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The Crystal and Molecular Structures of Tetraethylammonium [Heptakis(isothiocyanato)lanthanate(III) and -praseodymate(III)]·Benzene, $[(C_2H_5)_4N]_4[M(SCN)_7]\cdot C_6H_6$ (M=La, Pr), in a Unicapped Trigonal Prism Geometry

Fumiko Matsumoto,† Toshio Takeuchi,†† and Akira Ouchi*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†Department of Chemistry, School of Hygienic Sciences, Kitasato University, Kitasato, Sagamihara-shi, Kanagawa 228
††Department of Natural Sciences, Faculty of Science and Technology, Sophia University, Kioi, Chiyoda-ku, Tokyo 102

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Synopsis. The crystals of the title new lanthanum(III) complex, $LaC_{45}H_{86}N_{11}S_7$, F.W. 1144.59, are orthorhombic, space group $Bm2_1b$, a=17.438(7), b=21.507(9), c=16.616(6) Å, U=6232(4) Å^3, Z=4, D_m=1.21(3), D_x=1.22 g cm^{-3}, and μ(Mo $K\alpha$)=9.63 cm^{-1}. The central lanthanum(III) atom has a unicapped trigonal-prism 7N-hepta-coordination geometry: seven thiocyanato nitrogen atoms are ligated. There are no bridgings between the complexes and/or counter cations. Each benzene molecule is surrounded by the thiocyanate ions and ethyl groups of the cations. Although these crystals lose benzene at about 60 °C, they are stable for more than several weeks at ambient temperature, and can be regarded as a kind of inclusion compound. The isomorphous praseodymium(III) complex was also obtained.

The hexa-coordinated isothiocyanato(SCN) complexes of lanthanoids, $[(C_4H_9)_4N]_3[M(NCS)_6]$ (M=Pr—Yb), reported about 20 years ago,[1] are thought to have a specific structure, since in common complexes of lanthanoids the coordination numbers are in most cases 8, 9 or higher:[2] the SCN does not seem to be as massive as the one which should have a lower coordination number. In cases of the aqua-SCN mixed complexes, their coordination numbers were found to be eight.[3–5] The structures of the anionic thiocyanato complexes of cadmium are different from each other, depending on the kinds of their counter cations.[6,7] We recently found a new hepta-coordinated (in pentagonal bipyramidal form) isothiocyanato complexes of lanthanoids $[(CH_3)_4N]_4[M(NCS)_7]$ (M=Dy—Yb).[5] Therefore, we expected to find other types of new complexes from their tetraethylammonium salts, and obtained the title complexes. From preliminary chemical analyses, we found that they include the metal, SCN ions, and benzene in a mole ratio of 1 : 7 : 1, and were expected to have interesting structures. Therefore, their crystal and molecular structures were examined by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Tetraethylammonium Heptakis(isothiocyanato)lanthanate(III)·Benzene (1). Lanthanum and tetraethylammonium thiocyanates were obtained as previously reported.[4] Into a methanolic solution (15 cm^3) containing 1.0 mmol of lanthanum(III) thiocyanate and 0.8 g (4.3 mmol) of tetraethylammonium thiocyanate, 10 cm^3 of an ethanol-benzene mixed solution (1 : 1=v/v) was added and dried up at about 80 °C using a rotary vacuum evaporator. The sirupy residue was dissolved into 15 cm^3 of dried methanol and was left standing in benzene vapor at ambient temperature. Although no precipitates appeared during several weeks, crystals of the title complex were deposited after several months. Yield: 0.6 g (0.52 mmol, 52%). The praseodymium complex (**2**) was also obtained by almost the same technique, and almost in the same yield. Attempts to synthesize the isomorphous neodymium or the heavier lanthanoid complexes using the same technique have not been successful. Calcd for $MC_{45}H_{86}N_{11}S_7$: M=La (**1**), La, 12.14; C, 47.22; H, 7.57; N, 13.46%; M=Pr (**2**), Pr, 12.29; C, 47.14; H, 7.56; N, 13.44%. Found: **1**, La, 12.02; C, 46.85; H, 7.42; N, 13.45%; **2**, Pr, 12.30; C, 46.91; H, 7.40; N, 13.33%.

