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Syntheses, and Crystal and Molecular Structures of Tetramethylammonium [Aquamethanolhexakis(isothiocyanato)lanthanoidates(III)], $[(CH_3)_4N]_3[M(NCS)_6(CH_3OH)(H_2O)]$ (M=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er), and Tetramethylammonium [Heptakis(isothiocyanato)lanthanoidates(III)], $[(CH_3)_4N]_4[M(NCS)_7]$(M=Dy, Er, Yb)

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The title complexes were synthesized and their crystal and molecular structures were determined by the X-ray diffraction method using their single crystals. The crystals of the former ten hexakis(isothiocyanato) complexes of lanthanum through dysprosium(III) and erbiun(III) are isomorphous with each other: monoclinic, space group $P2_1$, $Z=2$. The central metal atom is octa-coordinated, in a square-antiprism geometry, to six nitrogen atoms of thiocyanato (SCN) ions and two oxygen atoms of methanol and water molecules. The two oxygen atoms take the positions of the most approaching apexes of two squares. The latter three heptakis(isothiocyanato) complexes of dysprosium, erbium, and ytterbium are in another isomorphous form with each other: orthorhombic, space group $P2_1nb$, $Z=4$. The central metal atom is hepta-coordinated, in a deformed pentagonal-bipyramidal geometry, to seven nitrogen atoms of SCN ions.

The study of the molecular structures of the metal complexes of thiocynate (SCN) is one of the very interesting fields due to their variety of coordinated forms and bridging structures. The structure of tetrabutylammonium [hexakis(isothiocyanato)lanthanoidates(M)] (M=Pr—Yb, and Y) has already been elucidated by Martin and others.[1] It has a coordination number of six, although almost all lanthanoids have a coordination number 8—9 in almost all of thier complexes.

On the other hand, in anionic complexes of tetrapotassium [tetraaquatetrakis(isothiocyanato)lanthanoidates(M)] thiocyanates (M=Nd, Eu), reported by Lazarev, the coordination number of the central metal atom is eight (square-antiprism geometry).[2] The authors have already shown that in tetraethylammonium [aquaheptakis(isothiocyanato)lanthanoidates-(M)] (M=La—Pr and Nd—Er) the central metal atom is in a cubic octa-coordination geometry.[3]

In this line of the study, the authors have tried to synthesize other types of thiocyanato complexes of lanthanoids, and have obtained the two series of the anionic complexes shown in the title. From now on, the former ten hexakis(isothiocyanato) complexes are called **A**-type complexes, while the latter three heptakis(isothiocyanato) complexes are called **B**-type.

In many cases a series of the isomorphous lanthanoid complexes were obtained only for a limited range of the members of the following series: for example, Sm—Yb for $[M(CH_3C_6H_4SO_3)_2(H_2O)_6](CH_3C_6H_4SO_3)\cdot 3H_2O$,[4] La—Gd for $[M\{(C_2H_5O)_2PS_2\}_2(C_6H_5CONH_2)_3][(C_2H_5O)_2PS_2]$,[5] La—Eu for $[\{M(ClCH_2CO_2)_3\}_3(H_2O)_5]$,[6] Gd—Yb for $[M_3(ClCH_2CO_2)_9(H_2O_4)]_n\cdot nH_2O$.[7] In a series of isomorphous lanthanoid complexes it was found that some structural detail changed, depending on the metal atomic number.[6,8,9] Since we had obtained ten members of isomorphous **A**-type complexes, we had planned to compare their detailed structures with each other. Moreover, by almost the same synthetic technique, the other type, **B**-type, complexes were obtained from the heavier lanthanoids. Therefore, a comparison of the **A**- and **B**-type complexes was also thought to be interesting.

Therefore, the authors investigated the crystal structures of the title two series of complexes by single-crystal X-ray diffraction.

Experimental

Synthesis of the A-Type Complexes: Tetramethylammonium [Aquamethanolhexakis(isothiocyanato)lanthanoidates-(III)], $[(CH_3)_4N]_3[M(NCS)_6(CH_3OH)(H_2O)]$(M=La—Er). Lanthanoid(III) thiocyanates and tetramethylammonium thiocyanate were obtained by the metathetical reaction between lanthanoid(III) chlorides or tetramethylammonium chloride and potassium thiocyanate in methanolic medium, respectively (as reported previously), to obtain cadmium and other metal thiocyanates.[10,11] The obtained lanthanoid thiocyantes were stored as their methanolic solution (0.5 mol dm^{-3}) without drying.

To synthesize the lanthanum(III) complex, to the methanolic solution (7 cm^3) of lanthanum thiocyanate (1.0 mmol), tetramethylammonium thiocyanate (0.41 g, 3.1 mmol), and water (0.1 cm^3, 6 mmol) were added. The mixture was then warmed and stirred until complete dissolution occured. The solution was left standing for several days in a silica gel desiccator for drying to about 1 cm^3 at room temperature. A square plate form crystals were deposited. Yield: 0.55 g (0.72 mmol, 72 %).

Crystals were also obtained when the above-mentioned starting solution was left standing in chlorobenzene vapor. Yield, 0.25 g, 0.33 mmol, 33%, started from 1 mmol of the metal salt.

The Ce through Dy complexes were obtained by the same technique in almost the same yield; even in the case of the Dy salt, only the **A**-type complex crystals were deposited, unless the starting solution was severely dried. (By the latter method, the **B**-type Dy complex was obtained.)

Both of the above-mentioned methods did not give the **A**-type erbium complex; only hexagonal thick plate crystals of the **B**-type complex were deposited within several days. The erbium complex was obtained by using a starting solution containing a little more water (0.5 cm^3 in place of 0.1 cm^3). The solvent was evaporated very slowly, over several months, at room temperature. Yield: 0.3 g (0.38 mmol, 38%) starting from 1.0 mmol of erbium thiocyanate.

