July, 1989] © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***62***, *2431—2433 (1989)* 2431

The Crystal and Molecular Structures of Tetraethylammonium [Tetraaquatetrakis(isothiocyanato)neodymate(III) and europate(III)], $[(C_2H_5)_4N][M(NCS)_4(H_2O)_4]$, (M=Nd, Eu)

Akira OUCHI
Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153

(Received December 1, 1988)

Synopsis. The crystal and molecular structures of the title new complexes were determined by means of a single-crystal X-ray diffraction method. The crystals of the neodymium(III) complex, $NdC_{12}H_{28}N_5O_4S_4$, F. W. 578.87, are triclinic, space group $P\bar{1}$, a=14.13(2), b=15.39(1), c=12.92(1) Å, α=106.81(8), β=114.70(9), γ=90.09(10)°, U=2418(5) Å^3, Z=4, D_m=1.57(3), D_x=1.59 g cm^{-3}, μ(Mo $K\alpha$)=25.22 cm^{-1}. The isomorphous europium(III) complex was also obtained: a=14.069(9), b=15.328(9), c=12.865(9) Å, α=106.98(5), β=114.57(5), γ=90.07(6)°, U=2390(3) Å^3, D_m=1.60(3), D_x=1.63 g cm^{-3}, μ(Mo $K\alpha$)=30.04 cm^{-1}. Two crystallographically independent neodymium(III) atoms in a unit cell have approximately the same coordination geometry: square antiprism 4*O*,4*N*-octa-coodination. A pair of the O atoms as well as N atoms are in cis positions on the top square and in trans positions on the bottom square of each polyhedron, where the lines connecting both pairs of the N atoms on both squares are approximately parallel.

The structures of metal thiocyanato complexes have already been actively investigated.[1,2] Among them, the lanthanoid complexes are interesting because of their specific coordination number (for example, six in tetrabutylammonium salts, $[(C_4H_9)_4N]_3[M(SCN)_6]$[3]), and of their coordination geometry (for example, cubic in $[(C_2H_5)_4N]_4[M(SCN)_7(H_2O)]$ (**1**[4])).

In this line of the study, we obtained another types of lanthanoid thiocyanato complexes (shown in the title), $[(C_2H_5)_4N][Nd(SCN)_4(H_2O)_4]$ (**2**), and the isomorphous europium(III) complex (**3**). It is very interesting that when using almost the same starting solution, crystals of **2** were obtained when this solution was kept in benzene vapor, while crystals of **1** were obtained when it was kept over silica gel. Although the structures of the complexes $K_4[M(SCN)_4(H_2O)_4]\cdot(SCN)_3\cdot nH_2O$ (M=Nd) (**4**), Eu (**5**)) have already been reported,[5] they are double salts in which, moreover, the counter cation is K^+: the coordination geometry of the anionic complexes is much affected by the kinds of counter cations.[6–8] We therefore examinted the structures of **2** and **3** by the single-crystal X-ray diffraction technique.

Experimental

Synthesis of Tetraethylammonium [Tetraaquatetrakis(isothiocyanato)neodymate(III)] (2). Neodymiun and tetraethylammonium thiocyanates were obtained as reported previously.[4] Into a methanolic solution (15 cm^3) containing 1.0 mmol of $Nd(SCN)_3$ and 0.2 cm^3 of water, 0.80 g (4.3 mmol) of $[(C_2H_5)_4N](SCN)$ was dissolved and left standing in a desiccator over benzene for several weeks: crystals of **2** were deposited. Yield: 0.46 g (0.80 mmol, 80%). The europium complex (**3**) was also obtained by the same technique and almost in the same yield. Attempts to synthesize types of La and the Pr complexes by this technique failed. Calcd for $MC_{12}H_{28}N_5S_4O_4$: M=Nd, Nd, 24.92; C, 24.90; H, 4.88; N, 12.10%; M=Eu, Eu, 25.91; C, 24.57; H, 4.81; N, 11.94%. Found: M=Nd, Nd, 24.98; C, 25.15; H, 5.05; N, 12.12%; M=Eu, Eu, 25.85; C, 24.57; H, 4.75; N, 11.78%.