Single Crystal X-Ray Structure Analysis. The crystal of **1** was colorless, parallelepiped (0.30×0.25×0.20 mm^3), D_m=1.21(3), and D_x=1.22 g cm^{-3}; and that of **2**, pale green in color, parallelepiped (0.30×0.20×0.12 mm^3), D_m=1.21(3), and D_x=1.23 g cm^{-3}. Intensities in the range $3<2\theta<60°$ were collected on a Rigaku AFC-6A automated 4-circle X-ray diffractometer using graphite monochromated Mo $K\alpha$ radiation (λ=0.71073Å) by means of an ω-2θ scan technique (scan speed (ω), 4° min^{-1}, and scan width (ω), 1.08+0.35 tanθ) for **1** and **2**. The intensities were corrected for Lorentz and polarization factors, but not for absorption and extinction. Of 4970 independent intensities collected, 1571 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination of **1**, while 1874 in 4956 reflections for that of **2**. The crystallographic data of **2** are: a=17.412(7), b=21.468(6), c=16.612(6) Å, U=6209(4) Å^3, μ(Mo $K\alpha$)=10.51 cm^{-1}.

All the 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.[8] The scattering factors were taken from Ref. 9.

The structure of **1** was solved by the heavy-atom method (positional and thermal parameters were refined by a block-

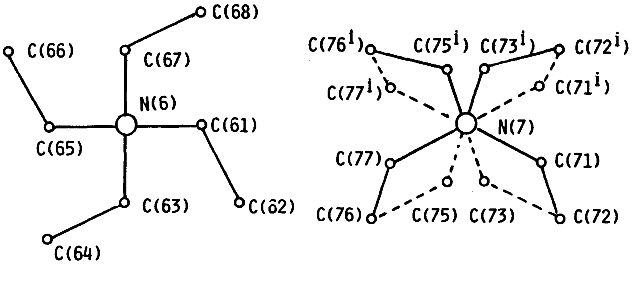

Fig. 1. Schematic presentation of the tetraethylammonium ions with the numbering scheme of the atoms.
A. The ion centered by N(6). **B**. The ion centered by N(7): the bonding and the numbering way are the same as the one centered by the N(8) atom. Key to the symmetry operation: i; $\bar{x}$, y, z.

diagonal least-squares method). No hydrogen atoms were included in the structure factor calculations. The structure of **2** was calculated starting from the final values of **1**. They were also refined. During the final stage of refinements, the movements of the respective parameters were less than one-third of the corresponding standard deviations, except for a few cases. The carbon atoms of the tetraethylammonium ions centered by N(7) and N(8) atoms are disordered, as shown in Fig. 1. The N(7) atom is bonded with four carbon atoms in two ways: with C(71), C(73$^{\rm i}$), C(75$^{\rm i}$), and C(77), or with C(71$^{\rm i}$), C(73), C(75), and C(77$^{\rm i}$), atoms (i, $-x$, y, z). The occupancy factors of both type structures are 0.5 due to symmetry. The final R and $R_{\rm w}$ (in parentheses) values[10] are: **1**, 0.091(0.071); **2**, 0.086 (0.070). Since the R and $R_{\rm w}$ values of the inversed chirality structures were, **1**, 0.093 (0.073); **2**, 0.089 (0.074), the structures were not adopted. Although the thermal parameters of some atoms were found to be large, such phenomena were sometimes found in the lanthanoid complexes, especially for the atoms relatively far from the central metal atom.[11]

The Other Measurements. Thermogravimetric (TG)-differential thermal analysis (DTA) simmultaneous measurement was carried out by the Rigaku "Thermoflex" M-8075 using samples weighing about 10 mg each at heating rate of 10 °C min^{-1} in air, α-alumina as the reference. Infrared spectra were obtained by means of a JASCO A-202 grating infrared spectrophotometer using paraffin oil and hexachloro-1,3-butadiene mull.