All attempts to synthesize the **A**-type complex of ytterbium were unsuccessful. Even when more water was added to the starting solution, the **B**-type complex was always deposited.

Synthesis of the B-Type Complex: Tetramethylammonium Heptakis(thiocyanato)dysprosium(III), $[(CH_3)_4N]_4[M(SCN)_7]$ (M=Er, Yb). The dysprosium complex was synthesized as follows. To the methanol solution (10 cm^3) of dysprosium thiocyanate (2.0 mmol) and tetramethylammonium thiocyanate (1.06 g, 8.0 mmol), 10 cm^3 of ethanol and 10 cm^3 of benzene were added, and the mixture was evaporated to dryness by a vacuum rotary evaporator at about 80 °C. The same process was repeated three times so as to remove the water completely. The residue was dissolved into 10 cm^3 of methanol (GR grade reagent of Wako Pure Chemicals Industry Ltd.: it contains at most 0.3% of water). The solution was dried to 2 cm^3 by standing in a silica gel desiccator for several days: crystals were deposited. These were washed with a small portion of ethanol and dried in a silica gel desiccator. Yield: 1.21 g, 1.40 mmol 70%. By the same synthetic method **B**-type Er and Yb complexes were also obtained in almost the same yield.

B-type complexs of terbium and the lighter lanthanoids

Table 1. Elemental Analyses (*n*/%)

A. **A**-type Complexes, $[(CH_3)_4N]_3[M(SCN)_6(CH_3OH)(H_2O)]$, $MC_{19}H_{42}N_9O_2S_6$ (The Calculated Values Are Shown in Parentheses)

M	M	C	H	N
La	18.10	29.85	5.55	16.60
	(18.28)	(30.03)	(5.57)	(16.59)
Ce	18.50	29.69	5.50	16.57
	(18.41)	(29.99)	(5.56)	(16.56)
Pr	18.45	29.55	5.50	16.75
	(18.50)	(29.95)	(5.56)	(16.55)
Nd	18.80	29.55	5.47	16.67
	(18.85)	(29.82)	(5.53)	(16.47)
Sm	19.19	29.39	5.46	16.01
	(19.49)	(29.59)	(5.49)	(16.34)
Eu	19.80	29.27	5.49	15.96
	(19.66)	(29.53)	(5.48)	(16.31)
Gd	19.92	29.01	5.27	16.17
	(20.21)	(29.32)	(5.44)	(16.20)
Tb	20.40	29.06	5.41	16.10
	(20.38)	(29.26)	(5.43)	(16.16)
Dy	20.50	28.82	5.36	15.80
	(20.74)	(29.13)	(5.40)	(16.09)
Er	21.40	28.67	5.29	16.19
	(21.22)	(28.95)	(5.37)	(15.99)

B. **B**-type Complexes, $[(CH_3)_4N]_4[M(SCN)_7]$, $MC_{23}H_{48}N_{11}S_7$ (The Calculated Values Are Shown in Parentheses)

M	M	C	H	N
Dy	18.34	31.69	5.54	17.55
	(18.77)	(31.91)	(5.59)	(17.80)
Er	18.90	31.41	5.45	17.48
	(19.22)	(31.74)	(5.56)	(17.70)
Yb	19.51	31.37	5.44	17.32
	(19.75)	(31.53)	(5.52)	(17.59)

Table 2. Crystallographic Data and Various Experimental Conditions for the **A**-Type Complexes, $[(CH_3)_4N]_3[M(SCN)_6(CH_3OH)(H_2O)]$, $MC_{19}H_{42}N_9O_2S_6$, Monoclinic, Space Group, $P2_1$, $Z=2$

M	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er
F. W.	759.87	761.09	761.87	765.21	771.33	772.93	778.22	779.89	783.47	788.23
$a(l/\text{Å})$	9.082(7)	9.061(2)	9.047(3)	9.044(2)	9.011(4)	8.999(4)	8.993(4)	8.980(4)	8.967(2)	8.948(3)
$b(l/\text{Å})$	22.59(6)	22.545(14)	22.542(17)	22.524(12)	22.497(15)	22.47(3)	22.460(13)	22.459(18)	22.43(5)	22.399(17)
$c(l/\text{Å})$	8.963(9)	8.950(4)	8.928(6)	8.929(4)	8.901(4)	8.899(3)	8.893(5)	8.874(5)	8.867(4)	8.846(4)
$\beta(\phi/^\circ)$	91.29(8)	91.19(3)	91.18(4)	91.06(2)	91.15(4)	91.11(4)	91.01(5)	91.09(5)	90.96(3)	90.98(3)
$U(v/\text{Å}^3)$	1838(5)	1827.9(15)	1820.4(19)	1818.6(12)	1804.0(17)	1798(2)	1795.8(16)	1789.4(19)	1783(4)	1772.8(16)
$D_\mathrm{m}(d/\mathrm{g\ cm^{-3}})$	1.35(3)	1.37(3)	1.37(3)	1.38(3)	1.42(3)	1.43(3)	1.43(3)	1.46(3)	1.45(3)	1.48(3)
$D_\mathrm{x}(d/\mathrm{g\ cm^{-3}})$	1.37	1.38	1.39	1.40	1.42	1.43	1.44	1.45	1.46	1.48
$\mu(\mathrm{Mo}\ K\alpha)$ $(n/\mathrm{cm^{-1}})$	15.41	16.16	17.00	18.05	20.14	21.21	22.69	23.89	25.43	28.29
N_m a)	6041	6004	5474	5691	5439	5918	6712	5871	5372	6621
N_c b)	4569	3957	3393	4397	4511	4661	4553	4277	4447	4461
R c)	0.081	0.077	0.078	0.052	0.052	0.051	0.066	0.060	0.052	0.059
V_c d) $(v/\mathrm{mm^3})$	0.35×0.33 ×0.33	0.28×0.25 ×0.25	0.21×0.21 ×0.20	0.30×0.30 ×0.22	0.35×0.32 ×0.23	0.33×0.33 ×0.33	0.32×0.31 ×0.30	0.30×0.30 ×0.20	0.33×0.33 ×0.35	0.30×0.30 ×0.29
S_w e) $(\omega/^\circ)$	1.16+ 0.5tanθ	1.25+ 0.35tanθ	1.15+ 0.5tanθ	1.12+ 0.5tanθ	1.15+ 0.5tanθ	1.20+ 0.35tanθ	1.30+ 0.5tanθ	1.30+ 0.35tanθ	1.25+ 0.35tanθ	1.16+ 0.5tanθ
S_R f) $(2\theta/^\circ)$	3—62	3—62	3—60	3—60	3—60	3—62	3—65	3—62	3—60	3—65

