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The Synthesis, and the Crystal and Molecular Structures of Tetraethylammonium [Aquaheptakis(thiocyanato)lanthanoidate(III)], $[(C_2H_5)_4N]_4[M(SCN)_7(H_2O)]$, (M=La, Ce, Pr; Nd, Dy, Er): The Complexes in a Cubic Octa-Coordination Geometry

Yoshikuni TATEYAMA,† Yasumitsu KUNIYASU,† Yasuo SUZUKI,† and Akira OUCHI*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Higashi-mita, Tama-ku, Kawasaki, Kanagawa 214
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The title complexes have been synthesized, and their crystal and molecular structures were determined by the X-ray diffraction method using their single crystals. Among them, the crystals of the La, Ce, and Pr complexes are isomorphous; cubic, space group $Pm\bar{3}$, $Z=1$, and the cell constants of the Pr complex, for example, are $a=11.513(2)$ Å, $U=1526.1(5)$ Å^3, and the final R value was 0.093. The Nd, Dy, and Er complexes, another group of the isomorphous complexes obtained almost by the same synthetic method, are tetragonal, space group $I4/m$, $Z=2$, and the cell constants of the Er complex, for example, are $a=11.564(2)$, $c=22.627(4)$ Å, $U=3026(3)$ Å^3, and the final R value was 0.071. The coordination geometry around the metal atoms of both types of complexes are almost the same: seven thiocyanato nitrogen and one water oxygen atoms are coordinated in a cubic geometry, being disordered as if each ligating atomic position is equally occupied by 1/8 atom of the water oxygen and 7/8 atoms of the thiocyanato nitrogen. In the lattice of the former three complexes, the tetraethylammonium nitrogen atoms occupy all Cl^- ionic positions of the NaCl-type lattice, while the metal atoms only the apex Na^+ ionic positions; not the face-center ones. The unit cells of the latter three complexes are apparently consist of the two former cubic type cells being piled on the c-axis direction, where the arrangement of the atoms is different from the former only on the plane where two original cells are contact: metal and ammonium nitrogen positions slide 0.5 both to a- and b-axis directions. Thus each metal atom of the both type complexes is surrounded by six tetraethylammonium nitrogen atoms on both sides of the a, b, and c-axis directions.

Lanthanoids(III) are known to be very hard elements,[1] and oxygen-coordinating ligands are most easily bonded to them. However, it is known that some nitrogen-containing ligands are also capable of being ligated to the metal atoms, forming stable complexes, when they are synthesized in anhydrous medium:[2] the structures of lanthanoid complexes with some such ligands were already reported.[3-5]

A thiocyanate ion (SCN) shows a variety of very interesting behaviors in its metal complexes: depending on the hardness of the metal, it is coordinated with its nitrogen or sulfur atom. In other cases it forms anionic complexes of the type $(M^{m+}(SCN)_n]^{(n-m)-}$ or the polymeric complexes connected by the [M-SCN-M']-type bridgings.[6] In some anionic thiocyanato complexes, the structure changes sensitively depending on the kinds of counter cations. For example, in the case of the tris(thiocyanato)cadmates, its rubidium, cesium, and tetramethylammonium salts have the respective types of network strucrtures.[7,8]

Only a few structural data of the thiocyanato complexes of lanthanoids(III) have been reported so far. The structures of the tetrabutylammonium salts of hexakis(thiocyanato)lanthanoidates(III), where the metals are praseodymium through ytterbium or yttrium, were reported: their metal atoms are ligated with six SCN nitrogen atoms being in an octahedral geometry.[9] It is very interesting that the coordination number of the metal atom is of such low value, even though the SCN ion is not a massive ligand. On the other hand, Lazarev has reported the structures of some aqua-thiocyanato mixed complexes of neodymium and europium, where four water oxygen as well as four SCN nitrogen atoms are ligated in a square-antiprism geometry.[10] In cases of the SCN complexes of uranium(IV), $[(C_2H_5)_4N]_4[U(SCN)_8]$, the central metal atom is in a cubic geometry, while in its cesium salt, the metal atom is in a square-antiprism geometry.[11,12] Referring to these data, it was thought to be interesting to study in more detail the structures of the thiocyanato complexes of lanthanoids.

Since we could obtain the crystals of the title complexes, their crystal and molecular structures were determined by the X-ray diffraction method, using their single crystals.

