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Syntheses, and Crystal and Molecular Structures of Tetraethylammonium [Hexakis(isothiocyanato)lanthanoidates(III)] Including Aromatic Hydrocarbon or Halohydrocarbon: $[(C_2H_5)_4N]_3[M(NCS)_6]\cdot G$ (M=Er, or Yb; G=Benzene, Fluorobenzene, Toluene, or Chlorobenzene)

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The title new complexes were synthesized and their crystal and molecular structures were determined by the single-crystal X-ray diffraction method. The crystal form of $[(C_2H_5)_4N]_3[Yb(NCS)_6]\cdot(C_6H_6)$, for example, is monoclinic, space group $P2_1/c$, a=19.458(12), b=14.046(6), c=18.288(7) Å, β=91.28(4)°, Z=4, and the final R value obtained was 0.064. The other seven crystals are isomorphous with each other. The central metal atom is in an octahedral hexa-coordination geometry: six nitrogen atoms of isothiocyanate ions are ligated to each metal atom. Each solvent molecule is arranged betweeen each pair of neighboring metal atoms along the $[1\ \bar{1}\ 0]$ axis in each crystal. The cations are arranged approximately between each pair of metal atoms along the [0 1 1], $[0\ \bar{1}\ 1]$, and [1 1 0] axes, respectively. They were stable for more than a few weeks at room temperature; however, when heated at about 80—90 °C, their guest molecules were lost.

Although lanthanoids are hard elements[1] and they prefer to be coordinated to oxygen donor ligands,[2] the nitrogen atom of a thiocyanate ion (SCN) can be ligated to the metal atom. The M-N(NCS) bond is relatively weak in aqueous solution;[3] however, it is more stable in some organic solvents used for the solvent extraction of the metals.[4]

The crystal and molecular structures of the tetrabutylammonium hexakis(isothiocyanato)lanthanoidates (III) (M=Pr—Yb) have already been elucidated: six nitrogen atoms of NCS are ligated to the central metal atom in an octahedral geometry.[5] However its coordination number (6) is rather abnormal, since the preferred coordination number of lanthanoid complexes is eight or nine, although seven, ten, and to a less extent, the other numbers are also found in the other complexes. Coordination numbers of six or lower are found only in the complexes when the ligand is too massive to take higher coordination numbers; however, the SCN ion is not large.

In cases of some aqua-isothiocyanato mixed complexes, the coordination number of the central lanthanoid atoms is eight: $K_4[M(NCS)_4(H_2O)_4](SCN)_3\cdot nH_2O$ (M=Nd, Eu),[6] $[(C_2H_5)_4N]_4[M(NCS)_7(H_2O)]$ (M=La, Ce, Pr; Nd, Dy, Er),[7] and $[(CH_3)_4N]_3[M(NCS)_6(CH_3OH)(H_2O)]$ (M=La—Er)[8] are examples. Recently, we obtained some anhydrous isothiocyanato complexes of lanthanoids in which the metal atom is hepta-coordinated, such as $[(CH_3)_4N]_4[M(SCN)_7]$ (M=Dy, Er, Yb),[8] and $[(C_2H_5)_4N]_4[M(SCN)_7]\cdot C_6H_6$ (M=La, Pr).[9] The last example is regarded as being a kind of inclusion compound, since it has one benzene molecule per one metal atom in a crystal, and no bonding has been recognized between the molecule and the cations or anions. Therefore, it seemed to be interesting to find some other such type adducts of complexes of lanthanoids. We were able to synthesize the title new complexes, and have investigated their properties by the thermoanalytical technique as well as by infrared spectra. Moreover, their crystal and molecular structures were determined by the single-crystal X-ray diffraction technique.

