1—5), while some bond lengths and angles as well as some interatomic distances, which are thought to be the hydrogen-bonding ones, are tabulated in Table 3.[14] A perspective drawing of the praseodymium(III) complex around the central

TABLE 2. FINAL ATOMIC COORDINATES (×10^4), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AND THEIR EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B_{eq}/Å^2)

1) [Hexaaquabis(2-naphthalenesulfonato) praseodymium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å^2[a)]
Pr	7227.9(2)	7500	5049.1(2)	1.8_1
S(1)	6068(1)	4470(3)	3160(1)	2.3_9
S(2)	6991(1)	11019(3)	6814(1)	2.4_4
S(3)	9585(1)	5042(3)	3319(1)	2.6_0
O(1)	6764(3)	5484(8)	3692(4)	3.0_8
O(2)	6109(3)	2659(13)	3545(4)	3.5_7
O(3)	5370(3)	5391(9)	3151(4)	3.2_6
O(4)	6808(3)	9463(8)	6158(4)	3.0_8
O(5)	6359(3)	12293(11)	6553(4)	3.4_4
O(6)	7724(3)	11837(8)	6853(4)	3.3_5
O(7)	8816(3)	4495(9)	3302(4)	3.6_7
O(8)	9877(4)	6553(10)	3939(4)	4.7_5
O(9)	10129(3)	3568(9)	3568(5)	4.3_6
O(W1)	8279(3)	7218(12)	4271(4)	4.3_7
O(W2)	8380(3)	8967(8)	6171(4)	3.2_5
O(W3)	7992(3)	4974(8)	5923(4)	3.5_9
O(W4)	5891(3)	8408(8)	4147(4)	3.1_3
O(W5)	7314(3)	10344(9)	4231(5)	4.3_1
O(W6)	6388(3)	5662(8)	5762(4)	3.7_7
O(W7)	4821(3)	6361(9)	5350(4)	3.9_1
O(W8)	9495(4)	4928(10)	6199(7)	6.2_2
O(W9)	8797(4)	11130(10)	4270(5)	4.9_0
C(1)	5473(4)	4865(11)	1169(6)	2.5_6
C(2)	6068(4)	4315(10)	1933(5)	2.2_2
C(3)	6754(4)	3524(11)	1776(5)	2.6_3
C(4)	6773(4)	3335(12)	824(6)	2.9_3
C(5)	6135(4)	3862(10)	0(5)	2.3_6
C(6)	6138(5)	3633(12)	−987(6)	3.2_9
C(7)	5518(5)	4089(12)	−1761(6)	3.3_5
C(8)	4854(5)	4847(13)	−1580(6)	3.3_8
C(9)	4845(5)	5107(12)	−637(6)	3.1_4
C(10)	5484(4)	4643(10)	186(5)	2.3_2
C(11)	7731(4)	10557(11)	8767(6)	2.7_3
C(12)	7074(4)	10194(10)	8001(5)	2.4_5
C(13)	6458(4)	9178(12)	8126(6)	2.9_8
C(14)	6502(4)	8583(12)	9046(6)	3.0_4
C(15)	7141(4)	8962(11)	9885(5)	2.9_1

Table 2. (Continued)

1) [Hexaaquabis(2-naphthalenesulfonato) praseodymium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
C(16)	7181(6)	8424(13)	10846(6)	4.2$_1$
C(17)	7812(7)	8864(16)	11636(7)	5.2$_2$
C(18)	8426(5)	9847(16)	11497(6)	4.6$_5$
C(19)	8413(5)	10361(14)	10576(6)	3.8$_1$
C(20)	7770(4)	9964(11)	9738(5)	2.8$_3$
C(21)	8903(4)	5247(11)	1333(5)	2.7$_4$
C(22)	9531(4)	5688(10)	2105(5)	2.4$_1$
C(23)	10147(4)	6702(11)	1949(6)	2.9$_6$
C(24)	10117(4)	7159(11)	1029(6)	3.2$_6$
C(25)	9489(4)	6717(11)	199(6)	3.0$_2$
C(26)	9449(5)	7194(14)	−771(6)	4.1$_0$
C(27)	8829(7)	6700(15)	−1561(7)	5.1$_2$
C(28)	8221(6)	5742(15)	−1401(7)	4.3$_1$
C(29)	8230(5)	5287(13)	−470(6)	3.6$_5$
C(30)	8871(4)	5733(11)	354(5)	2.7$_6$