a) Number of reflections measured. b) Number of reflections used for the calculation (reflections of $|F_\mathrm{o}|>3\sigma(|F_\mathrm{o}|)$ were used). c) $R=\sum||F_\mathrm{o}|-|F_\mathrm{c}||/\sum|F_\mathrm{o}|$. d) The size of the crystal (approximately parallelepiped). e) Scan width. f) Scanned range.

Table 3. Crystallographic Data and Various Experimental Conditions for the **B**-Type Complexes, $[(CH_3)_4N]_4[M(SCN)_7]$, $MC_{23}H_{48}N_{11}S_7$, Orthorhombic, Space Group, $P2_1nb$, $Z=4$

M	Dy	Er	Yb
F. W.	865.68	870.44	876.22
$a(l/\text{Å})$	12.800(5)	12.775(5)	12.762(2)
$b(l/\text{Å})$	26.180(9)	26.154(19)	26.119(5)
$c(l/\text{Å})$	12.715(8)	12.693(3)	12.674(2)
$U(v/\text{Å}^3)$	4261(3)	4242(4)	4224.7(12)
$D_m(d/\text{g cm}^{-3})$	1.36(3)	1.36(3)	1.35(3)
$D_x(d/\text{g cm}^{-3})$	1.35	1.36	1.38
$\mu(\text{Mo } K\alpha)$ (n/cm^{-1})	21.79	24.15	26.90
N_m[a)]	6402	6011	6144
N_C[b)]	3101	3053	3495
R[c)]	0.067	0.061	0.058
V_c[d)] (v/mm^3)	0.32×0.28 ×0.30	0.35×0.30 ×0.30	0.32×0.30 ×0.28
S_w[e)] $(\omega/°)$	1.23	1.30	1.15
S_R[f)] $(2\theta/°)$	3—55	3—57	3—57.5

a—f) See the footnotes of Table 2.

were not obtained, even when a strictly dried starting solution was used.

The results of elemental analyses of the **A**- and **B**-type complexes are shown in Table 1.

X-Ray Structure Analysis. Crystallographic data and various experimental conditions for collecting intensity data are listed in Tables 2 and 3.

Reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo *Kα* radiation (λ=0.71073 Å). In the case of the **A**-type complexes a ω-2θ scan technique was used, while for the **B**-type complexes a ω-scan was adopted. The intensities were corrected for the Lorentz and polarization factors, but not for absorption and extinction.

Structure Determination. The structure of the Nd complex in the **A**-type and that of the Yb complex in the **B**-type were solved by the heavy-atom method, respectively. The positions of the metal and some sulfur atoms were deduced from their three-dimensional Patterson maps; the other non-hydrogen atoms were located by successive Fourier syntheses. Their positional and thermal parameters were refined by a block-diagonal least-squares method. No hydrogen atoms were included in the structure factor calculations.

The structures of the other **A**-type complexes, Ce—Er complexes, were determined by starting from the final parameters of the neodymium complex. The structures of the **B**-type Dy and Er complexes were determined by starting from the final parameters of the ytterbium complex. In all cases, at the final cycle of the refinement the shifts of all the parameters were less than one third of the respective standard deviations.

Some thermal parameters of tetramethylammonium carbon atoms are relatively large in the **A**-type complexes, especially when the atomic number of the central lanthanoid atom is small. In the **B**-type complex the thermal parameters of some tetramethylammonium carbon atoms as well as the S(7) atom were large: the isotropic temperature factor was applied to the S(7) atom. Such large temperature factors of some atoms are also found in some other lanthanoid complexes, especially for their sulfur and carbon atoms, when they are loosely packed in the crystal.[12)]

All calculations were carried out on a HITAC M-682H computer at the Computer Center of the University of Tokyo using a local version of the UNICS program.[13)] The atomic scattering factors were taken from Ref. 14.