Experimental

Synthesis of Tetraethylammonium [Aquaheptakis(thiocyanato)praseodymate(III)]. The metal and tetraethylammonium thiocyanates were obtained by metathesis reactions between their hydrated chlorides and potassium thiocyanate in methanolic medium, as in the cases of the other metal thiocyanates.[13] As the starting metal thiocyanate, the obtained methanolic solution was used directly without drying up.

To the methanolic solution of the praseodymium thiocyanate (15 cm^3, containing 2.0 mmol of Pr), tetraethylammonium thiocyanate (1.5 g, 8.0 mmol), and 0.5 cm^3 of water were added. The mixed solution was left standing in a silica gel desiccator until the volume of the solution reduced to about 8 cm^3, and the deposited crystals were separated, washed with a little portion of methanol, and dried in air. Yield: 1.3 g (1.2 mmol, 60%). Almost by the same way, the isomorphous lanthanum and cerium salts were obtained: starting from 2.0 mmol of the lanthanum(III) or cerium(III)

thiocyanate in methanolic solution, 0.5 cm^3 of water, and tetraethylammonium thiocyanate (1.5 g, 8.0 mmol), the yield of their complexes were 1.5 g (1.4 mmol, 69%), and 1.4 g (1.3 mmol, 65%), respectively.

Their elemental analyses are shown in Table 1.

Although these complex crystals were not deposited from the severely dried medium, several tenths of a gram of water per one mmol of metal salt is sufficient to synthesize the products: the included water was hardly removed, even when they were left standing in a silica gel desiccator for several days; however, they became dehydrated after a longer time. On the other hand, the use of the solvent containing more water (the authors have tried up to 2 : 1=v/v in concentration of the methanol-water mixture) gave the same product; however, as the complexes were readily soluble in such a solvent, we had to evaporate the solvent more, and the yield as well as the purity were inferior.

Attempts to synthesize such complexes of the heavier lanthanoids were not successful: in such cases, the complexes written in the following section were always obtained.

The Synthesis of Tetraethylammonium [Aquaheptakis-(thiocyanato)erbate(III)]. The starting materials, metal and tetraethylammonium thiocyanates, were obtained in the same way. To a methanolic solution of erbium(III) thiocyanate (15 cm^3, including 2.0 mmol of Er), tetraethylammonium thiocyanate (1.5 g, 8.0 mmol), and 0.5 cm^3 of water were added and dissolved. The solution was kept in a silica-gel desiccator until about 80% of the solvent was evaporated off. The deposited crystals were separated, washed with a small portion of methanol, and dried in air. Yield: 1.2 g (1.1 mmol, 54%). The neodymium and the dysprosium salts were obtained almost in the same way: started from 2.0 mmol of neodymium or dysprosium thiocyanate in methanolic solution, the yields of the complexes were 1.6 g (1.5 mmol, 74%), and 1.4 g (1.3 mmol, 63%), respectively.

Their elemental analyses are shown in Table 1.

In these cases, too, when more water was added into the solution, the yields of the products were lowered. By this synthetic process, neither lanthanum through prasedymium complexes of this type were obtained.

X-Ray Structure Analysis. The crystallographic data, the sizes of the used crystals (approximately parallelepiped in shape, and the colors are; the Pr salt, pale green, the Nd salt, pale violet; the Er salt, pale pink; the others, colorless), and various experimental conditions are listed in Tables 2A and 2B. Reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ=0.71073 Å), ω-2θ scan technique being employed (scan speed was 4° min^{-1} (θ)). The intensities were corrected for Lorentz and polarization factors, but no correction was made for the absorption and extinction.