2) [Hexaaquabis(2-naphthalenesulfonato) europium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Eu	2772.4(4)	2500	4957.7(5)	1.5$_9$
S(1)	3919(2)	5538(5)	6820(3)	2.0$_7$
S(2)	3008(2)	−992(5)	3212(3)	2.1$_4$
S(3)	415(2)	4991(6)	6671(3)	2.4$_2$
O(1)	3228(6)	4479(16)	6307(8)	2.6$_6$
O(2)	3879(7)	7401(30)	6417(8)	3.6$_7$
O(3)	4635(6)	4656(18)	6823(8)	3.0$_9$
O(4)	3193(7)	608(16)	3868(7)	2.7$_5$
O(5)	3648(6)	−2234(22)	3467(7)	2.9$_3$
O(6)	2259(7)	−1793(16)	3202(8)	3.2$_1$
O(7)	1193(6)	5514(17)	6679(8)	2.9$_9$
O(8)	114(9)	3454(20)	6040(9)	5.0$_9$
O(9)	−131(7)	6466(19)	6397(10)	3.9$_0$
O(W1)	1750(6)	2828(22)	5735(8)	3.5$_5$
O(W2)	1632(6)	1071(17)	3857(8)	2.8$_9$
O(W3)	2024(6)	5061(17)	4102(9)	3.1$_4$
O(W4)	4094(6)	1646(16)	5829(8)	2.6$_8$
O(W5)	2696(8)	−239(18)	5771(10)	4.2$_6$
O(W6)	3586(6)	4299(15)	4276(8)	2.7$_6$
O(W7)	5168(6)	3687(18)	4650(9)	3.4$_5$
O(W8)	524(8)	5124(20)	3848(13)	5.5$_4$
O(W9)	1222(7)	−1074(21)	5731(10)	4.5$_1$
C(1)	4524(9)	5123(21)	8800(11)	2.0$_5$
C(2)	3905(8)	5692(20)	8062(10)	1.8$_5$
C(3)	3244(9)	6494(23)	8214(11)	2.4$_8$
C(4)	3231(9)	6715(24)	9163(12)	2.5$_8$
C(5)	3863(8)	6144(22)	9994(11)	2.2$_2$
C(6)	3859(10)	6411(23)	10994(12)	2.7$_8$
C(7)	4483(10)	5903(26)	11780(12)	3.1$_3$
C(8)	5135(10)	5180(25)	11607(12)	3.0$_6$
C(9)	5170(10)	4935(22)	10635(12)	2.8$_3$
C(10)	4509(9)	5408(21)	9810(12)	2.2$_1$
C(11)	2273(9)	−522(22)	1256(11)	2.3$_6$
C(12)	2915(8)	−161(21)	2024(10)	1.9$_0$
C(13)	3533(9)	822(24)	1895(12)	2.5$_0$
C(14)	3508(10)	1454(24)	949(12)	3.0$_7$
C(15)	2862(9)	1079(24)	115(12)	2.8$_2$
C(16)	2818(12)	1630(30)	−859(13)	4.1$_7$
C(17)	2206(12)	1105(31)	−1638(14)	4.3$_1$
C(18)	1578(11)	163(31)	−1513(13)	3.9$_9$
C(19)	1561(13)	−345(31)	−545(14)	4.7$_5$
C(20)	2215(9)	54(21)	278(12)	2.5$_5$
C(21)	1094(9)	4747(22)	8665(11)	2.3$_8$
C(22)	474(8)	4292(22)	7887(11)	2.1$_8$

2) [Hexaaquabis(2-naphthalenesulfonato) europium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
C(23)	−158(9)	3362(23)	8049(12)	2.7$_2$
C(24)	−118(9)	2875(23)	8964(12)	3.0$_1$
C(25)	496(9)	3278(22)	9822(11)	2.4$_3$
C(26)	578(10)	2860(20)	10789(12)	3.1$_6$
C(27)	1204(13)	3326(28)	11565(13)	4.4$_9$
C(28)	1756(12)	4234(28)	11438(13)	3.9$_5$
C(29)	1793(10)	4744(25)	10467(13)	3.1$_3$
C(30)	1137(10)	4328(22)	9639(11)	2.6$_0$