Infrared Absorption Spectrum Measurements. The infrared absorption spectra were obtained by means of a JASCO 202-A grating infrared spectrophotometer using paraffin oil and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic positional and thermal parameters

Table 4. Final Atomic Coordinates (×10^4, for Er ×10^5) and Equivalent Isotropic Temperature Factors ($B_{eq}/\text{Å}^2$) of the Atoms of Tetramethylammonium [Aquamethanolhexakis(isothiocyanato)erbate(III)] with Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^2$ [a)]
Er	15240(4)	25000	44128(4)	2.7
S(1)	3410(4)	412(2)	2899(5)	5.9
S(2)	862(5)	810(2)	8253(5)	6.1
S(3)	2947(5)	3556(2)	9410(4)	5.6
S(4)	−3564(4)	1683(2)	2621(4)	5.5
S(5)	−3338(4)	3357(2)	6565(5)	6.5
S(6)	2670(6)	4615(2)	2416(5)	7.8
O(1)	4188(7)	2561(7)	4287(9)	5.7
O(2)	1553(11)	2589(7)	1697(8)	6.4
N(1)	2489(11)	1554(4)	3540(12)	4.6
N(2)	1036(12)	1794(4)	6360(11)	4.6
N(3)	2480(11)	2964(5)	6686(10)	4.2
N(4)	−734(11)	2043(5)	3413(12)	5.0
N(5)	−595(11)	3020(5)	5414(12)	5.1
N(6)	1981(12)	3509(5)	3651(11)	5.0
N(7)	5643(13)	1374(6)	7947(13)	6.2
N(8)	7410(14)	3965(6)	1486(15)	6.8
N(9)	8871(11)	22(4)	3133(11)	4.2
C(1)	2872(11)	1091(5)	3267(12)	3.6
C(2)	981(12)	1380(5)	7117(13)	3.9
C(3)	2675(12)	3187(5)	7829(12)	3.8
C(4)	−1935(12)	1906(5)	3074(12)	3.8
C(5)	−1730(13)	3155(5)	5938(13)	4.2
C(6)	2286(14)	3959(6)	3141(13)	4.7
C(21)	1145(22)	2175(7)	560(15)	7.9
C(71)	4800(20)	1915(8)	8452(22)	8.5
C(72)	5048(23)	1071(11)	6449(18)	9.6
C(73)	7265(20)	1516(14)	8026(33)	15.0
C(74)	5305(29)	904(8)	9119(18)	10.1
C(81)	6375(21)	3396(8)	1677(20)	7.9
C(82)	6697(20)	4351(8)	340(19)	7.8
C(83)	8913(22)	3860(16)	1088(34)	15.9
C(84)	7533(40)	4303(14)	2981(23)	15.6
C(91)	7208(13)	−70(8)	3193(17)	5.9
C(92)	9250(16)	305(7)	1640(14)	5.6
C(93)	9339(16)	450(7)	4386(14)	5.5
C(94)	9704(15)	−563(6)	3334(16)	5.4

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

Table 5. Final Atomic Coordinates (×10^4, for Yb ×10^5) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) of the Atoms of the Tetramethylammonium Heptakis(isothiocyanato)ytterbate with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq} or B_{iso}/Å^2 [a,b]	Atom	x	y	z	B_{eq} or B_{iso}/Å^2 [a,b]
Yb	25000	11954(4)	19922(4)	3.9	N(11)	6288(13)	2275(7)	482(14)	9.6
S(1)	3249(7)	3076(2)	2492(6)	10.8	N(21)	4457(13)	−484(5)	4519(12)	7.4
S(2)	1428(7)	−640(2)	2489(7)	11.9	N(31)	5683(10)	2107(5)	5163(10)	5.5
S(3)	−1176(4)	1678(3)	3092(5)	8.9	N(41)	8536(11)	5061(5)	4064(10)	6.3
S(4)	3025(7)	1018(3)	5946(4)	13.5	C(11)	5460(21)	2257(12)	1190(21)	13.8
S(5)	6344(4)	907(3)	2775(5)	8.2	C(12)	7283(21)	2254(13)	789(28)	16.8
S(6)	3768(8)	1736(3)	−1605(5)	12.6	C(13)	6068(27)	2679(9)	−298(19)	13.4
N(1)	2916(11)	2037(4)	2329(10)	6.0	C(14)	6333(27)	1740(13)	−1(30)	17.2
N(2)	2198(11)	327(5)	2151(11)	6.8	C(21)	3368(21)	−421(13)	4951(27)	16.7
N(3)	870(11)	1441(5)	2603(10)	6.0	C(22)	5182(21)	−362(12)	5369(22)	14.4
N(4)	2685(16)	1118(4)	3830(8)	5.9	C(23)	4337(24)	−135(14)	3650(25)	17.5
N(5)	4265(10)	939(5)	2201(10)	5.5	C(24)	4657(37)	−1024(10)	4199(24)	16.9
N(6)	3339(12)	1433(6)	429(10)	6.7	C(31)	5890(21)	1573(7)	5583(23)	12.7
N(7)	1350(12)	1031(6)	592(10)	6.8	C(32)	5264(19)	2418(8)	6097(16)	9.4
C(1)	3085(13)	2463(6)	2386(12)	5.4	C(33)	4872(16)	2078(7)	4329(15)	7.9
C(2)	1865(13)	−73(6)	2316(13)	5.5	C(34)	6592(19)	2339(9)	4706(17)	10.2
C(3)	−1(13)	1540(6)	2819(11)	5.1	C(41)	7754(19)	5300(11)	4706(18)	13.5
C(4)	2836(12)	1073(5)	4700(11)	5.6	C(42)	7959(21)	4671(9)	3507(26)	13.8
C(5)	5110(11)	919(5)	2441(12)	4.3	C(43)	8972(21)	5420(10)	3336(21)	11.7
C(6)	3451(14)	1577(5)	−414(12)	5.7	C(44)	9328(22)	4818(7)	4787(18)	10.5
C(7)	837(15)	1104(8)	−73(15)	8.1	S(7)[b]	18(11)	1222(4)	−1028(10)	17.91(4)

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3$ $(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}=2hkB_{12}+2hlB_{13}+2klB_{23})]$. b) The isotropic temperature factor was used for S(7) in the refinement. c) C (11—14; 21—24; 31—34, and 41—44) are the methyl carbon atoms bonded to the N(11, 21, 31, and 41) atoms, respectively.