Experimental

Synthesis of Tetraethylammonium [Hexakis(isothiocyanato)erbate(III)]·Benzene (1), the Isomorphous Benzene Adduct of Ytterbate(III) (2), and the Isomorphous Complexes Including Fluorobenzene (3,4), Toluene (5,6), or Chlorobenzene (7,8).[§] The starting erbium(III) thiocyanate (in methanolic solution) and solid tetraethylammonium thiocyanate were obtained (as mentioned in a previous paper).[7] Into a methanolic solution (10 cm³) of erbium thiocyanate (1.0 mmol) tetraethylammonium thiocyanate (0.61 g, 3.2 mmol) was added and dissolved. To the solution, the ethanol-benzene mixture (1 : 1=v/v, 20 cm³) was added and the mixture was dried up using a rotary evaporator at about 80 °C. The dehydration process was repeated twice, and the residue was dissolved into 10 cm³ of methanol (GR grade reagent of Wako Pure Chemical Ind. Ltd.: it contains at most 0.2% of water). After a trace of insoluble matter was filtered off, the solution was left standing in the benzene-vapor moiety for several days. The precipitate was

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[§] Odd number ones are erbate, and even number ones are ytterbate.

separated, washed with a small portion of ethanol, and dried in a silica-gel desiccator overnight. Yield: 0.72 g (0.73 mmol, 73%). The isomorphous ytterbium complex (**2**) was obtained by almost the same technique.

The other six isomorphous adducts, the respective erbium (odd number ones) and ytterbium complexes (even number ones) including fluorobenzene, toluene, or chlorobenzene, were also synthesized by the same technique: keeping the starting solution in a desiccator over respective solvents.

In Table 1, are shown their elemental analyses and the numbering of the complexes. The yields of complexes **2**—**8**, starting from 1.0 mmol of the respective metal thiocyanates, are: **2**, 0.65 g, 66%; **3**, 0.83 g, 83%; **4**, 0.76 g, 75%; **5**, 0.55 g, 55%; **6**, 0.60 g, 60%; **7**, 0.50 g, 49%; and **8**, 0.45 g, 44%.

All of them are pale orange in color and are relatively stable: their crystals could be kept at room temperature for at least a few weeks without decomposition, although they lost their guests and became pulverized after a longer time. When they were kept in a stoppered bottle at about 6 °C or lower, they were stable for more than six months.

Attempts to synthesize the isomorphous complexes of dysprosium or of lighter lanthanoids, including any of the above-mentioned guests have not yet been successful.

X-Ray Structure Analysis. Crystallographic data of **1**—**8**, the size of the used crystal (approximately parallelepiped), and some experimental conditions for the X-ray structure analyses of **1**—**6** are listed in Table 2.

Reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer, with graphite monochromated Mo*Kα* radiation (λ=0.71073 Å), an ω-2θ scan technique being employed (scan speed 4° min^{-1}). The used crystals were coated with a cyanoacrylate resin to

Table 1. Elemental Analyses (Calculated Values in Parentheses) (n/%) and the Numbering of the Complexes, $[(\mathrm{C_2H_5})_4\mathrm{N}]_3[\mathrm{M(NCS)_6}]\cdot\mathrm{G}$

No.	G	M	Formula	M	C	H	N
1	$\mathrm{C_6H_6}$	Er	$\mathrm{ErC_{36}H_{66}N_9S_6}$	16.89	43.61	6.71	12.70
				(16.99)	(43.92)	(6.76)	(12.80)
2	$\mathrm{C_6H_6}$	Yb	$\mathrm{YbC_{36}H_{66}N_9S_6}$	17.59	43.26	6.59	12.61
				(17.47)	(43.66)	(6.72)	(12.73)
3	$\mathrm{C_6H_5F}$	Er	$\mathrm{ErC_{36}H_{65}N_9S_6F}$	16.81	42.76	6.53	12.73
				(16.68)	(43.13)	(6.54)	(12.57)
4	$\mathrm{C_6H_5F}$	Yb	$\mathrm{YbC_{36}H_{65}N_9S_6F}$	17.12	42.55	6.43	12.43
				(17.16)	(42.88)	(6.50)	(12.50)
5	$\mathrm{C_7H_8}$	Er	$\mathrm{ErC_{37}H_{68}N_9S_6}$	16.65	44.24	6.79	12.88
				(16.75)	(44.50)	(6.86)	(12.62)
6	$\mathrm{C_7H_8}$	Yb	$\mathrm{YbC_{37}H_{68}N_9S_6}$	17.10	43.93	6.72	12.56
				(17.23)	(44.25)	(6.82)	(12.55)
7	$\mathrm{C_6H_5Cl}$	Er	$\mathrm{ErC_{36}H_{65}N_9S_6Cl}$	16.48	42.08	6.44	12.56
				(16.41)	(42.43)	(6.43)	(12.37)
8	$\mathrm{C_6H_5Cl}$	Yb	$\mathrm{YbC_{36}H_{65}N_9S_6Cl}$	16.81	42.16	6.42	12.39
				(16.88)	(42.19)	(6.39)	(12.30)