Single Crystal X-Ray Structure Analysis. The crystal of **2** used for a structure analysis was pale violet in color, and parallelepiped in shape (0.30×0.30×0.28 mm^3); that of **3** was colorless and in a similar shape (0.29×0.29×0.29 mm^3). The intensities in the range $3<2\theta<50°$ (2θ) were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer using graphite monochromated Mo $K\alpha$ radiation (λ= 0.71073 Å) by means of a ω–2θ scan technique (scan speed, 4° min^{-1} (ω); scan width (ω), 1.07+0.35tanθ° for **2**, and 1.15+0.35tanθ° for **3**). The intensities were corrected for Lorentz and polarization factors, but not for absorption or extinction. Of 8576 independent intensities collected, 6453 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination of **2**, and 6438 in 8465 reflections for that of **3**.

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.[9] The scattering factors were taken from Ref. 10.

The structure of **2** was solved by the heavy-atom method, and the positional and thermal parameters were refined by a block-diagonal least-squares method. No hydrogen atom was included in the structure factor calculations. The structure of **3** was refined in the same way, starting from the final values of **2**. At the final stage of the refinement, the shifts of the parameters were less than one third of the corresponding standard deviations. The final R values applying anisotropic temperature factors were 0.040 (R_w=0.052) for **2**, and 0.055 (R_w=0.061) for **3**.[11]

If only complex anions were considered, the centers of symmetry of the crystal exist at the middle points of both pairs of the respective kinds of complex metal atoms, Nd(1) and Nd(2). The tetraethylammonium ions centered by the N(3) atoms are also distributed so as to take the same positions as the centers of symmetry. On the other hand, the central nitrogen atoms, N(4) and N(5), of the other two kinds of tetraethylammonium ions exist just at the centers of symmetry. As these cations were found not to be cetrosymmetric, we had to assume that the respective eight ethyl carbon atoms around each central nitrogen atom were disordered at two positions with equal occupancy factors. On the calculation, the positions of the N(4) and N(5) atoms were fixed at 0.5, 0.5, 0.5 and 0.5, 0, 0.5, respectively.

Results and Disccusion

Selected bond lenghts of **2** and **3** are shown in Table 1. A perspective drawing of a complex centered by the Nd(1) atom is shown Fig. 1, and a projection of the unit cell of the neodymium complex along the c-axis is shown in Fig. 2.[1)]

There are two kinds of crystallographically independent complexes; however, they are approximately in the same form. All the complexes are in a square-

Table 1. Selected Bond Lengths (l/Å) of the Complexes, with the Standard Deviations in Parentheses

M=	Nd	Eu	M=	Nd	Eu
M(1)-N(11)	2.504(8)	2.453(11)	M(1)-O(11)	2.457(7)	2.403(9)
M(1)-N(12)	2.504(7)	2.455(10)	M(1)-O(12)	2.470(9)	2.424(12)
M(1)-N(13)	2.493(7)	2.445(10)	M(1)-O(13)	2.492(8)	2.442(11)
M(1)-N(14)	2.505(8)	2.470(10)	M(1)-O(14)	2.465(8)	2.420(11)
M(2)-N(21)	2.486(11)	2.46(2)	M(2)-O(21)	2.454(7)	2.392(9)
M(2)-N(22)	2.503(7)	2.455(9)	M(2)-O(22)	2.468(7)	2.418(10)
M(2)-N(23)	2.498(8)	2.450(10)	M(2)-O(23)	2.485(6)	2.428(7)
M(2)-N(24)	2.503(9)	2.459(13)	M(2)-O(24)	2.493(9)	2.444(12)

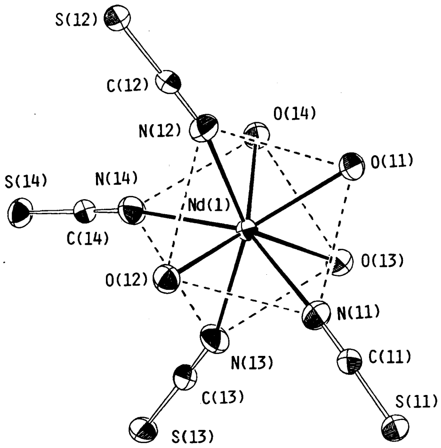

Fig. 1. Perspective drawing of the neodymium(III) complex anion centered by Nd(1) atom, with the numbering scheme of the atoms: 30% probability ellipsoids are shown for the atoms in the figure.