(B_{eq}(Å)) of the **A**-type erbium(III) and of the **B**-type ytterbium(III) complexes are listed in Tables 4 and 5, and the selected bond lengths and bond angles of the **A**- and **B**-type complexes are given in Tables 6 and 7, respectively. Perspective drawings of the **A**-type Er complex as well as that of the **B**-type Yb complex are shown in Figs. 1 and 2, together with a numbering scheme of their atoms.

The crystal structures of the **A**-type Er and the **B**-type Yb complexes projected along the b-axis are shown in Figs. 3 and 4.[15]

The Structure of the A-Type Complexes. In the **A**-type erbium complex the central metal atom is octa-coordinated, in a square-antiprism geometry, to six nitrogen atoms of SCN ions, and two oxygen atoms of one water and one methanol molecules. The two ligated oxygen atoms take positions at the most approaching apexes of the respective bottom squares, obeying the empirical rule that the same kind of ligating atoms preferably take the neighboring posi-

Table 6. Selected Bond Lengths and Bond Angles of the **A**-Type Complexes, $[(CH_3)_4N]_3[M(SCN)_6(CH_3OH)(H_2O)]$, with the Standard Deviations in Parentheses

A. Bond lengths (l/Å) M	La	Ce	Pr	Nd	Sm
M-O(1)	2.530(9)	2.537(8)	2.526(9)	2.498(6)	2.466(6)
M-O(2)	2.547(12)	2.558(11)	2.522(13)	2.496(8)	2.472(19)
M-O (Sum of Shannon's ionic radii)	2.51	2.49	2.48	2.46	2.43
M-N(1)	2.589(14)	2.514(12)	2.466(15)	2.531(9)	2.504(9)
M-N(2)	2.554(15)	2.477(14)	2.465(16)	2.484(9)	2.470(10)
M-N(3)	2.536(15)	2.567(14)	2.551(14)	2.514(9)	2.495(19)
M-N(4)	2.561(15)	2.498(13)	2.476(16)	2.504(9)	2.493(9)
M-N(5)	2.587(14)	2.599(13)	2.569(15)	2.508(10)	2.478(10)
M-N(6)	2.540(16)	2.622(14)	2.603(14)	2.515(9)	2.468(9)
M-N(n) (n=1—6) (average)	2.561	2.546	2.522	2.509	2.485
M-N (Sum of Shannon's ionic radii)	2.62	2.60	2.59	2.57	2.54
N(n)-C(n) (n=1—6) (average)	1.15	1.14	1.15	1.146	1.138
	(1.09(2)—1.21(2))	(1.11(2)—1.18(2))	(1.12(2)—1.22(2))	(1.125(13)—1.166(14))	(1.101(13)—1.166(13))
C(n)-S(n) (n=1—6) (average)	1.612	1.618	1.614	1.616	1.623
	(1.563(15)—1.647(15))	(1.578(14)—1.639(15))	(1.539(17)—1.662(18))	(1.593(10)—1.638(10))	(1.587(10)—1.655(10))

A. Bond lengths (l/Å)					
M	Eu	Gd	Tb	Dy	Er
M-O(1)	2.452(6)	2.434(8)	2.424(7)	2.408(7)	2.393(6)
M-O(2)	2.468(8)	2.444(11)	2.439(10)	2.410(9)	2.411(9)
M-O (Sum of Shannon's ionic radii)	2.42	2.40	2.40	2.38	2.35
M-N(1)	2.424(9)	2.478(12)	2.468(11)	2.439(12)	2.419(10)
M-N(2)	2.393(10)	2.449(13)	2.410(12)	2.410(11)	2.385(10)
M-N(3)	2.507(9)	2.465(12)	2.429(10)	2.449(11)	2.407(10)
M-N(4)	2.434(9)	2.461(12)	2.442(11)	2.428(10)	2.419(10)
M-N(5)	2.508(10)	2.438(12)	2.459(11)	2.430(11)	2.407(11)
M-N(6)	2.530(9)	2.444(12)	2.427(11)	2.417(11)	2.395(11)
M-N(n) (n=1—6) (average)	2.466	2.456	2.439	2.429	2.405
M-N (Sum of Shannon's ionic radii)	2.53	2.51	2.50	2.49	2.46
N(n)-C(n) (n=1—6) (average)	1.147	1.144	1.147	1.143	1.143
	(1.131(13)	(1.138(17)	(1.125(16)	(1.113(15)	1.120(15)
	1.161(13))	1.172(18))	1.170(17))	1.160(15))	1.163(16))
C(n)-S(n) (n=1—6) (average)	1.620	1.622	1.620	1.623	1.623
	(1.592(10)—	(1.601(14)—	(1.593(14)—	(1.589(12)—	(1.585(12)—
	1.632(12))	1.654(16))	1.655(15))	1.650(14))	1.642(14))