Table 2. Crystallographic Data and Various Experimental Conditions for the Complexes, $[(\mathrm{C_2H_5})_4\mathrm{N}]_3[\mathrm{M(NCS)_6}]\cdot\mathrm{G}$, Space Group, $P2_1/c$, Z=4

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**[13]	**8**[13]
M=	Er	Yb	Er	Yb	Er	Yb	Er	Yb
G=	$\mathrm{C_6H_6}$	$\mathrm{C_6H_6}$	$\mathrm{C_6H_5F}$	$\mathrm{C_6H_5F}$	$\mathrm{C_7H_8}$	$\mathrm{C_7H_8}$	$\mathrm{C_6H_5Cl}$	$\mathrm{C_6H_5Cl}$
F. W.	984.64	990.42	1002.60	1008.38	998.63	1004.41	1019.05	1024.83
$a(l/\text{Å})$	19.516(5)	19.458(12)	19.489(17)	19.466(10)	19.769(9)	19.763(8)	19.662(19)	19.644(14)
$b(l/\text{Å})$	14.091(4)	14.046(6)	14.030(15)	14.036(14)	14.111(4)	14.115(7)	14.067(14)	14.064(6)
$c(l/\text{Å})$	18.647(6)	18.288(7)	18.471(19)	18.42(3)	18.398(6)	18.360(9)	18.555(14)	18.548(8)
$\beta(\phi/°)$	91.20(2)	91.28(4)	90.86(8)	90.95(8)	92.04(3)	92.22(4)	91.70(7)	91.85(5)
$U(v/\text{Å}^3)$	5046(2)	4998(4)	5050(9)	5032(9)	5129(3)	5118(4)	5130(7)	5121(5)
$D_\mathrm{m}(d/\mathrm{g\,cm^{-3}})$	1.30(3)	1.31(3)	1.32(3)	1.32(3)	1.29(3)	1.29(3)	1.31(3)	1.34(3)
$D_\mathrm{x}(d/\mathrm{g\,cm^{-3}})$	1.30	1.32	1.32	1.33	1.29	1.30	1.32	1.33
$\mu(\mathrm{Mo}\,K\alpha)$ $(n/\mathrm{cm^{-1}})$	20.00	22.43	20.03	22.33	19.69	21.92	20.20	22.42
N_m[a]	9266	6889	6957	6939	9484	7079		
N_c[b]	3066	2814	2510	2311	2314	2353		
R[c]	0.068	0.064	0.074	0.069	0.091	0.079		
V_c[d]$(v/\mathrm{mm^3})$	0.33×0.32 ×0.20	0.35×0.33 ×0.30	0.30×0.25 ×0.20	0.32×30 ×0.30	0.31×0.31 ×0.31	0.32×0.31 ×0.31		
S_w[e]$(\omega/°)$	1.16+ 0.5 tanθ	1.07+ 0.5 tanθ	1.08+ 0.35 tanθ	1.15+ 0.35 tanθ	1.27+ 0.5 tanθ	1.21+ 0.5 tanθ		
S_R[f]$(2\theta/°)$	3—50	3—45	3—45	3—45	3—50	3—45		

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 used (approximately in parallelepiped in shape). e) Scan width (ω). f) Scanned range (2θ).

prevent the escape of the guest; however, it was not necessary to seal the crystal in a glass capillary. During the intensity collection (about 5—7 days) a decrease in the standard reflection intensities was not recognized in the cases of complexs **1**—**4**, and less than 8% in the cases of the complexes **5** and **6**. The intensities were corrected for Lorentz and polarization factors, though no corrections were made for absorption.

Structure Determination. The structure of **2** was solved by the heavy-atom method. The positions of the metal and some sulfur atoms were deduced from the three-dimensional Patterson map, and the other atoms were located by successive Fourier syntheses. Their positional and thermal parameters were refined by a block-diagonal least-squares method. No hydrogen atom was included in the structure factor calculations.