Table 1. Elemental Analyses of the Complexes $[(C_2H_5)_4N]_4[M(SCN)_7(H_2O)]$, $MC_{39}H_{82}N_{11}OS_7$ (M=La, Ce, Pr, Nd, Dy, and Er) (*n*/%)

M		M	C	H	N
La	Found	13.06	43.15	7.42	14.24
	Calcd	12.81	43.19	7.62	14.21
Ce	Found	12.66	42.69	7.36	13.89
	Calcd	12.91	43.14	7.61	14.19
Pr	Found	13.17	42.70	7.34	13.98
	Calcd	12.97	43.11	7.61	14.18
Nd	Found	13.11	42.87	7.37	14.19
	Calcd	13.23	42.98	7.58	14.14
Dy	Found	14.70	41.92	7.21	13.83
	Calcd	14.66	42.27	7.46	13.90
Er	Found	15.09	42.10	7.28	13.90
	Calcd	15.03	42.09	7.43	13.84

Table 2. Crystallographic Data and Various Experimental Conditions to Obtain the Reflection Intensities

A. Light Lanthanoid Complexes $[(C_2H_5)_4]_4[M(SCN)_7(H_2O)]$, $MC_{39}H_{82}N_{11}OS_7$, (M=La, Ce, Pr), Cubic, $Pm\bar{3}$, Z=1

M=	La	Ce	Pr
F. W.	1084.5	1085.7	1086.5
a(*l*/Å)	11.540(4)	11.530(4)	11.513(2)
U(*v*/Å^3)	1536.7(9)	1532.8(10)	1526.1(5)
D_m(*d*/g cm^{-3})	1.16(3)	1.19(3)	1.19(3)
D_x(*d*/g cm^{-3})	1.17	1.18	1.18
μ(Mo$K\alpha$)(*n*/cm^{-1})	9.74	10.15	10.65
N_m[a]	2266	3143	3137
N_c[b]	449	683	589
R[c]	0.124	0.099	0.093
V_c[d](*v*/mm^3)	0.30×0.30 ×0.15	0.20×0.35 ×0.12	0.30×0.20 ×0.25
S_W[e](θ/°)	1.30+0.5tanθ	1.10+0.5tanθ	1.30+0.5tanθ
S_R[f](2θ/°)	3—60	3—65	3—65

B. Heavy Lanthanoid Complexes $[(C_2H_5)_4]_4[M(SCN)_7(H_2O)]$, $MC_{39}H_{82}N_{11}OS_7$, (M=Nd, Dy, Er), Tetragonal, $I4/m$, Z=2

M=	Nd	Dy	Er
F. W.	1089.9	1108.1	1112.9
a(*l*/Å)	11.569(2)	11.556(2)	11.564(2)
c(*l*/Å)	22.755(4)	22.605(4)	22.627(4)
U(*v*/Å^3)	3046(2)	3018.7(11)	3026(3)
D_m(*d*/g cm^{-3})	1.19(3)	1.21(3)	1.21(3)
D_x(*d*/g cm^{-3})	1.19	1.22	1.23
μ(Mo$K\alpha$)(*n*/cm^{-1})	11.23	15.55	17.16
N_m[a]	3094	2207	3056
N_c[b]	839	783	793
R[c]	0.0771	0.0807	0.0707
V_c[d](*v*/mm^{-3})	0.30×0.30 ×0.25	0.40×0.20 ×0.20	0.35×0.22 ×0.22
S_W[e](θ/°)	1.12+0.5tanθ	1.30+0.5tanθ	1.21+0.5tanθ
S_R[f](2θ/°)	3—65	3—60	3—65

a) Number of reflections measured (all positive *hkl* region was surveyed). b) Reflections used for the calculation (reflections of $|F_o|>3\sigma(|F_o|)$ were used). c) $R=\sum||F_o|-|F_o||/\sum|F_o|$. d) Size of crystals used. e) Scan width. f) Scanned range.

Structure Determination. The crystal system of the La, Ce, and Pr complexes, which are isomorphous with each other, was ascertained by the facts that the respective Weisenberg photographs rotated around three unit-cell axes are the same, and that the measured intensities of the corresponding reflections are almost the same. The space group of the Nd, Dy, and Er complexes, which are isomorphous with each other, was ascertained by the regular extinction of the reflections, and the comparison of the measured intensities of the corresponding reflections of both the Weisenberg pho-

tographs rotated around the unit cell axes, as well as of the intensity data obtained by a diffractometer.

The structures of the praseodymium and the erbium salts were solved by the heavy-atom method, respectively. The positions of the metal and sulfur atoms were deduced from their three-dimensional Patterson map; other non-hydrogen atoms were located by successive Fourier syntheses. Their positional, isotropic and, then, anisotropic thermal parameters were refined by a block-diagonal least-squares method. All hydrogen atoms were excluded from the structure factor calculations. The structure analyses of the other isomorphous salts were started from their final positional and final isotropic thermal parameters of the praseodymium or the erbium complex; they were refined in the same way.