3) [Hexaaquabis(2-naphthalenesulfonato) gadolinium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Gd	2773.3(1)	2500	4959.8(1)	1.6$_0$
S(1)	3917(1)	5528(2)	6815(1)	2.1$_3$
S(2)	3003(1)	−996(2)	3219(1)	2.1$_7$
S(3)	420(1)	4979(2)	6665(1)	2.3$_8$
O(1)	3224(2)	4483(6)	6295(3)	2.6$_3$
O(2)	3867(3)	7345(9)	6417(3)	3.3$_4$
O(3)	4630(2)	4645(7)	6824(3)	2.8$_0$
O(4)	3185(2)	570(6)	3885(3)	2.7$_6$
O(5)	3641(2)	−2264(8)	3486(3)	3.1$_7$
O(6)	2262(3)	−1818(6)	3178(3)	2.9$_5$
O(7)	1190(2)	5540(7)	6693(3)	3.1$_5$
O(8)	134(3)	3442(8)	6040(3)	4.3$_5$
O(9)	−135(3)	6432(7)	6400(4)	4.0$_0$
O(W1)	1750(2)	2820(8)	5724(3)	3.6$_9$
O(W2)	1640(2)	1108(7)	3863(3)	2.7$_6$
O(W3)	2024(2)	4973(7)	4107(4)	3.2$_7$
O(W4)	4076(2)	1612(6)	5828(3)	2.7$_9$
O(W5)	2689(3)	−251(7)	5778(4)	3.9$_7$
O(W6)	3587(2)	4298(6)	4261(4)	3.1$_6$
O(W7)	5163(3)	3663(8)	4640(4)	3.7$_2$
O(W8)	513(3)	5091(8)	3816(5)	5.5$_8$
O(W9)	1213(3)	−1064(8)	5742(4)	4.4$_3$
C(1)	4516(3)	5143(8)	8815(4)	2.2$_4$
C(2)	3902(3)	5698(8)	8057(4)	2.1$_5$
C(3)	3238(3)	6469(9)	8217(4)	2.4$_4$
C(4)	3221(3)	6690(9)	9173(4)	2.7$_4$
C(5)	3860(3)	6150(8)	10003(4)	2.3$_6$
C(6)	3869(4)	6387(10)	10997(5)	2.9$_6$
C(7)	4486(4)	5913(11)	11766(5)	3.4$_5$
C(8)	5149(4)	5177(10)	11584(5)	3.2$_7$
C(9)	5157(4)	4891(9)	10635(4)	2.7$_7$
C(10)	4513(3)	5377(8)	9812(4)	2.1$_5$
C(11)	2271(3)	−528(8)	1250(4)	2.3$_7$
C(12)	2920(3)	−164(8)	2021(4)	2.1$_1$
C(13)	3545(3)	830(9)	1900(4)	2.6$_3$
C(14)	3497(4)	1437(9)	965(5)	2.9$_9$
C(15)	2858(4)	1044(9)	137(4)	2.7$_0$
C(16)	2814(5)	1591(11)	−852(5)	4.0$_6$
C(17)	2191(5)	1133(13)	−1642(5)	4.6$_9$
C(18)	1560(5)	166(13)	−1497(5)	4.4$_6$
C(19)	1586(4)	−359(11)	−557(5)	3.6$_9$
C(20)	2234(3)	61(9)	277(4)	2.5$_7$
C(21)	1094(3)	4780(8)	8661(4)	2.5$_5$
C(22)	465(3)	4319(8)	7884(4)	2.2$_9$
C(23)	−148(3)	3332(9)	8036(5)	2.7$_2$
C(24)	−125(3)	2840(9)	8977(5)	3.0$_3$
C(25)	511(4)	3304(9)	9811(4)	2.7$_7$
C(26)	556(4)	2829(10)	10800(5)	3.5$_0$
C(27)	1168(5)	3325(11)	11579(5)	4.3$_2$
C(28)	1791(4)	4268(12)	11425(5)	3.8$_1$
C(29)	1776(4)	4736(11)	10482(5)	3.4$_7$
C(30)	1127(3)	4288(8)	9647(4)	2.5$_3$

TABLE 2. (Continued)