It was found that several atoms have relatively large temperature factors, although this phenomenon had already been found for atoms loosely packed in the crystal in some other lanthanoid complexes.[10] Although the intensity measurement process was repeated for **2** using another crystal, the result was not improved: the temperature factors of some atoms were still very large. The occupancy factors of the atoms of the guest molecule were examined by a full-matrix least squares method; they converged to approximately 1.0.

After repeated refinement steps, some parameters were still moving over 3 times of their respective standard deviations, though their values almost converged. Therefore, at the final refinement steps, such parameters were fixed in the structure calculations.[13]

The structure of **1** was determined starting from the final parameters of **2**, and refined in a similar way.

The structures of **3** and **5** were obtained starting from the final parameters of **2**, and refined in a similar way. The positions of the fluorine atom of **3** and the methyl carbon atom of **5** were obtained from their difference synthesis maps. The structures of **4** and **6** were obtained starting from the final parameters of **3** and **5**, respectively, and their parameters were refined in the same way.

In **3** and **4**, from their difference synthesis map, the position of the fluorine atom was divided into two, F(1A) and F(1B), which were bonded to C(63) and C(66), respectively, with an equal occupancy factor.

In **5**, or **6**, from their difference synthesis maps, the position of the methyl carbon atom of toluene molecule was found to be not disordered, which is bonded to C(66).

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

Other Measurements. Their infrared absorption spectra

Table 3. Final Atomic Coordinates ($\times 10^4$) and Isotropic or Equivalent Isotropic Temperature Factors ($B_{eq}/\text{Å}^2$) of Tetraethylammonium [Hexakis(isothiocyanato)ytterbate(III)]·Benzene with Estimated Standard Deviations in Parentheses

Atom[c)]	x	y	z	$B_{eq}/\text{Å}^{2\,a)}$	Atom[c)]	x	y	z	$B_{eq}/\text{Å}^{2\,a)}$
Yb(1)	0.0	0.0	0.0	8.0	C(35)	2571(12)	891(15)	−231(13)	10.3
Yb(2)	5000.0	5000.0	0.0	5.0	C(36)	3144(13)	272(13)	−559(14)	10.7
S(11)	1839(4)	873(7)	1807(4)	13.3	C(37)	2898(12)	2265(17)	−1135(11)	10.4
S(12)	−1695(4)	554(6)	1967(4)	11.7	C(38)	2251(12)	2138(16)	−1575(11)	10.4
S(13)	386(5)	3336(7)	−639(7)	19.3	C(41)	5384(10)	3874(13)	2782(10)	7.2
S(21)	6918(3)	5316(4)	1848(3)	8.0	C(42)	4949(13)	4183(18)	3413(12)	10.9
S(22)	3390(4)	4297(5)	2032(3)	10.5	C(43)	6225(11)	2976(16)	3593(10)	9.1
S(23)	5380(4)	1516(4)	432(3)	8.9	C(44)	6773(12)	3743(19)	3520(12)	11.7
N(11)	845(9)	259(14)	813(8)	9.9	C(45)	6170(10)	2755(14)	2200(9)	7.4
N(12)	−764(9)	306(14)	872(9)	10.3	C(46)	6584(13)	1864(18)	2234(12)	11.8
N(13)	68(10)	1572(15)	−316(11)	12.4	C(47)	5273(12)	2117(14)	3115(11)	8.8
N(21)	5893(7)	5294(10)	813(8)	7.2	C(48)	4723(12)	1979(16)	2483(13)	10.9
N(22)	4253(8)	4798(9)	956(8)	6.7	C(61)	7254(14)	3749(19)	−246(15)	13.4
N(23)	5199(7)	3399(10)	85(8)	6.7	C(62)	7708(12)	3794(17)	−780(14)	11.4
N(31)	2790(7)	1971(11)	−288(8)	7.2	C(63)	8263(14)	3085(22)	−767(14)	14.2
N(41)	5777(7)	2925(10)	2909(7)	6.4	C(64)	8257(11)	2419(17)	−232(15)	11.5
N(51)	−340(10)	3604(13)	1857(9)	10.8	C(65)	7741(13)	2322(17)	286(14)	12.1
C(11)	1259(10)	551(16)	1240(11)	8.4	C(66)	7221(13)	3019(18)	205(13)	11.4
C(12)	−1143(11)	398(15)	1345(11)	8.3	C(51)[b)]	−110(13)	2502(17)	1821(13)	11.3
C(13)	174(11)	2234(15)	−472(13)	9.3	C(52)[b)]	422(13)	2688(17)	2565(13)	11.3
C(21)	6305(9)	5268(11)	1240(9)	5.6	C(53)[b)]	140(13)	4298(18)	2012(13)	11.3
C(22)	3897(10)	4571(13)	1417(10)	6.6	C(54)[b)]	684(13)	4106(18)	1298(13)	11.3
C(23)	5285(9)	2610(13)	245(9)	5.7	C(55)[b)]	−672(13)	3801(18)	2603(13)	11.3
C(31)	3492(11)	2175(17)	83(13)	10.8	C(56)[b)]	−1395(13)	3294(17)	2502(13)	11.3
C(32)	3468(11)	1885(16)	913(11)	9.5	C(57)[b)]	−685(12)	3556(18)	1181(13)	11.3
C(33)	2182(11)	2501(16)	43(13)	10.2	C(58)[b)]	−1191(13)	4459(19)	1129(13)	11.3
C(34)	2330(12)	3616(15)	42(13)	10.6					

