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The Syntheses, Crystal and Molecular Structures, and Their Thermal Properties of Tetramethylammonium [Octakis(isothiocyanato)lanthanoidates(III)]·benzene (1/2), $[(CH_3)_4N]_5[M(NCS)_8]\cdot 2C_6H_6$ (M=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy)

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Synopsis. The titled series of isomorphous complexes, the first octakis(isothiocyanato) complexes of lanthanoids, were obtained. Their crystals are tetragonal, space group $P4nc$, Z=2. The cell dimensions of the praseodymium complex, for example, are a=15.871(7), c=11.543(6) Å, U=2908(3) Å^3, and D_m=1.29(3), D_x=1.29 g cm^{-3}, μ(Mo $K\alpha$)= 11.60 cm^{-1}, with a final R value of 0.069. The metal atom is octa-coordinated by eight isothiocyanate ions in an intermediate geometry between cube and square-antiprism. The benzene included in the praseodymium complex crystals was retained up to 174 °C (DTA), and was not removed even after being heated for 12 h at 110 °C. In cases of the other isomorphous members, the benzene was removed at lower temperatures, respectively. The isomorphous fluorobenzene adduct was obtained only for the lanthanum complex.

Since Martin et al. reported the structure of tetrabutylammonium [hexakis(isothiocyanato)lanthanoidates],[1] it has been widely believed that the octahedral hexa-coordination is the only geometry of such complexes.[2–4] Recently, the authors reported the structures of crystals including $[M(NCS)_7]^{4-}$ ions;[5,6] as the next step we expected to obtain crystals including $[M(NCS)_8]^{5-}$ ions by using light lanthanoids and tetramethylammonium cation.

From preliminary tests, the title praseodymium complex crystals were found to include benzene; this was hard to remove, even after being heated for 12 h at 110 °C. This thermal stability of the adduct was abnormal, because the included benzene was always removed under 100 °C from all of the type adducts previously reported.[5,7] We have therefore synthesized a series of its isomorphous complexes, and have examined their crystal and molecular structures, as well as their thermal properties.

Experimental

Praseodymium and tetramethylammonium thiocyanates were obtained as previously reported.[6] The methanol solution (7 cm^3) including praseodymium thiocyanate (1.0 mmol) and tetramethylammonium thiocyanate (0.69 g, 5.2 mmol) was left standing for several days in benzene vapor, and pale-green crystals of $[(CH_3)_4N]_5[Pr(NCS)_8]\cdot 2C_6H_6$ were deposited. The yield was 0.9 g (0.80 mmol, 80%). The isomorphous complexes from lanthanum to dysprosium were obtained in the same way and almost in the same yield.[8] By this method, the isomorphous erbium and ytterbium complexes were not precipitated; instead, $[(CH_3)_4N]_4[M(NCS)_7]$ (M=Er, Yb) were deposited.[6] When the starting solution was left standing in fluorobenzene vapor, the isomorphous complex was obtained only for the lanthanum.[8]

In the X-ray structure analysis, the intensities were measured on a Rigaku AFC-6A automated 4-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), the ω-2θ scan technique being employed (ω-scan speed=4° min^{-1}). The intensities were corrected for Lorentz and polarization factors, but not for absorption. The structure of the gadolinium complex was first solved by the heavy-atom method. Hydrogen atoms were not included in the structure calculations. The block-diagonal least-squares method was used for the refinement. The position of the metal atom was fixed at the origin, and the x and y coordinates of the N(31) atom of a cation, were fixed to be zero. The methyl carbon atoms around N(31), C(31), and C(32), were disordered into two with occupancy factors of 0.5, considering the site symmetry. The structures of the other isomorphous complexes were obtained by starting from the final positional and thermal parameters of the gadolinium complex: they were refined in the same way. The fluorine atom of the fluorobenzene adduct of the lanthanum complex was obtained from its difference synthesis map: it is bonded to C(61), which is also disordered into two, considering the site symmetry.[8] All of 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.[9] The atomic-scattering factors were taken from Ref. 10.