4) [Hexaaquabis(2-naphthalenesulfonato) erbium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Er	7226.3(2)	7500	5031.8(2)	1.48
S(1)	6092(1)	4479(3)	3203(2)	1.99
S(2)	6998(1)	10986(3)	6755(2)	2.05
S(3)	9579(1)	5013(4)	3342(2)	2.22
O(1)	6787(4)	5548(11)	3730(5)	2.57
O(2)	6145(4)	2671(16)	3602(5)	3.14
O(3)	5383(4)	5350(11)	3205(5)	2.77
O(4)	6823(4)	9410(10)	6095(5)	2.55
O(5)	6361(4)	12267(12)	6486(5)	2.95
O(6)	7735(4)	11810(10)	6783(5)	2.88
O(7)	8810(4)	4437(11)	3322(5)	3.06
O(8)	9858(6)	6570(12)	3961(6)	4.52
O(9)	10144(4)	3553(11)	3615(6)	3.63
O(W1)	8230(4)	7171(11)	4294(5)	3.20
O(W2)	8344(4)	8844(10)	6122(5)	2.52
O(W3)	7962(4)	5055(10)	5849(6)	3.01
O(W4)	5941(4)	8411(10)	4161(4)	2.36
O(W5)	7308(4)	10191(11)	4220(6)	3.58
O(W6)	6432(4)	5748(10)	5742(5)	2.84
O(W7)	4847(4)	6334(12)	5366(6)	3.67
O(W8)	9471(4)	4912(12)	6170(8)	4.81
O(W9)	8784(5)	11017(13)	4267(6)	4.26
C(1)	5492(5)	4854(13)	1200(6)	1.97
C(2)	6107(5)	4304(13)	1959(6)	2.07
C(3)	6770(5)	3522(14)	1792(7)	2.38
C(4)	6785(5)	3308(14)	841(7)	2.50
C(5)	6140(5)	3854(12)	5(6)	2.02
C(6)	6141(6)	3614(15)	−1002(7)	2.81
C(7)	5517(7)	4072(16)	−1776(7)	3.11
C(8)	4852(6)	4800(16)	−1597(7)	3.09
C(9)	4840(6)	5089(15)	−647(7)	2.73
C(10)	5492(5)	4633(12)	199(7)	2.02
C(11)	7731(5)	10514(14)	8738(7)	2.39
C(12)	7085(5)	10152(13)	7953(6)	1.92
C(13)	6456(5)	9152(14)	8081(7)	2.33
C(14)	6495(6)	8560(14)	9017(8)	2.86
C(15)	7147(6)	8961(15)	9865(7)	2.59
C(16)	7192(7)	8398(16)	10842(8)	3.65
C(17)	7806(8)	8871(18)	11641(8)	4.06
C(18)	8441(7)	9842(20)	11495(8)	4.04
C(19)	8425(6)	10358(17)	10557(8)	3.18
C(20)	7773(5)	9946(14)	9716(7)	2.37
C(21)	8904(5)	5224(14)	1333(7)	2.33
C(22)	9534(5)	5668(13)	2122(7)	2.18
C(23)	10157(5)	6664(15)	1962(7)	2.63
C(24)	10128(5)	7161(12)	1031(8)	2.72
C(25)	9494(5)	6692(14)	189(7)	2.42
C(26)	9452(6)	7193(16)	−796(8)	3.32
C(27)	8830(8)	6683(18)	−1596(8)	4.02
C(28)	8206(7)	5722(19)	−1430(8)	3.63
C(29)	8220(6)	5267(16)	−483(7)	3.13
C(30)	8872(5)	5696(13)	350(6)	2.07

5) [Hexaaquabis(2-naphthalenesulfonato) ytterbium(III)] 2-Naphthalenesulfonate Trihydrate