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: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$. b) Their B_{iso} was all fixed at the value, 11.3 Å^2. c) The numbering of the tetraethylammonium atoms are as follows: the ethyl carbon atoms, C(n1), C(n3), C(n5), and C(n7), which are bonded to the carbon atoms C(n2), C(n4), C(n6), and C(n8) respectively, are located around the central nitrogen atom N(n1) tetrahedrally (n=3—5). The benzene carbon atoms are numbered from C(61) to C(66) succesively.

Table 4. Selected Bond Lengths (l/Å) and Bond Angles (ϕ/°) of the Adducts of Tetraethylammonium Hexakis(isothiocyanato)erbate(III) and -ytterbate(III), (**1**—**6**), $[(C_2H_5)_4N]_3[M(NCS)_6]\cdot G$ (M=Er, Yb; G=Benzene, Fluorobenzene, or Toluene), with the Standard Deviations in Parentheses

No.[a)]	**1**	**2**	**3**	**4**	**5**	**6**
M=	Er	Yb	Er	Yb	Er	Yb
G=	C_6H_6	C_6H_6	C_6H_5F	C_6H_5F	C_7H_8	C_7H_8
M(1)-N(11)	2.27(2)	2.22(2)	2.27(3)	2.23(3)	2.27(4)	2.25(3)
M(1)-N(12)	2.29(2)	2.25(3)	2.31(3)	2.28(3)	2.26(4)	2.32(3)
M(1)-N(13)	2.32(2)	2.29(2)	2.22(4)	2.19(3)	2.34(3)	2.32(3)
M(2)-N(21)	2.31(2)	2.30(2)	2.33(3)	2.37(3)	2.28(3)	2.23(3)
M(2)-N(22)	2.33(2)	2.32(2)	2.32(3)	2.25(3)	2.35(4)	2.24(3)
M(2)-N(23)	2.32(1)	2.29(1)	2.29(2)	2.28(2)	2.35(2)	2.28(2)
M-N (av.)[b)]	2.31	2.28	2.29	2.27	2.31	2.27
N(*n*)-C(*n*) (av.)[b)]	1.09	1.13	1.12	1.12	1.11	1.11
	(0.91—1.15)	(1.00—1.16)	(1.06—1.18)	(1.03—1.21)	(1.02—1.22)	(1.03—1.23)
C(*n*)-S(*n*) (av.)[b)]	1.61	1.60	1.62	1.61	1.59	1.60
	(1.57—1.65)	(1.56—1.64)	(1.54—1.70)	(1.54—1.69)	(1.49—1.67)	(1.48—1.69)
N(11)-M(1)-N(12)	88.1(8)	89.1(9)	88.0(11)	89.8(11)	89.1(13)	90.8(11)
N(11)-M(1)-N(13)	88.6(8)	88.0(8)	87.2(13)	85.6(12)	85.6(12)	86.2(11)
N(12)-M(1)-N(13)	92.0(9)	92.1(8)	92.0(13)	90.8(12)	91.3(12)	91.7(10)
N(21)-M(2)-N(22)	90.4(7)	90.7(7)	92.1(10)	90.8(10)	89.2(12)	88.9(12)
N(21)-M(2)-N(23)	90.0(6)	90.5(6)	90.1(8)	90.5(8)	89.5(10)	89.2(10)
N(22)-M(2)-N(23)	86.3(6)	86.4(6)	85.1(8)	85.0(9)	86.4(11)	87.0(10)
M(1, 2)-N(*n*)-C(*n*) (av.)[b)]	170	170	170	170	168	169
	(167—176)	(167—175)	(165—174)	(166—178)	(164—172)	(166—174)
N(*n*)-C(*n*)-S(*n*) (av.)[b)]	177	176	175	175	173	176
	(175—178)	(174—178)	(172—177)	(171—179)	(171—176)	(168—179)