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

A crystal-packing diagram of the praseodymium complex projected along the c-axis is shown in Fig. 1.[8,11]

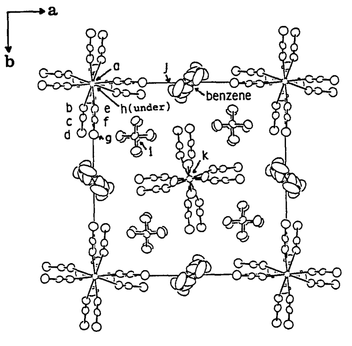

Fig. 1. Projection of the unit cell of the praseodymium complex along the c-axis. Notation of the atoms: a, Pr; b, N(1); c, C(1); d, S(1); e, N(2); f, C(2); g, S(2); h, N(31); i, N(41); j, C(61); k, N(31^i). (i=0.5−x, 0.5+y; 0.5+z).

Table 1. Cell Dimensions and M-N Bond Lengths of the Complexes $[(CH_3)_4N]_5[M(NCS)_8]\cdot 2G$ (M=La—Dy, G=C_6H_6; M=La, G=C_6H_5F[a])

M=	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	La[a]
F.W.	1130.49	1131.71	1132.50	1135.83	1141.95	1143.55	1148.84	1150.51	1154.09	1166.47
a/Å	15.888(5)	15.879(8)	15.871(7)	15.872(9)	15.859(3)	15.857(9)	15.860(7)	15.856(8)	15.848(6)	15.922(8)
c/Å	11.579(2)	11.548(3)	11.543(6)	11.527(4)	11.479(2)	11.447(5)	11.468(4)	11.454(3)	11.443(4)	11.546(4)
U/Å^3	2923(1)	2912(3)	2908(3)	2904(3)	2887(1)	2886(3)	2884(2)	2879(3)	2874(2)	2924(3)
M-N(1) (l/Å)	2.59(2)	2.57(2)	2.57(1)	2.54(2)	2.53(1)	2.50(1)	2.48(2)	2.46(1)	2.45(1)	2.58(2)
M-N(2) (l/Å)	2.56(2)	2.53(2)	2.50(1)	2.50(2)	2.41(2)	2.46(1)	2.43(2)	2.43(1)	2.43(2)	2.57(2)

a) The isomorphous fluorobenzene adduct of the lanthanum complex.

The cell dimensions and the M-N bond lengths of all the isomorphous complexes are shown in Table 1. Both of the Pr-N bond lengths, for example, are slightly shorter than the sum of the Shannon's crystal radii, 2.59 Å.[12] In the $[Pr(NCS)_8]^{5-}$ ion, the metal atom is octa-*N*-coordinated in an intermediate geometry between a cube and a square-antiprism. The intersecting angle between the projections on the ab-plane of the diagonals of the top and the bottom squares of the ligating N-atoms was 26°. The isothiocyanate ions are arranged approximately on [011] or [01$\bar{1}$]. The N(31) atom is in the middle of a pair of neighboring metal atoms along the c-axis, and the N(41) atom of the other cation is in the middle of a metal and the N(31) atom approximately along [110]. The center of the benzene ring, 0.5, 0, 0, is in the middle of a pair of neighboring metal atoms along the a-axis.

The relations between the average M-N bond lengths, a- and c-axis lengths, and the Shannon's metal crystal radii of the complexes[12] are shown in Fig. 2. They decrease as the metal atomic number, though the a-axis length changes quite slowly. Since benzene molecules are arranged along the a-axis, its length is thought to be sensitive to the size of the space where the benzene ring is included, and the range of the optimum size is quite likely to be limited.