All calculations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo, using a local version of the UNICS progrm.[14] The atomic scattering factors were taken from Ref. 15.

In the case of the praseodymium complex, according to the request of the symmetry regulations of the space group, many positional as well as anisotropic thermal parameters were fixed or equated with each other. Other than the ruled ones, the x and z coordinates of C(11) and C(13) atoms are assumed to be equal to the x and y coordinates of the C(12) and C(14) atoms, respectively, because they take equivalent positions around the nitrogen atom from each other.

The metal atom is at the center of symmetry, 0 0 0, and the atoms of the SCN ions are restricted to be arranged on the [±1±1±1] axes. However, from the result of their elemental analyses, as well as from the charge balance aspect, each complex contains only seven SCN ions; one water atom is coordinated to the metal atom other than the SCN ions. Attempted structure analyses assuming other lower symmetry space groups did not result in much improvement, except in some cases where a slightly better R values were obtained. However, these may only have been due to increase in the number of parameters. Therefore, we have assumed the disorder of the water molecule and the thiocyanate ions: respective eight coordinating positions around the metal atom are occupied equally by 1/8 molecules of water and 7/8 ions of SCN. Excepting this comples, in $[Co(NCS)(NH_3)_5]Cl_2$[16] too, all six coordinating positions around the cobalt atom are occupied equally by a disordered SCN ion (1/6) and ammonia molecules (5/6). During the calculation, the input positional parameters of the ligating oxygen atom was fixed as if the atom was on the [111] axis, and the distance from the metal atom is the sum of the metal (coordination number is 8, valence is 3+), and an oxygen (coordination number is 2, valence is 2−) atomic radii proposed by Shannon.[17]

There are crystallographically two independent kinds of tetraethylammonium ions; their ethyl carbon atoms are also disordered. The positions of the carbon atoms around the N(11) and N(21) atoms are shown schematically in Figs. 1A and 1B, respectively. Although one possible selection of the four ethyl group position are shown in the respective figures by thick lines, there are many other possible selections keeping the tetrahedrally bonding geometry around the nitrogen atom as well as the sp^3 angles of the N-C-C bonds: we have assumed that all equivalent positions of the respective carbon atoms are equally occupied. The multiplicities of the respective atoms used in the calculation are shown in Table 3.

In the cases of the erbium and its isomorphous salts, their

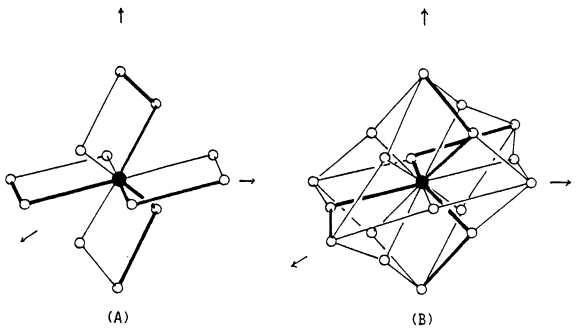

Fig. 1. Schematic presentation of the arrangements of the ethyl carbon atoms around, (A) N(11) atom of the praseodymium complex, and N(11) and N(21) atoms of the erbium complex; (B) N(21) atom of the praseodymium complex. ●, nitrogen atom; ○, carbon atom. Thick bonding lines mean one of the possible selection of the bondings.

Table 3. Final Atomic Coordinates (×10³), Multiplicities Used in the Calculation, and Equivalent Isotropic Temperature Factors (B_{eq}/Å²), with Estimated Standard Deviations in Parenthesess, of the Praseodymium Complex

Atom	G[g]	x	y	z	B_{eq}/Å²[h]
Pr	1/24	0	0	0	2.1_8
S(1)[i]	7/8	260.4(9)	260.4	260.4	10.6_9
C(1)[i]	7/8	186(3)	186	186	7.2_8
N(1)[i]	7/8	125(3)	125	125	12.2_3
N(11)	1/8	500	0	0	8.5_8
N(21)	1/24	500	500	500	5.7_8
C(11)[j]	1/4	421(3)	0	97(3)	10.6_3
C(12)[j]	1/4	421	97	0	10.6_3
C(13)[j]	1/4	500	0	214(3)	13.9_4
C(14)[j]	1/4	500	214	0	13.9_4
C(21)	1/6	410(5)	413(5)	500	8.1_5
C(22)	1/6	500	282(3)	500	9.2_5
O(1)[k]	1/8	12.4	12.4	12.4	8.0

g) Multiplicities. h) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$. i) $x=y=z$. j) As C(11) and C(12), and C(13) and C(14) are equivalent respectively, x and z of the formers are defined to be the same as x and y of the latters, respectively. k) O(1) was fixed at the position.