a) Numbers of the complexes (see Table 1). b) Average of the six values of the all SCN ions.

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

Results and Discussion

The final atomic coordinates and isotropic or equivalent isotropic temperature factors (B_{eq}/Å^2) of **2** are tabulated in Table 3; some selected bond lengths and bond angles of **1**—**6** are listed in Table 4. Perspective drawings of complex **2** around atoms Yb(1) and Yb(2) are shown in Figs. 1 and 2, and a projection of its unit cell along the b-axis in Fig. 3.[13)]

In **2**, both of the crystallographically independent metal atoms, Yb(1) and Yb(2), are at the centers of symmetry, and are hexa-coordinated in an octahedral geometry: six nitrogen atoms of SCN ions are in coordination. The average M-N bond length is 2.28 Å (2.22—2.32 Å), which is a little shorter than the sum of the Shannon's crystal radii, 2.33Å.[14)] The average bond angles, Yb-N-C and N-C-S, are 170 (167—175) and 176 (174—178)°, respectively.

Among the six coordinated SCN ions, four ions are situated approximately on a plane parallel to the ac-plane and are arranged approximately to [1 0 1] and [$\bar{1}$ 0 1]; the other two SCN ions are arranged approximately along the b-axis.

The tetraethylammonium ions around the N(41) and N(51) atoms are arranged approximately between each pair of neighboring metal atoms along [0 1 1] and [0 $\bar{1}$ 1]: the N(41) atoms are between the Yb(2)

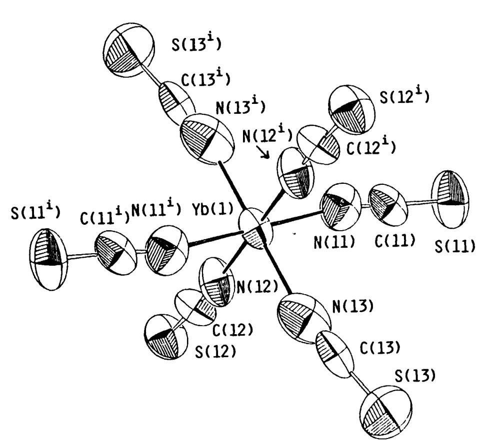

Fig. 1. Perspective drawing of tetraethylammonium [hexakis(isothiocyanato)ytterbate(III)]·benzene (**2**) around Yb(1) atom together with the numbering scheme of the atoms. Key to the symmetry operation: i, $-x$, $-y$, $-z$.

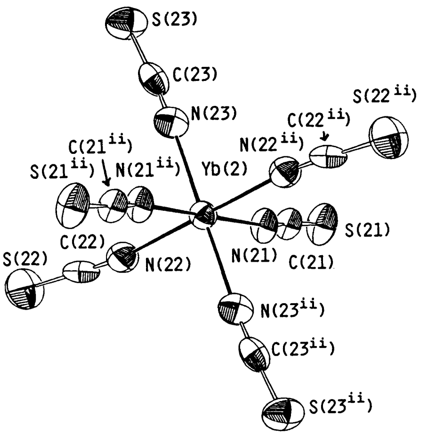

Fig. 2. Perspective drawing of tetraethylammonium [(hexakis(isothiocyanato)ytterbate(III)]·benzene (**2**) around Yb(2) atom together with the numbering scheme of the atoms. Key to the symmetry operation: i, 1−*x*, 1−*y*, −*z*.