B. Bond angles (ϕ/°)					
M	La	Ce	Pr	Nd	Sm
O(1)-M-O(2)	88.3(3)	84.9(3)	84.6(4)	85.8(2)	85.5(2)
O(1)-M-N(1)	71.7(4)	72.4(3)	72.7(4)	71.5(3)	70.7(3)
O(1)-M-N(6)	76.6(4)	75.0(4)	74.2(4)	75.7(2)	75.9(2)
O(2)-M-N(1)	77.7(4)	75.8(4)	75.7(5)	74.8(3)	73.5(3)
N(1)-M-N(2)	71.6(4)	74.2(4)	73.8(5)	73.8(3)	74.8(3)
N(1)-M-N(3)	122.0(4)	122.6(4)	122.0(5)	121.8(3)	122.2(3)
N(1)-M-N(4)	79.8(5)	82.4(4)	82.4(5)	80.1(3)	79.4(3)
N(1)-M-N(5)	145.9(4)	147.4(4)	147.5(5)	145.8(3)	147.0(3)
M-N(n)-C(n) (n=1—6) (average)	168.1	168.9	169.3	168.7	167.6
	(164.4(13)—	(164.4(12)—	(165.1(14)—	(166.3(9)—	(164.6(9)—
	171.8(14))	172.0(11))	171.5(13))	171.8(8))	170.7(9))
N(n)-C(n)-S(n) (n=1—6) (average)	174.6	174.5	175.8	177.3	177.1
	(168.9(16)—	(173.5(14)—	(173.5(17)—	(175.7(9)—	(176.9(10)—
	178.7(17))	176.9(17))	177.6(16))	178.0(11))	178.3(10))

B. Bond angles (ϕ/°)					
M	Eu	Gd	Tb	Dy	Er
O(1)-M-O(2)	85.4(2)	84.3(3)	85.5(3)	8 5.1(3)	85.5(3)
O(1)-M-N(1)	71.7(3)	70.8(3)	71.2(3)	70.4(3)	71.0(3)
O(1)-M-N(6)	74.8(2)	76.2(3)	75.6(3)	76.5(3)	76.0(3)
O(2)-M-N(1)	75.8(3)	74.2(4)	75.1(3)	74.3(3)	75.2(3)
N(1)-M-N(2)	75.7(3)	74.3(4)	74.2(4)	74.4(4)	73.8(3)
N(1)-M-N(3)	122.9(3)	122.3(4)	121.9(4)	122.4(4)	121.4(3)
N(1)-M-N(4)	81.3(3)	79.5(4)	79.4(4)	79.2(4)	79.2(3)
N(1)-M-N(5)	148.1(3)	145.8(4)	146.1(4)	146.3(4)	146.0(4)
M-N(n)-C(n) (n=1—6) (average)	168.6	168.5	168.9	168.7	168.7
	(165.1(9)—	(168.4(11)—	(166.6(11)—	(165.2(10)—	(165.9(10)—
	171.2(9))	170.5(12))	171.8(11))	171.1(10))	172.8(10))
N(n)-C(n)-S(n) (n=1—6) (average)	175.5	176.5	177.0	177.6	177.3
	(175.5(11)—	(175.0(13)—	(175.1(12)—	(176.7(11)—	(175.8(11)—
	179.7(11))	177.7(13))	178.3(12))	178.8(12))	178.8(11))

tions.[17] A schematic presentation which shows the coordinating positions of the ligating atoms around the erbium atom is given in Fig. 5.

The complex, where an alcohol and a water molecules are coordinated to the same metal atom, had already been found in neodymium(III) 1-hydroxy-2-naphthoate;[16] however, it was readily decomposed in open air, missing the alcohol ligand. The crystal used for the intensity collection had to be sealed in a glass capillary. On the other hand, these **A**-type complexes are more stable in the open, and do not decompose in open air during the intensity collection process (about one week) without a cover.

Angle O(1)-Er-O(2) is 85.5 °, and the Er-O(1) and Er-O(2) bonds are approximately directed to the next metal atoms in the a- and c-axis directions, respectively.

As shown in Table 6, the Er-O distance is 2.402 Å

Table 7. Selected Bond Lengths and Bond Angles of the **B**-Type Complexes, $[(CH_3)_4N]_4[M(SCN)_7]$, with the Standard Deviations in Parentheses

A. Bond length (l/Å)

M	Dy	Er	Yb
M-N(1)	2.394(15)	2.361(14)	2.302(12)
M-N(2)	2.307(14)	2.277(14)	2.310(13)
M-N(3)	2.363(18)	2.294(17)	2.311(14)
M-N(4)	2.376(16)	2.383(15)	2.350(12)
M-N(5)	2.394(15)	2.412(14)	2.364(13)
M-N(6)	2.344(19)	2.363(18)	2.336(14)
M-N(7)	2.354(19)	2.345(17)	2.343(15)
M-N(av.)[a]	2.362	2.348	2.331
N(*n*)-C(*n*) (*n*—7) (av.)[a]	1.136 (1.05(3)—1.19(3))	1.126 (1.07(3)—1.18(3))	1.133 (1.08(3)—1.17(2))
C(*n*)-S(*n*) (*n*=1—7) (av.)[a]	1.611 (1.53(2)—1.68(2))	1.618 (1.57(2)—1.69(2))	1.612 (1.581(17)—1.631(14))

B. Bond angle (ϕ/°)

M	Dy	Er	Yb
N(1)-M-N(2)	162.8(5)	163.3(5)	163.9(5)
N(1)-M-N(3)	83.8(6)	83.3(5)	83.1(5)
N(2)-M-N(3)	96.6(6)	96.9(5)	95.4(5)
N(3)-M-N(4)	76.8(6)	77.2(6)	77.5(5)
N(4)-M-N(5)	77.0(5)	76.6(5)	76.7(4)
N(5)-M-N(6)	75.6(6)	74.4(6)	74.5(5)
N(6)-M-N(7)	71.8(7)	72.0(6)	72.2(5)
N(3)-M-N(7)	75.6(6)	76.7(6)	74.9(5)
M-N(*n*)-C(*n*) (*n*=1—7)(av .)[a]	166.6 (160.8(18)—172.8(8))	166.9 (158.1(17)—173.0(14))	167.2 (159.3(16)—175.8(13))
N(*n*)-C(*n*)-S(*n*) (*n*=1—7)(av.)[a]	175.4 (173(2)—177.5(17))	175.7 (171.2(19)—178.7(19))	176.9 (176.4(15)—179.1(15))

a) Average of the seven values of the all SCN ions.