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Yb	7726.4(2)	7500	5028.4(2)	1.65
S(1)	6098(1)	4500(3)	3212(2)	2.21
S(2)	7000(1)	11003(3)	6743(2)	2.23
S(3)	9579(1)	5028(3)	3349(2)	2.44
O(1)	6786(3)	5571(10)	3734(5)	2.80
O(2)	6155(4)	2672(17)	3618(5)	3.56
O(3)	5383(3)	5375(10)	3199(5)	2.88
O(4)	6822(4)	9439(9)	6082(4)	2.75
O(5)	6362(4)	12271(12)	6472(5)	3.18
O(6)	7738(4)	11830(9)	6790(5)	3.15
O(7)	8809(4)	4460(11)	3317(5)	3.17
O(8)	9863(5)	6563(12)	3968(5)	4.79
O(9)	10143(4)	3595(11)	3623(6)	3.95
O(W1)	8229(4)	7180(9)	4274(5)	2.95
O(W2)	8332(3)	8867(9)	6097(5)	2.62
O(W3)	7960(4)	5113(9)	5857(5)	3.18
O(W4)	5954(3)	8413(9)	4180(4)	2.50
O(W5)	7311(4)	10197(10)	4207(6)	3.64
O(W6)	6435(4)	5768(9)	5723(5)	3.15
O(W7)	4849(4)	6362(11)	5363(5)	3.65
O(W8)	9471(4)	4912(12)	6158(7)	4.96
O(W9)	8773(4)	11059(12)	4255(6)	4.44
C(1)	5493(5)	4877(12)	1192(7)	2.34
C(2)	6105(5)	4354(12)	1965(6)	2.05
C(3)	6778(5)	3562(13)	1794(7)	2.56
C(4)	6788(5)	3328(14)	828(7)	2.87
C(5)	6142(5)	3867(12)	6(6)	2.18
C(6)	6140(6)	3613(15)	−1001(7)	3.19
C(7)	5509(6)	4113(15)	−1773(7)	3.29
C(8)	4848(6)	4838(15)	−1592(7)	3.40
C(9)	4837(6)	5130(14)	−636(7)	2.90
C(10)	5493(5)	4642(12)	193(6)	2.14
C(11)	7724(5)	10546(13)	8724(7)	2.29
C(12)	7084(5)	10173(12)	7957(6)	1.95
C(13)	6451(5)	9158(14)	8073(7)	2.47
C(14)	6499(5)	8568(14)	9011(7)	2.98
C(15)	7141(5)	8974(13)	9856(7)	2.71
C(16)	7184(6)	8452(16)	10855(8)	3.79
C(17)	7818(7)	8882(18)	11645(7)	4.37
C(18)	8450(7)	9864(18)	11500(8)	4.15
C(19)	8421(6)	10387(15)	10550(8)	3.49
C(20)	7771(5)	9964(13)	9705(7)	2.51
C(21)	8901(5)	5224(13)	1340(7)	2.59
C(22)	9530(5)	5677(12)	2121(7)	2.18
C(23)	10158(5)	6690(13)	1975(7)	2.61
C(24)	10129(5)	7184(12)	1023(7)	2.79
C(25)	9491(5)	6721(13)	190(7)	2.63
C(26)	9454(6)	7185(14)	−807(7)	3.49
C(27)	8836(8)	6722(17)	−1587(8)	4.30
C(28)	8206(7)	5756(18)	−1434(8)	3.92
C(29)	8222(6)	5293(15)	−484(8)	3.53
C(30)	8867(5)	5715(13)	350(7)	2.57

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

metal atom, as well as the numbering scheme, is shown in Fig. 1. The crystal packing diagram is shown in Fig. 2, and the linkages between the complex molecules, in Fig. 3, schematically.

The central metal atom is octa-coordinated and is in a deformed square-antiprism geometry, where two oxygen atoms of the respective 2-naphthalenesulfonato ligand, as well as six water-oxygen atoms, are ligated. The naphthyl group of the ligand is large and is, moreover, non-polar compared with the polar moiety around the central metal atoms. Therefore, two coor-

Table 3. Selected bond lengths and bond angles of the $[M(C_{10}H_7SO_3)_2(H_2O)_6](C_{10}H_7SO_3)\cdot 3H_2O$ complexes