anionic complex ions are approximately in a cubic (though not exact cube) coordination geometry around their metal atoms, which are at the centers of symmetry, 0 0 0 and 0.5 0.5 0.5. To these complexes, too, the same type of disorder of the water molecule and of the SCN ions around each metal atom is assumed: each coordination position is occupied by 1/8 atom of the water oxygen and 7/8 atoms of the SCN nitrogen atoms. The position of the coordinated water oxygen atom was fixed as in the case of the light lanthanoid complexes. The ethyl carbon atoms around a central tetraethylammonium nitrogen atom are also disordered. Arrangements of the ethyl carbon atoms around both N(11) and N(21) atoms are in the type schematically shown in Fig. 1A, and the occupancies of the respective equivalent positions of the car-

bon atoms are assumed to be equal. The multiplicities used in the calculations are shown in Table 4. Attempts to perform structure factor calculations using other lower symmetry space groups did not yield improved results.

As shown in the results, the atomic positions as well as the temperature factors of these complexes did not converged well as the usual crystals: this was probably due to the existence of much disordering of the atoms.

Infrared Absorption Spectrum Measurements. They were obtained by means of JASCO A-202 grating infrared spectrophotometer, using liquid paraffin and hexachloro-1,3-butadiene mull.

Results and Discussion

The final positional parameters, their multiplicities used in the calculation, and their isotropic equivalent temperature factors of the praseodymium and erbium complexes are shown in Tables 3 and 4; selected interatomic distances as well as bond angles of the six complexes are shown in Tables 5 and 6. The perspective drawings of the praseodymium and the erbium complexes and their numbering scheme of the atoms are shown in Figs. 2 and 4, while their crystal packing diagrams in Figs. 3 and 5, respectively.[18]

In the praseodymium complex, the metal atom (at 0 0 0) is octa-coordinated being in a cubic geometry: seven SCN nitrogen atoms, and one water oxygen atoms are ligated to the metal atom, being disordered to occupy the eight positions equally, as shown in the previous paragraph. Since the SCN ions are arranged on the [±1±1±1] axes, the angles M-N(1)-C(1) as well as N(1)-C(1)-S(1) angles are 180°.

The Pr-N(1) bond length is 2.50(2) Å, which is shorter than the sum of their Shannon's ionic radii, 2.58 Å,[17] while the Pr-O(1) bond length is fixed as 2.477 Å.[17] The interatomic distance S(1)···S(1^{v}), the edge length of the complex anion cube, is 6.00(2) Å.

Table 4. Final Atomic Coordinates (×10^4), Multiplicities Used in the Calculation, and Equivalent Isotropic Temperature Factors (B/Å^2), with Estimated Standard Deviations in Parentheses, of the Erbium Complex

Atom	G[g]	x	y	z	B_{eq}/Å^2 [h]
Er	1/8	0	0	0	5.3_6
S(1)	7/8	2510(5)	2520(5)	1308(2)	12.0_5
C(1)	7/8	1755(13)	1794(13)	907(6)	8.9_4
N(1)	7/8	1171(16)	1211(18)	588(6)	17.4_7
N(11)	1/4	0	5000	0	11.6_8
N(21)	1/4	0	0	2576(8)	8.4_3
C(11)	1/4	939(43)	5686(42)	0	12.4_7
C(12)	1/4	1014(54)	4142(33)	0	14.3_1
C(13)	1/2	46(34)	4215(22)	511(12)	12.6_2
C(14)	1/2	2171(23)	4904(27)	0	14.5_4
C(15)	1/2	0	5000	1103(10)	15.1_8
C(21)	1/2	−22(44)	997(25)	2150(9)	10.7_0
C(22)	1/2	−59(41)	987(25)	2982(9)	10.6_7
C(23)	1/2	39(16)	2207(13)	2548(8)	13.3_1
O(1)[k]	1/8	118	118	60	4.0_3

g), h), and k): see the footnotes of Table 3.