Results and Discussion

Selected bond lengths and bond angles are listed in Table 1. A perspective drawing of the anionic complex is shown in Fig. 2, and a projection of the unit cell along b-axis in Fig. 3.[12]

The metal atom is in a unicapped trigonal prism hepta-coordination geometry, as shown by the broken lines in Fig. 2: seven N atoms of SCN ions are ligated. The atoms of the metal and the SCN ions following N(1), N(4), and N(2) (cap position) are on planes parallel to the bc-plane; the other two pairs of the SCN ions (following N(3), and N(3$^{\rm i}$); and N(5) and N(5$^{\rm i}$)) are at the respective mirror image positions with each other on both sides of the planes. The triangle planes of the prism are approximately parallel to the ac-plane.

Table 1. Selected Bond Lengths and Bond Angles of the Complexes with the Standard Deviations in Parentheses

Bond length(l/Å) M=	La	Pr	M=	La	Pr
M-N(1)	2.57(3)	2.57(2)	M-N(2)	2.56(7)	2.52(6)
M-N(3)	2.60(2)	2.58(2)	M-N(4)	2.47(3)	2.37(3)
M-N(5)	2.45(2)	2.37(2)	N(1)-C(1)	1.19(4)	1.14(3)
N(2)-C(2)	1.14(9)	1.14(9)	N(3)-C(3)	1.13(3)	1.11(2)
N(1)-C(1)	1.00(5)	1.09(5)	N(5)-C(5)	1.18(3)	1.18(3)
C(1)-S(1)	1.51(3)	1.54(3)	C(2)-S(2)	1.62(7)	1.61(6)
C(3)-S(3)	1.59(2)	1.59(2)	C(4)-S(4)	1.92(4)	1.85(5)
C(5)-S(5)	1.61(2)	1.63(2)			

Bond angl (ϕ/°) M=	La	Pr
M-N(1)-C(1)	178(2)	173(2)
M-N(2)-C(2)	164(6)	173(6)
M-N(3)-C(3)	171(2)	168(1)
M-N(4)-C(4)	151(3)	158(3)
M-N(5)-C(5)	171(2)	168(2)
N(1)-C(1)-S(1)	177(3)	179(2)
N(2)-C(2)-S(2)	163(7)	175(6)
N(3)-C(3)-S(3)	175(2)	179(2)
N(4)-C(4)-S(4)	175(4)	179(4)
N(5)-C(5)-S(5)	169(2)	170(2)

The average M-N bond lengths to the three N atoms at the apexes of one bottom triangle are short (**1**, 2.46, and **2**, 2.37Å, on the average), and the other four, to the N atoms at the apexes of the other bottom triangle and at the cap position, are long (**1**, 2.58, and **2**, 2.56Å, on the average). The averages of the M-N-C and N-C-S angles are: **1**, 167 and 172; **2**, 168 and 176°, respectively. These are not much deviated from 180°.

It is an interesting fact that $[\mathrm{Dy(SCN)_7}]^{4-}$ ion in tetramethylammonium salt has an approximately pentagonal bipyramidal geometry around its metal atom, while the present $[\mathrm{Pr(SCN)_7}]^{4-}$ in tetraethylammonium salt a unicapped trigonal prism.