M=	Pr	Eu	Gd	Er	Yb
Bond length	(l/Å)	(l/Å)	(l/Å)	(l/Å)	(l/Å)
M-O(1)	2.389(10)	2.351(19)	2.335(8)	2.278(12)	2.255(12)
M-O(4)	2.441(10)	2.38(2)	2.370(8)	2.333(13)	2.332(12)
M-O(W1)	2.495(13)	2.44(3)	2.427(10)	2.362(13)	2.372(12)
M-O(W2)	2.472(7)	2.424(14)	2.399(5)	2.355(8)	2.329(8)
M-O(W3)	2.452(7)	2.441(14)	2.388(6)	2.338(8)	2.303(8)
M-O(W4)	2.477(5)	2.424(11)	2.400(5)	2.372(7)	2.342(6)
M-O(W5)	2.455(10)	2.369(19)	2.383(8)	2.330(12)	2.338(11)
M-O(W6)	2.492(10)	2.403(18)	2.416(7)	2.373(12)	2.344(11)
Av. of M-O(Wn)[a]	2.474(10)	2.416(20)	2.402(8)	2.355(11)	2.338(10)
Av. of all M-O[b]	2.459(10)	2.403(24)	2.390(8)	2.343(12)	2.327(11)
M-O calcd.[c]	2.476	2.416	2.403	2.354	2.335
S(1)-O(1)	1.475(6)	1.473(12)	1.470(5)	1.480(8)	1.468(7)
S(1)-O(2)	1.456(12)	1.50(3)	1.460(8)	1.499(15)	1.463(15)
S(1)-O(3)	1.444(7)	1.456(15)	1.449(5)	1.439(9)	1.441(8)
S(2)-O(4)	1.465(9)	1.486(18)	1.471(7)	1.467(11)	1.458(10)
S(2)-O(5)	1.455(7)	1.443(14)	1.454(5)	1.454(8)	1.447(8)
S(2)-O(6)	1.456(7)	1.482(15)	1.463(5)	1.457(9)	1.450(8)
S(3)-O(7)	1.454(7)	1.461(15)	1.448(6)	1.449(9)	1.441(8)
S(3)-O(8)	1.433(10)	1.45(2)	1.443(8)	1.443(13)	1.429(12)
S(3)-O(9)	1.455(7)	1.453(14)	1.449(5)	1.460(5)	1.442(8)
Av. of coord. S-O[d]	1.470(8)	1.480(15)	1.471(6)	1.474(10)	1.463(9)
Av. of all S-O[e]	1.455(9)	1.467(19)	1.456(6)	1.455(11)	1.449(10)
O(7)···O(W1)[f]	2.798(17)	2.76(3)	2.804(12)	2.824(18)	2.798(16)
O(W7)···O(W4^{ii})[f]	2.767(12)	2.77(2)	2.782(9)	2.789(14)	2.807(13)
O(9)···O(W2^{iv})[f]	2.646(8)	2.654(18)	2.652(7)	2.655(11)	2.669(10)
O(W8)···O(8^{iv})[f]	2.809(11)	2.77(2)	2.797(9)	2.797(14)	2.792(13)
O(W5)···O(2^{vi})[f]	2.735(10)	2.71(2)	2.725(8)	2.734(12)	2.714(12)
O(W9)···O(7^{vi})[f]	2.878(14)	2.89(3)	2.873(11)	2.876(17)	2.857(16)
Bond angle	(ϕ/°)	(ϕ/°)	(ϕ/°)	(ϕ/°)	(ϕ/°)
M-O(1)-S(1)	140.9(7)	140.6(14)	140.7(5)	141.2(9)	141.3(9)
M-O(4)-S(2)	146.4(6)	145.5(12)	146.8(5)	147.2(7)	147.3(7)
M-O(W1)···O(7)	135.2(4)	136.9(8)	136.7(3)	137.3(4)	137.3(4)
M-O(W5)···O(2^{vi})[f]	124.0(4)	124.5(8)	124.6(3)	125.3(5)	124.7(5)
M-O(W2)···O(9^{v})[f]	132.4(5)	132.8(9)	133.9(4)	134.4(6)	134.9(5)

a) The average of M-O(Wn)(n=1—6), where the oxygen atom are ligated to the metal atom. b) The average of the bond lengths between the central metal atom and all the ligated oxygen atoms around it. c) The sum of the metal (tripositive, octacoordinated) and the oxygen (dinegative, dicoordinated) ionic radii proposed by Shannon.[15] d) The average of the S(1)-O(1) and S(2)-O(4), where both the oxygen atoms are ligated. e) The average of all nine S-O bond lengths of the sulfonate ions in the complex. f) Keys to the symmetric operations: ii, 1.0−x, −0.5+y, 1.0−z; iv, 2.0−x, −0.5+y, 1.0−z; v, 2.0−x, 0.5+y, 1.0−z; vi, x, 1.0+y, z for the Pr, Er and Yb comolexes, and the corresponding ones for the Eu and Gd complexes, which have the opposite structure.

dinated sulfonato ligands, and consequently the ligated O(1) and O(4) atoms, take the positions around the metal atom the most separated from each other.

As is shown in Table 3, the M-O distances to the ligated sulfonato oxygen atoms are shorter than those to the ligated water-oxygen atoms. The latter distances almost exactly agree with the sum of the respective metal (M^{3+}, in octa-coodination) and oxygen (O^{2-}, in di-coordination) ionic radii reported by Shannon.[15] On the other hand, as the former M-O bond lengths are shorter than the respective sums, the bondings can be expected to be stronger than the common M-O bonds of the lanthanoid complexes. Although the M-O(1) bond length is clearly shorter than the sum, even in the heavy lanthanoid complexes, the differeces between the M-O(4) bond length and the sum of the ionic radii are not very large, especially in the erbium and ytterbium complexes. In the case of the tetraacetato complexes of lanthanoids (M=La···Sm), the weakest M-O bond length in the complex was found to increase with the decrease in the atomic number of the central metal atom because of the loss of its coordination space around the metal atom, while the other M-O bond lengths decrease depending on the decrease in the metal atomic radius caused by the lanthanoid contraction.[3] In this case, the same tendency was recognized: the M-O(1) bond length, which is supposed to be stronger than M-O(4), is always shorter than the metal-aqueous oxygen-atom bond lengths, while the weaker M-O(4) bond is weakened to almost the same extent as the metal-water oxygen-atom ones when the atomic number of the central metal atom increases.