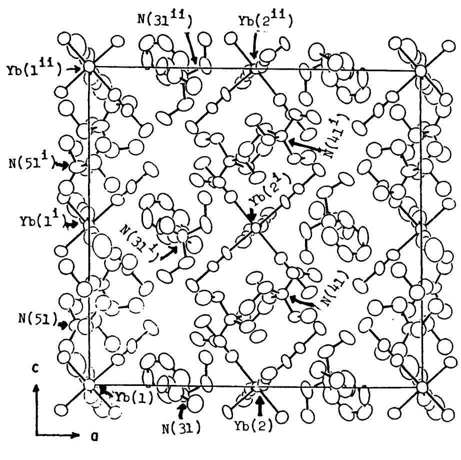

Fig. 3. Projection of the unit cell of tetraethylammonium [hexakis(isothiocyanato)ytterbate(III)]·benzene (**2**) along b-axis. The numbering scheme of some metal and ammonium nitrogen atoms are also shown. Key to the symmetry operations: i, *x*, 0.5−*y*, 0.5+*z*; ii, *x*, *y*, 1+*z*.

atoms, while the N(51) atoms are between the Yb(1) atoms. Another tetraethylammonium ion around the N(31) atom and the benzene molecule are arranged between each pair of Yb(1) and Yb(2) atoms along [1 1 0] and [$\bar{1}$ 1 0], respectively.

The structure of the isomorphous erbium complex (**1**) has essentially the same structure as **2**, although the average Er-N bond length is 2.31 Å (2.27(2)—2.33(2) Å) which is longer than the corresponding length of **2**, due to the longer metal crystal radii (the sum of the Shannon's crystal radii of Er-N is 2.35 Å). The reported Er-N(SCN) bond length of $[Er(SCN)_6]^{3-}$ ion in its tetrabutylammonium salt is 2.34(2) Å, which is a little longer than that of **1**.[5] Other than the metal ionic size and, consequently, the M-N bond lengths and the unit-cell volume, the structures of **1** and **2** are approximately the same.

We can compare with each other the relative volumes (where the organic molecules are included) from their unit-cell volumes of the same metal complexes, ytterbium ones: the unit-cell volumes of **2**, **4**, **6**, and **8** are 4998(4), 5032(9), 5118(4), and 5121(5) Å^3, respectively. Therefore, the space for the guest is expanded a little, depending on the increase in the volume of the guest molecule.

Although the unit cell of each erbium complex is a little larger than that of the corresponding ytterbium complex, almost no difference could be recognized between the thermal properties of the corresponding adducts of both metals (as shown in the later part of this paper). However, the same type inclusion compounds of dysprosium or smaller atomic number lanthanoids were not obtained. The formation of this kind of adduct is likely only for a limited range of sizes of the complex: the distance between the cations and anions should be kept to an appropriate value.

Qualitatively, we guess that, in cases of the isothiocyanato complexes of lanthanoids, when the organic groups of the cations are sufficiently large to supply enough non-polar moiety in the crystal, the coordinated SCN ions, which also contain a non-polar part (sulfur and carbon atoms), are capable of moving around their regular positions. As a result, the SCN ions are sufficiently bulky to be in hexa-coordination to lanthanoid metals. The structure of $[(C_4H_9)_4N]_3[M(NCS)_6]$ can be explained in terms this hypothesis. In cases of the present complexes, although the ethyl group of the cation is not sufficiently large, the central metal atom is relatively small (Er or Yb); moreover, some non-polar hydrocarbon or halohydrocarbon molecules are included. As a result, the SCN ions assume an octahedral geometry.