Table 5. Selected Interatomic Distances and Bond Angles of the Light Lanthanoid Complexes with the Standard Deviations in Parentheses

A. Interatomic distances (l/Å) M=	La	Ce	Pr
M-N(1)	2.60(3)	2.568(16)	2.50(2)
M-N (Shannon)[l]	2.62	2.60	2.58
M-O(1)[m]	2.482	2.480	2.477
S(1)-C(1)	1.48(3)	1.538(14)	1.49(2)
C(1)-N(1)	1.14(4)	1.10(2)	1.21(3)
S(1)···S(1^{v})	6.03(3)	6.012(17)	6.00(2)
N(1)···N(1^{v})	3.007(1)	2.966(1)	2.888(1)
M··· N(11)	5.870(2)	5.765(2)	5.757(1)
B. Bond angles (ϕ/°) M=	**La**	**Ce**	**Pr**
M-N(1)-C(1)	180	180	180
N(1)-C(1)-S(1)	180	180	180
N(1)-M-N(1^{v})	70.5(8)	70.5(5)	70.5(7)
N(1)-M-N(1^{v})	109.5(8)	109.5(5)	109.5(7)

Key to the symmetry operations: i, −x, −y, z; v, x, y, −z. l) Sum of the Shannon's ionic radii.[17] m) O(1) atom is fixed assuming the M-O(1) bond length is the same as the sum of the metal and oxygen ionic radii.[17]

Table 6. Selected Interatomic Distances and Bond Angles of the Heavy Lanthanoid Complexes with the Standard Deviations in Parentheses

A. Interatomic distances (l/Å) M=	Nd	Dy	Er
M-N(1)	2.49(3)	2.40(3)	2.36(3)
M-N (Shannon)[l]	2.57	2.49	2.46
M-O(1)[m]	2.46	2.38	2.35
S(1)-C(1)	1.51(3)	1.49(3)	1.51(3)
C(1)-N(1)	1.15(4)	1.19(4)	1.20(4)
S(1)···S(1^{iv})	5.98(3)	5.93(3)	5.92(3)
S(1)···S(1^{ii})	5.912(13)	5.837(13)	5.817(12)
N(1)···N(1^{iv})	2.85(9)	2.74(8)	2.66(9)
N(1)···N(1^{ii})	2.88(4)	2.79(4)	2.76(4)
M···N(11)	5.785(1)	5.778(1)	5.782(1)
M···N(21)	5.81(2)	5.80(2)	5.828(17)
B. Bond angles (ϕ/°) M=	**Nd**	**Dy**	**Er**
M-N(1)-C(1)	179(3)	176(2)	177(2)
N(1)-C(1)-S(1)	176(3)	176(2)	179(2)
N(1)-M-N(1^{ii})	70.9(8)	71.0(8)	71.4(8)
N(1)-M-N(1^{i})	110.2(10)	110.4(10)	111.3(10)

Key to the symmetry operations: i, −x, −y, z; ii, −y, x, z; iv, x, y, −z. l) and m): see the footnote of Table 5.

As shown schematically in Fig. 6, the crystal lattice of this complex resembles that of rock salt. The tetraethylammonium nitrogen atoms occupy the Cl^- ionic position, the N(11) atoms are at the midpoints of the respective edges, and the N(21) atom is at the body center of the unit cell. The metal atoms occupy only the apex Na^+ ionic positions of the NaCl-type crystal lattice, and the face center positions are vacant. Therefore, each metal atom is surrounded by six N(11) atoms from both sides of the a, b, and c axis directions. No bridging was found between these anions and cations.

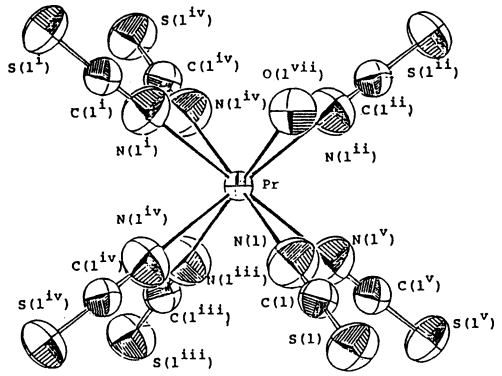

Fig. 2. A perspective drawing of the praseodymium complex around the metal atom (one of the possible arrangement). The key to the symmetry operations are: i, $-x$, $-y$, z; ii, $-x$, y, $-z$; iii, x, $-y$, $-z$; iv, $-x$, $-y$, $-z$; v, x, y, $-z$; vi, x, $-y$, z; vii, $-x$, y, z.