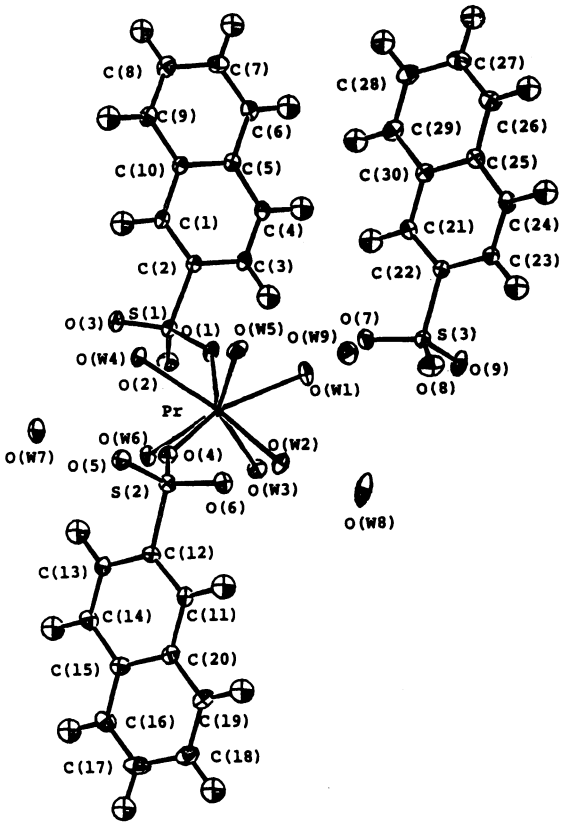

Fig. 1. A perspective drawing of the praseodymium (III) complex with the numbering scheme.

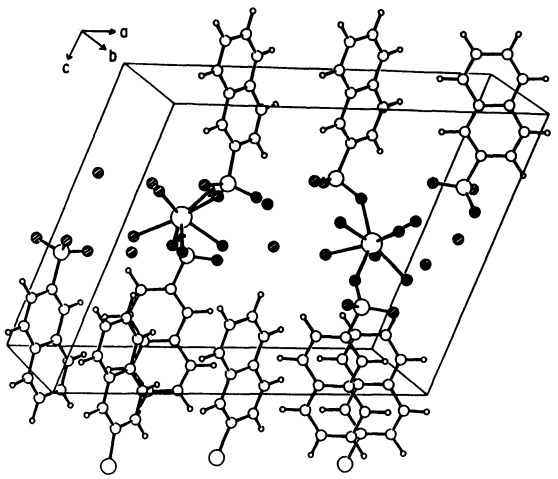

Fig. 2. Crystal packing diagram of the praseodymium(III) complex.

The planarity of the square of the square-antiprism geometry around the metal atom including O(1) is not so exact as that containing O(4). The deformation is caused by the M–O(1) bond, which is stronger than the M–O(4) bonding.

As is shown in Fig. 2, the crystal is composed of alternate layers of hydrophilic and hydrophobic groups parallel to the ab plane. The metal atoms are almost on the plane (0 0 2), and the oxygen atoms are coordinated from both sides of the plane. The oxygen atoms on each side form a hydrogen-bonding network; although there are some hydrogen bondings between the two networks, there are not many.

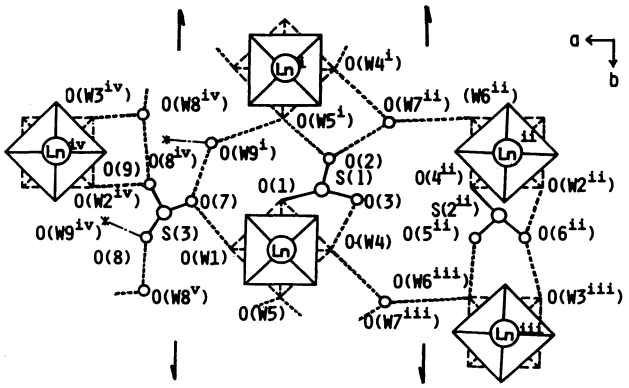

Fig. 3. The schematic presentation of the bridgings between the lanthanoid(III) complex molecules. The network shown in the figure is that in the layer lower than the metal atom plane. As the two-fold screw axes exist, which are shown in the figure, the same type of the linkage-network exists also in the upper layer. Keys to the symmetric operations: i, x, $-1.0+y$, z; ii, $1.0-x$, $-0.5+y$, $1.0-z$; iii, $1.0-x$, $0.5+y$, $1.0-z$; iv, $2.0-x$, $-0.5+y$, $1.0-z$; v, $2.0-x$, $0.5+y$, $1.0-z$.