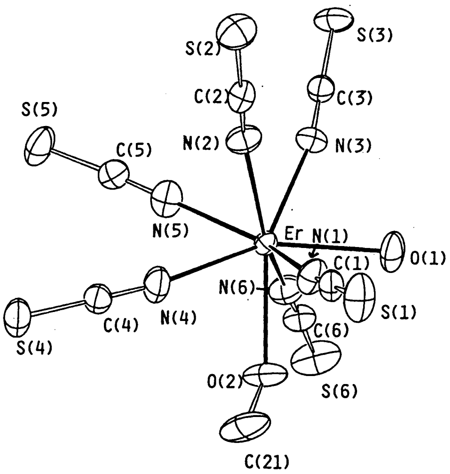

Fig. 1. A perspective drawing of the **A**-type erbium(III) complex around the metal atom, with the numbering scheme of the atoms.

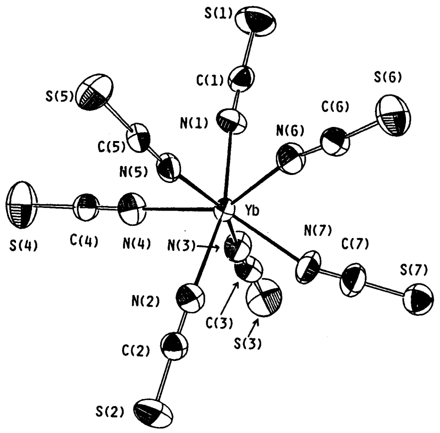

Fig. 2. A perspective drawing of the **B**-type ytterbium(III) complex around the metal atom, with the numbering scheme of the atoms.

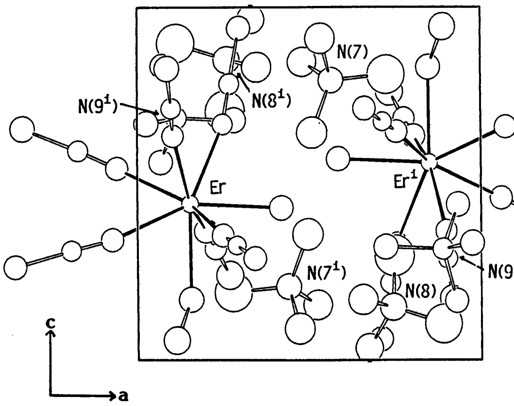

Fig. 3. A projection of the unit cell of the **A**-type erbium(III) complex along b-axis.

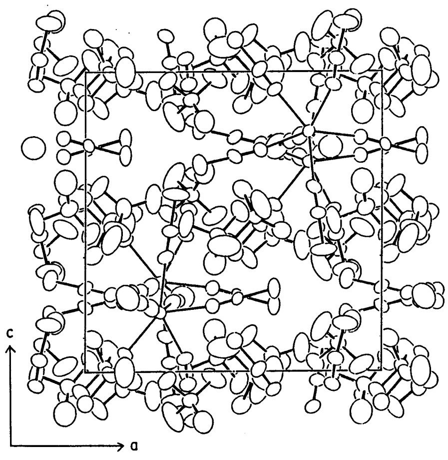

Fig. 4. A projection of the unit cell of the **B**-type ytterbium(III) complex along b-axis.

(on the average), where Er-O(water) is 0.018 Å shorter than Er-O(methanol). Judging from these bond lengths, although methanol is coordinated to the metal atom more weakly than water, the diffence in the bond strengths does not seem to be great.

Although the Er complex is the last member of the **A**-type isomorphous complexes, the Er-N bond lengths are in the range 2.385(10)—2.419(10) Å (2.405 Å on the average): abnormally long bonds, which were found in some carboxylato complexes of lantha-

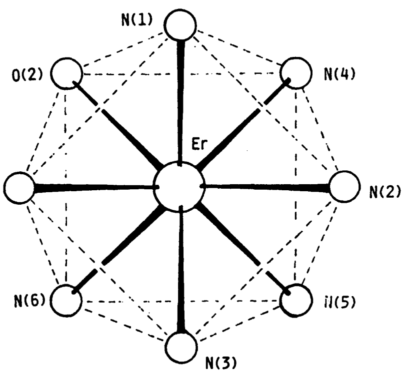

Fig. 5. Schematic presentation of the **A**-type erbium(III) complex to show the coordination geometry around the metal atom.

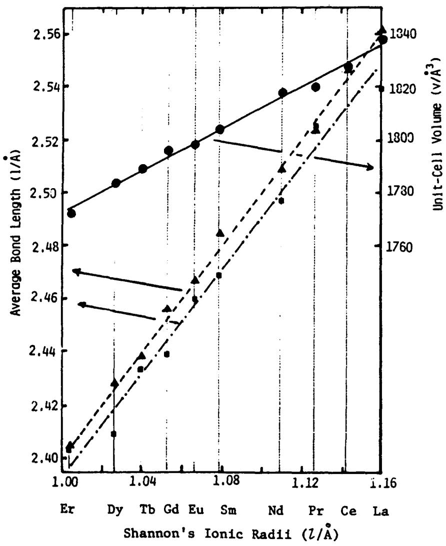

Fig. 6. The relation between the interatomic distances, M-N and M-O, as well as the unit cell volumes, and the Shannon's ionic radii of the central metal atom of the **A**-type complexes (unit cell volume (—●—); M-N bond length (---▲---); and average M-O bond length (-·-■-·-).

noids, do not exist.[6,18]