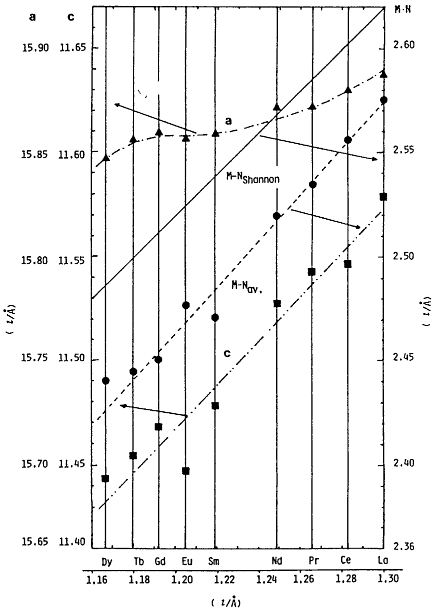

Fig. 2. The relation between the Shannon's crystal radii of the central metal atom, and the a- and c-axis lengths (shown by **a** and **c**) and M-N bond lengths (average of the observed values of the respective complexes and the sums of the respective Shannon's crystal radii).

The fluorobenzene molecule, which is larger than benzene, can be included only in a complex of lanthanum which has the largest metal crystal radius.

The features of the TG and DTA curves of the praseodymium complex are shown in Fig. 3. It lost benzene (judging from the weight loss) at point **1** of TG (165 °C) and at peak **11** of DTA (174 °C). The temperatures were much higher than expected, since benzene was not expected to make any effective hydrogen bonds in the crystal. At **2** of TG and **12** of DTA, one mole of $[(CH_3)_4N](SCN)$ was removed (judging from the weight loss). At **3** of TG, and **13**, **14**, and some other small peaks near them of DTA, the complex decomposed completely; after the sample was heated up to 1000 °C the residue was metal oxide.

The features of the TG and DTA curves of the other isomorphous complexes are approximately the same, except for the temperatures at **1** and **11**. The relation between the temperatures and the Shannon's metal crystal radii of the complexes are shown in Fig. 4. The praseodymium complex showed maximum values. The fluorobenzene was removed from its adduct at approximately the same temperature as the benzene adduct of lanthanum.

The high thermal stability of the praseodymium complex crystals was also examined by heating for 12 h at 110 °C: neither the weight loss nor any changes of

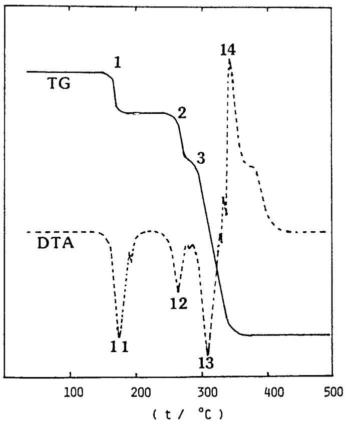

Fig. 3. TG(——) and DTA(----) curves of the praseodymium complex. Mass loss of the TG was taken downwards and the exothermic change of DTA was taken upwards.

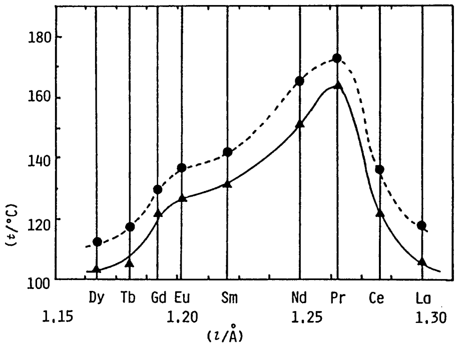

Fig. 4. The corresponding temperatures of the respective complexes at the points **I** and **II** of Fig. 3. The abscissa of the figure is taken as proportional to the crystal radii of the central metal atom.

the infrared spectral peaks (3090, 3050, 1030, and 680 cm^{-1} peaks of the included benzene and 2060, 740, and 475 cm^{-1} peaks of isothiocyanate ions) were recognized. As was expected from the thermo-analytical result, the isomorphous neodymium complex also showed almost the same thermal stability, though the europium complex lost half of its benzene within 10 h, and the gadolinium complex lost all of it within 6 h at 110 °C. The benzene in the lanthanum, cerium, terbium, and dysprosium complexes, as well as the fluorobenzene in the lanthanum adduct, were completely removed within 2 h at 110 °C.

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