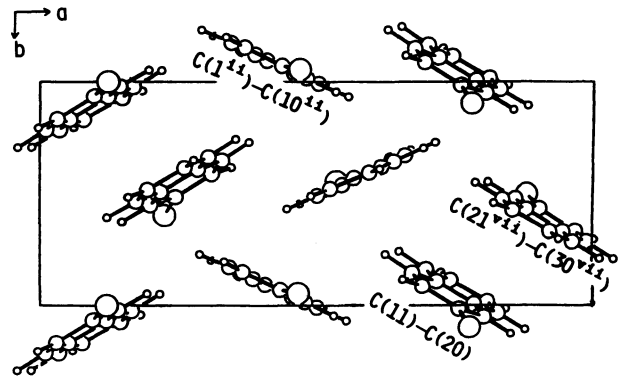

Fig. 4. Packing projection of the naphthalene rings together with the sulfonato sulfur atoms of the anions on the (0 0 1) plane. Keys to the symmetry operations: ii, $1.0-x$, $-0.5+y$, $1.0-z$; vii, x, y, $1.0+z$.

Figure 4 shows the packing of the naphthalene rings projected on the ab plane. They stand almost perpendicular to the ab plane. The angles between the ab plane and the C(1)–C(10), C(11)–C(20), and C(21)–C(30) rings are 89.1, 81.6, and 84.3° respectively in the praseodymium(III) complex. There is a tendency for these angles to become larger with the decrease in the unit-cell volumes. The C(11)–C(20) ring is almost parallel to the C(21)–C(30) ring, and when the former ring is projected on the latter plane, about 33% of the area overlaps. In the case of the praseodymium(III) complex, the distance between these rings is from 3.387 to 3.619 Å, which is almost the same as the thickness of the aromatic molecules;[16] however, the distance decreases with the decrease in

Table 4. The interfacial distances (l/Å) and the angles (ϕ/°) to the 001 plane of the sulfonato naphthalene rings

M=	Pr	Eu	Gd	Er	Yb
Interfacial min.	3.387	3.360	3.374	3.380	3.370
distances[a] max.	3.619	3.581	3.608	3.575	3.561
Angles of planes[b]					
C(1)-C(10)	89.09	89.18	89.27	89.35	89.52
C(11)-C(20)	81.59	82.02	81.85	82.02	82.06
C(21)-C(30)	84.33	84.25	84.41	84.28	84.25

a) The respective maximum and minimum interfacial distances between the naphthalene rings, C(11)-C(20) and C(21^{vii})-C(30^{vii}),[b,c] which are almost parallel to each other. b) Respective naphthalene rings are shown by the included carbon atoms. c) Key to the symmetric operation: vii x, y, 1.0+z.

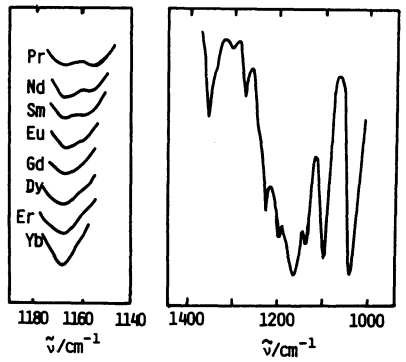

Fig. 5. Infrared absorption spectra of the complexes in the ν(S=O) region. Right; the spectrum of the gadolinium(III) complex in the region. Left; the peak of ν(S=O) of the complexes (the name of the central metal atoms are shown in the figure).

the unit-cell parameters because of the lanthanoid contraction of the central metal ion. The interfacial distances and the angles to the ab plane of the naphthalene rings are shown in Table 4. Thus, the naphthalene rings are packed quite closely to form a hydrophobic layer between hydrophilic layers.

The infrared spectrum of the ν(S=O) region of the gadolinium(III) complex is shown in Fig. 5; the general features of the spectra of the other complexes are almost the same throughout the region from 400 to 4000 cm^{-1}. A slight difference between them was, however, found in those of the peaks at about 1100 cm^{-1}; the peak at 1100 cm^{-1} is identified as one of the ν(S=O) peak of the sulfonato group.[17] The peak of the praseodymium(III) complex split into two; 1167 and 1156 cm^{-1}. The latter peak is weakened when the atomic number of the central metal atom increases; in the case of the ytterbium(III) complex, only a slight shoulder was observed at the lower-wave-number side of the 1167 cm^{-1} peak.

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