The centers of cations, N(7) and N(8) atoms, as well as the centers of benzene rings are on planes parallel to the bc-plane. The benzene ring is arranged approximately parallel to the ab-plane and is mirror-symmetrical to the bc-plane. The benzene ring is

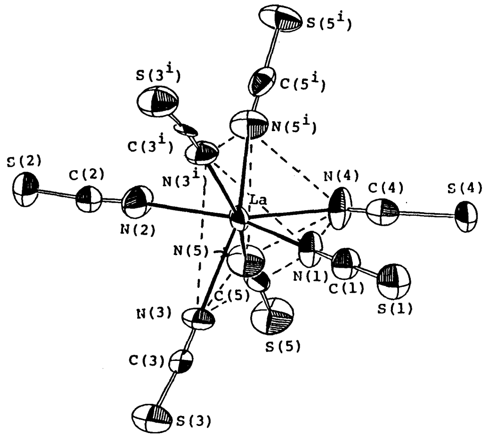

Fig. 2. The perspective drawing of the anionic complex with the numbering scheme of the atoms. (i; $\bar{x}$, y, z.)

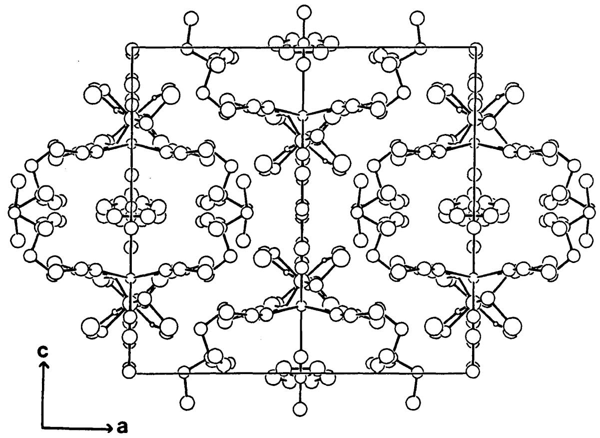

Fig. 3. Projection of the unit-cell along b-axis.

situated between two cations centered by N(7) and N(8) atoms in the c-axis direction. Moreover, on both sides of the ring along b-axis, there are the SCN ions bonded to the cap-positions of the complexes which are neighboring along [011] or [0$\bar{1}$1] axis.

The metal and a center of the cation, N(6), atoms are on planes parallel to the ac-plane intersecting the b-axis at 0 and 0.5, while the benzene molecules and the other cations (centered by N(7) and N(8) atoms) are sandwitched between the former planes: both kinds of layers are arranged alternately along b-axis.

The general feature of the TG and DTA curves of **1** and **2** are approximately the same: they decompose in two steps. At the first step of TG curve (at, **1**, 60; **2**, 103 °C) they lose benzene (corresponding DTA endothermic peaks are at, **1**, 65; **2**, 120 °C). At the second step of TG curve (at, **1**, 264; **2**, 274 °C) they seem to decompose in a one-step reaction into their oxides. However, as the corresponding DTA curve shows an endothermic followed by exothermic peaks, the reaction is likely to consist of several complicated steps.

When **1** and **2** were heated at 110 °C for several hours, they lost only benzene, judging from their mass loss. In the infrared spectra of their heating residue, peaks of SCN were found (ν(CN), 2035; ν(CS), 730(sh); δ(SCN), 482 cm^{-1}) as well as those of the $[(C_2H_5)_4N]^+$ ion (for example, strong peaks at 1490, 1395, 1364, 1170, 997, and 780 cm^{-1}). Those for benzene, found in the spectra of **1** or **2** (for example peaks at 1480, 680 (splitted into two) cm^{-1}), disappeared.

On the other hand, at room temperature, these complexes were stable, and the included benzene was not removed after, at least, several weeks (when they were kept in a stoppered glass bottle in a refrigerator, they were not decomposed even after six months).

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10) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, where $w=1/[\{\sigma(|F_o|)\}^2+(F_w\times F_o)^2]$, $F_w=0.015$ for **1** and **2**.

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12) The positional and isotropic equivalent as well as anisotropic temperature factors, the final F_o and F_c tables, and some additional data of bond lengths and bond angles of **1** and **2** are deposited as Document No. 8876 at the Office of the Editor of Bull. Chem. Soc. Jpn.