The sums of the Shannon's ionic radii are 2.35 and 2.46 Å for Er-O and Er-N (coordination number of Er is 8), respectively.[19] Therefore, the observed Er-O is longer and the observed Er-N, is shorter than the sums of the Shannon's ionic radii, respectively. In many carboxylato complexes of lanthanoids the M-O bond lengths are not much different from the sums of Shannon's ionic radii.[6,7,18] Therefore, in these complexes, the M-O bonds are a little weaker than those of the usual oxygen donor complexes. In the other aqua-isothiocyanato mixed complex, $K_4[M(SCN)_4(H_2O)_4](SCN)_3 \cdot nH_2O$ (M=Nd, Eu), the average Nd-O and Eu-O bonds are reported to be 2.60 and 2.51 Å, respectively, which are much longer than the sums of the Shannon's ionic radii, 2.46 and 2.42 Å.[2] The shortening of the Er-N bonds are also found in the other isothiocyanato complexes. For example, the sums of the Shannon's ionic radii and the observed bond lengths of $[(C_2H_5)_4N]_4[Er(SCN)_7(H_2O)]$ are 2.46 and 2.36(3) Å, respectively.[3] However, in $[(C_4H_9)_4N]_3[Er(SCN)_6]$, these values are 2.35 and 2.34(2) Å, respectively, not much different from each other.[1]

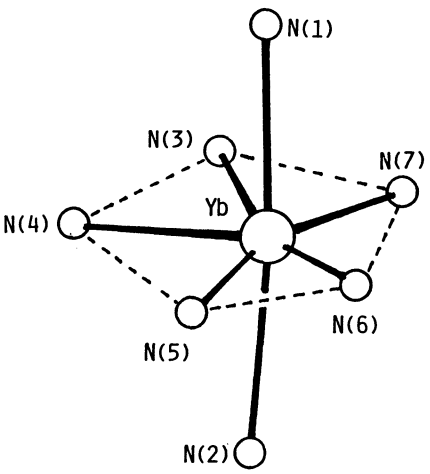

Fig. 7. Schematic presentation of the **B**-type ytterbium (III) complex to show the coordination geometry around the metal atom.

The bond angles of Er-N-C and of N-C-S are 168.7° on the average (165.9(10)—172.8(10)°), and 177.3° on the average (175.8(11)—178.8(11)), respectively. They are not very far from 180°.

The relations between the Shannon's ionic radii of the central metal atom and the unit cell volume, as well as the average M-O and M-N bond lengths of the **A**-type complexes, are shown in Fig. 6. No irregular changes were found among the series of isomorphous complexes. However, the earlier members decomposed more easily than the later member ones when left standing in open air.

The Structure of the B-Type Coiplexes. In the **B**-type ytterbium complex, the central metal atom is hepta-coordinated in a deformed pentagonal-bipyramidal geometry to seven nitrogen atoms of SCN ions, as shown schematically in Fig. 7. The deviations of the atomic positions from the mean-square plane of the six atoms, five equatorially ligated SCN nitrogen atoms and the central metal atom, are 0.344 Å on the average (0.037—0.927 Å). The plane is approximately parallel to the ac-plane. The axis angle, N(1)-Yb-N(2), is 163.9(5)°, and the axis of the complex is directed approximately parallel to the b-axis.

The tetramethylammonium ions are approximately sandwitched between pentagon planes consisting of five equatorially coordinated SCN ions of the complexes, where the central nitrogen atoms of the cations are arranged on several layers parallel to the ac-plane and between the pentagon planes. Consequently, layers of the complexes and of the cations are piled up alternately in the b-axis direction.

The M–N bond lengths of the ytterbium complex are, as shown in Table 7, 2.331 Å on the average (2.302(12)—2.364(13) Å), which is much shorter than the sum of the Shannon's ionic radii, 2.39 Å,[19] as in the case of the **A**-type complexes.

The Yb–N–C and N–C–S bond angles are, on the average, 167.2 and 176.9 °, respectively.

There are no systematic changes of the respective bond lengths and bond angles through the series of the **B**-type three complexes, except for the change of the M–N bond length due to a decrease in the metal ionic radii, depending on the metal atomic number. The three **B**-type complexes can be considered to have the same type structure. All members of the three **B**-type complexes are stable in open air for at least several weeks.

General Remark. Though the 6N-hexa-coordinated hexakis(thiocyanato) lanthanoidate(III) ion was found in its tetrabutylammonium salt,[1] deduced from the results of this and several related studies, the central metal atoms of thiocyanato complexs are not always in the hexa-coordination. Their coordination number can be seven or eight, depending on the kinds of counter cations, and of the included guest molecule, such as benzene, in the crystal,[20] or of the ligands other than the SCN ions of the complex.

Infrared Spectra. The general feature as well as the maximum wavenumbers of the infrared spectra of the **A**- and **B**-type complexes are not much different from each other, except for the strong ν(O–H) bands of the **A**-type complexes caused by including methanol and water, which appeared at about 3320—3350 $\mathrm{cm^{-1}}$. The bands due to the N-bonded SCN ion appear almost in the same region as the other metal complexes:[21] ν(CN)(s), 2060 and 2100 $\mathrm{cm^{-1}}$ for the **A**-type, and 2060 and 2070 $\mathrm{cm^{-1}}$ for the **B**-type complexes; ν(CS), 730 $\mathrm{cm^{-1}}$, and δ(SCN), 480 $\mathrm{cm^{-1}}$ for both type complexes. The bands due to the tetramethylammonium ion appear at 1488(s), 1433(m), 1163(m), 942(s), and 720(m) $\mathrm{cm^{-1}}$. These bands are approximately the same as those found in the spectra of the other tetramethylammonium salts.

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