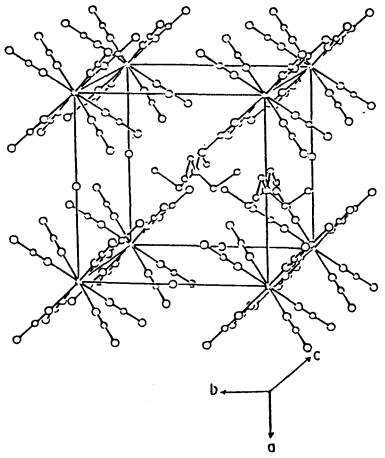

Fig. 3. Crystal packing diagram of the praseodymium complex.

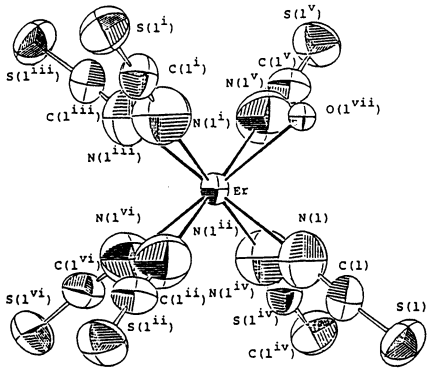

Fig. 4. A perspective drawing of the erbium complex around the metal atom (one possible arrangement). The key to the symmetry operations are: i, $-x$, $-y$, z; ii, $-y$, x, z; iii, $-x$, $-y$, $-z$; iv, x, y, $-z$; v, y, $-x$, $-z$; vi, $-y$, x, $-z$; vii, y, $-x$, z;

The structure of the isomorphous lanthanum and cerium complexes are fundamentally the same as that of the praseodymium complex. However, as the cell volume decreases, depending on the atomic number of the metal atom, the M···N(11) distance (the separation between the cation and anion) decreases in the order. The M-N(1) bond length (La-N(1), 2.60(3); Ce-N(1), 2.568(16); Pr-N(1), 2.50(2) Å) also decreases in the same order; it decreases more rapidly than the sum of their Shannon's ionic radii (La-N, 2.62; Ce-N, 2.60; Pr-N, 2.58 Å).[17]

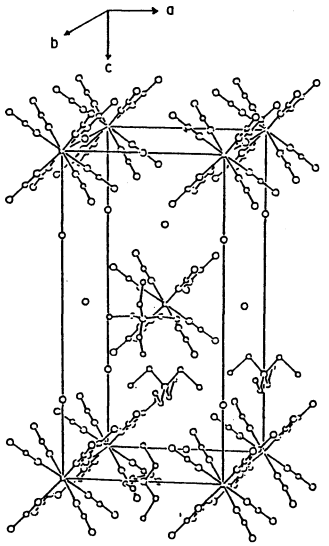

Fig. 5. Crystal packing diagram of the erbium complex.

The complex ion of the erbium salt has approximately the same structure as that of the light lanthanoid complexes. The metal atoms (at 0 0 0 and 0.5 0.5 0.5) are octa-coordinated, being approximately in a cubic geometry: seven SCN nitrogen and one water oxygen atoms are ligated to the metal atom, being disordered to occupy all eight coordinating positions equally.

The edge lengths of the complex anion cube are: S(1)···S(1^{ii}), 5.817(12); and S(1)···S(1^{iv}), 5.92(3) Å (key to the symmetry operations: ii, $-y$, x, z; iv, x, y, $-z$). The bond length of Er-N(1) is 2.36(3) Å, which is shorter than the sum of the Shannon's ionic radii, 2.46 Å.[17] The Er-O(1) distance was fixed as 2.35 Å.[17] The bond angles Er-N(1)-C(1), and N(1)-C(1)-S(1) are 177(2) and 179(2)°, respectively, which are almost 180°. The bond angles N(1)-Er-N(1^{i}) and N(1)-Er-N(1^{ii}) are 111.3(10) and 71.4(8)°, respectively (key to the symmetry operations: i, $-x$, $-y$, z; ii, $-y$, x, z).