In infrared absorption spectra of the complexes **1**—**8**, the bands due to the N-bonded SCN ion appear in the same region as the other metal complexes:[15] ν(CN), 2050(s); ν(CS), 730(shoulder, partly overlapped with the peak of the cation); δ(SCN), 480 cm^{-1}. The bands due to the tetraethylammonium ion are commonly found in the specta of **1**—**8**, at about 1490(s), 1440(s), 1395(s), 1364(m), 1170(s), 1052(m), 997(s), 780(s), and 720(m) cm^{-1}. The peak of the mode of the out-of-plane deformation of the benzene ring is characteristic to complexes **1**—**8**, and is useful for identifying whether the complex really includes a guest or not. The peaks of **1** and **2** appear at 687 cm^{-1}, which is a liitle blue shifted from that of the free benzene (673 cm^{-1}). Such a shift in the peak of a guest molecules around 680—690 cm^{-1} was not observed in the spectra of **3**—**8**. The peaks of the guests in the infrared spectra are as follows: **3** and **4**, 683, 750, 805, 899, 1220, 1500, and 1598 cm^{-1}; **5** and **6**, 460, 693, 722, 1030, and 1080 cm^{-1}; and **7** and **8**, 682, 701, 1022, 1085, 1450, 1481, and 1584 cm^{-1} peaks, respectively. None of them shift much from the peak wavenumbers of the respective free guests.

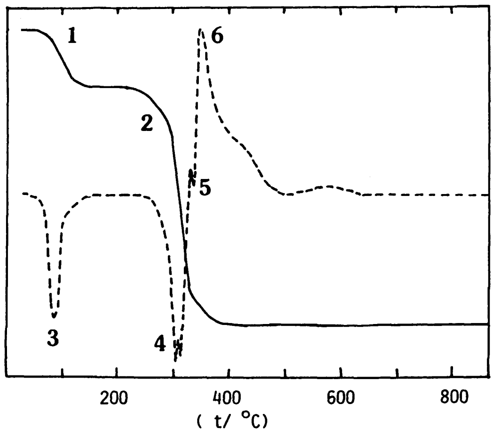

Fig. 4. TG(——) and DTA(----) curves of tetraethylammonium [hexakis(isothiocyanato)ytterbate(III)]·benzene (**2**). Mass loss of TG was taken downward and the exothermic change of DTA was taken upward. The temperature corresponding with the points numbered from **1** to **6** of the runs with the complexes **1**, **2**, **4**, **6**, and **8** are shown in Table 5.

Table 5. Thermal Analytical Data of the Complexes

Complex	**1**[b]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	**6**[b]	*R*[c]
1[a]	81	297	93	303, 312	333	351	22
2[a]	88	285	99	304, 315	330	353	22
4[a]	82	288	94	305		330	24
6[a]	81	288	91	311	335	351	20
8[a]	83	285	95	302		343	23

a) Complexes shown in Table 1. b) The points shown in Fig. 4 (the temperatures in the table are shown in the unit of (t/°C)). c) The weight of residue after heating the samples up to 1000 °C (shown in weight %).

The simultaneous TG-DTA curves of complex **2** is shown in Fig. 4. The general feature of the curves of the other complexes are almost the same. The corresponding temperatures at points **1**—**6** shown in Fig. 4 (of the complexes **1**, **2**, **4**, **6**, and **8**) are listed in Table 5.

From these results, it was shown that when the temperature was increased, all kinds of guest molecules in them were removed at about 80—90 °C: no serious difference was found between their degradation temperatures. The change was found to be endothermic from their DTA curves, and the mass loss of this step of each complex approximately coincided with the molecular weight of each guest.

Between the first and second mass-loss steps, the vacant cage structure, $[(C_2H_5)_4N]_3[M(NCS)_6]$ (M=Er, Yb), was thought to be stable. In the respective infrared spectra of the residues after heating complexes **1**—**8**, about 2—5 h at 110 °C, the peaks of the guests completely disappeared, while the peaks of the SCN^- and $[(C_2H_5)_4N]^+$ ions were retained almost in the same wavenumber region. Each mass loss by this heating process also corresponded approximately with the weight of the included guest calculated from its formula.

At about 280—290 °C the complexes decomposed by one-step degradation, as shown by the TG curve; however, it consists of several complicated endo- and exothermic steps, judging from their DTA curves.

After the second step of decomposition, no specific changes were observed on the TG and DTA curves, and the residues after being heated to 1000 °C were mainly the respective metal oxides.

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