As shown in Fig. 6, the crystal lattice of the erbium complex is a modified form of the praseodymium complex lattice. Its unit cell apparently consists of two latter cubic cells piled along the c-axis direction, and the positions of the metal and ammonium nitrogen atoms on the contact plane of the original two cells are shifted as shown in the following. The relative arrangement of the metal and the tetraethylammonium nitrogen atoms on the plane **1** and **2** (see Fig. 6) of the erbium complex, which are parallel to the ab-plane and intersect the c-axis at 0.0 and 0.5, is the same, but all of their positions on plane **2** are shifted

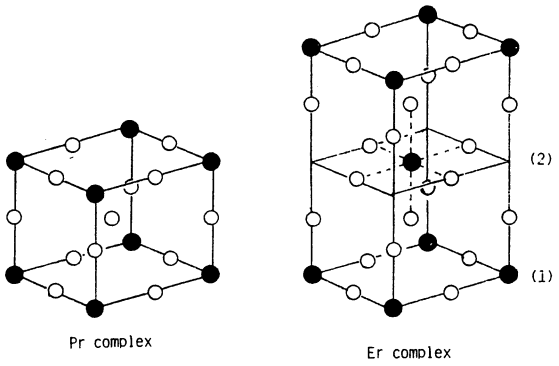

Fig. 6. Schematic presentation of the metal and tetraethylammonium nitrogen atomic positions in the crystal lattices of the praseodymium and erbium complexes. ●: metal atoms, ○: tetraethylammonium nitrogen atoms.

by 0.5 along both the a- and b-axis directins from the respective positions on plane 1. The **1** and **2** type planes appear alternately along the c-axis. On the other hand, in the erbium complex, the N(11) atoms at the midpoint of the c-edge as well as the body-centered N(21) atoms of the praseodymium complex are apparently kept at their positions: they are on the planes parallel to the ab-plane intersecting the c-axis at about 0.25 and 0.75, respectively.

As a result, as shown in Fig. 6, in the erbium complex, too, the metal atom is surrounded by six tetraethylammonium nitrogen atoms in about equidistances on both sides along a-, b-, and c-axis directions: Er···N(11), 5.782(1); Er···N(21), 5.828(17) Å.

The neodymium and dysprosium complexes have essentially the same type of structure. The M-N(1) bond lengths (Nd-N(1), 2.49(3); Dy-N(1), 2.40(3); and Er-N(1), 2.36(3) Å) are shorter than the respective sums of the Shannon's ionic radii (Nd-N, 2.57; Dy-N, 2.49; Er-N, 2.46 Å), and the differences are larger than the values found in the series of the light lanthanoid complexes. Therefore, it is likely that, through the both series of these complexes, the M-N(SCN) bonds have the more covalent-bonding character in the higher metal-atomic-number complexes.

The infrared absorption spectra of these complexes were examined. Not only the general feature, but also the maximum wavenumbers of the respective peaks of the title six complexes were not much different from each other. Therefore, the respective average wavenumbers of the peak maxima will be discussed.

Although some of them partially overlapped with the bands due to the tetraethylammomium ion, the typical bands due to the SCN ion were observed: ν(CN), 2050(s); ν(CS), 735(sh); and δ(NCS), 475(m) cm^{-1}, respectively (here, s, strong; sh, shoulder; m, medium). These values are all in a reasonable region for the bands of the N-bonded SCN ions.[19] The ν(OH) band of the coordinated water was found at about 3370 cm^{-1} in the spectra of all of these complexes, although it is broad and weak. The maximum wavenumbers of the tetraethylammonium ion peaks, 1490, 1440, 1393, 1170, 1050, 998, 780, and 720 cm^{-1}, were not much different from those of tetraethylammonium chloride.

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18) The atomic positional parameters of the lanthanum, cerium, neodymium, and dysprosium complexes, the thermal parameters, the final F_o-F_c tables and some additional data of bond lengths and bond angles of the all complexes are deposited as Document No. 8811 at the office of the Editor of Bull. Chem. Soc. Jpn.
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