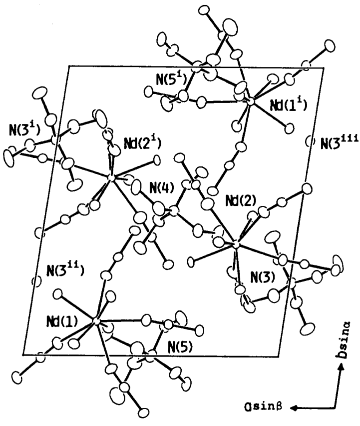

Fig. 2. A projection of the unit-cell of the neodymium(III) complex along c-axis. The numbering of the metal and the tetraethylammonium nitrogen atoms are also shown. Only one in possible two arrangements are shown for the tetraethylammonium carbon atoms around the N(4) and N(5) atoms, respectively. The carbon atoms around the N(3^{ii}) and N(3^{iii}) atoms are not shown. Key to the symmetry operations: i, $1-x$, $1-y$, $1-z$; ii, $1+x$, y, z; iii, $-x$, $1-y$, $1-z$.

antiprism 4*N*,4*O*-octa-coordination. On a top square of each coordination polyhedron, the two N atoms as well as the two O atoms take a cis configuration, respectively, while on the bottom square they take a trans configuration: the lines through two N atoms on the respective faces are approximately parallel. The mean squares planes of the respective four atoms at the apexes of the top and the bottom squares of each coordination polyhedron are nearly parallel (dihedral angles are: 3.5, 3.2° for **2**, and 2.7, 3.1° for **3**). As shown in Table 1, the M-N and the M-O bond lengths of **2** and **3** are distributed over a relatively wide range, and the longest or shortest members are not always the same in both complexes.

The average of the eight bond lengths are: **2**, Nd-N, 2.500 (2.486(11)—2.504(8)); Nd-O, 2.473 (2.454(7)—2.493(9)) Å; **3**, Eu-N, 2.456 (2.445(9)—2.470(10)); Eu-O, 2.421 (2.392(9)—2.444 (12)) Å. These M-N(SCN) and M-O(H_2O) bond lengths are not much different from the corresponding ones of the related compounds.[4,5,13] However, as mentioned above, in **2** and **3** the average M-O bond length is a little shorter than the average M-N length in each complex. This tendency is also found in the tetramethylammonium salts, $[(CH_3)_4N]_3[M(SCN)_6(CH_3OH)(H_2O)]$, (M=La through Er), which are also in the square antiprism coordination geometry.[13] On the other hand, in **4** and **5**, although the anionic complexes have the same chemical composition and the coordination geometry, their M-O(H_2O) is reported to be longer than M-N(SCN) in each complex.[5] Probably this fact is caused by the types of counter cations. Since the tetramethyl- and tetraethylammonium ions are surrounded by hydrocarbon groups, they are less polar than the potassium ions.

The average M-N-C and N-C-S angles are: **2**, 163.4 (158.4(9)—170.5(5)) and 178.8 (177.3(6)—179.5(7))°; **3**, 164.3 (157.6(14)—171.6(8)) and 178.2 (176.8(10)—178.8(11))°, respectively.

In the crystals of **2** and **3** the metal atoms are arranged approximately on lines parallel to the b-axis (intersecting the ac-plane at about 0.25, 0, 0, and 0.75, 0, 0). The dihedral angles between the top or the bottom square planes of the coordination polyhedrons and the ab-plane are small (**2**, 10.4—14.2; **3**, 10.9—14.0°). The N atoms of the counter cations are also arranged approximately on lines parallel to the b-axis, intersecting the ac-plane at about 0, 0, 0.5 and 0.5, 0, 0.5). Thus, in the crystal, the layers of the anions and the cations are piled alternately along the a-axis as well as c-axis.

References

1) A. F. Wells, "Structural Inorganic Chemistry," 5th ed, Clarendon Press, Oxford, U. K. (1984), p. 935.

2) K. Vrieze and G. van Koten, "Comprehensive Coordination Chemistry," ed by Sir G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, U. K. (1987), Vol. 2, p. 225.

3) J. L. Martin, L. C. Thompson, L. J. Radonovich, and M. D. Glick, *J. Am. Chem. Soc.*, **90**, 4493 (1968).

4) Y. Tateyama, Y. Kuniyasu, Y. Suzuki, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **61**, 2805 (1988).

5) P. I. Lazarev, L. A. Aslanov, V. M. Ionov, and M. A. Porai-Koshits, *Koord. Khim.*, **1**, 710 (1975), also *Struct. Report*, **41A**, 210 (1975).

6) G. Thiele and D. Messer, *Z. Anorg. Allg. Chem.*, **464**, 255 (1980).

7) Y. Kuniyasu, Y. Suzuki, M. Taniguchi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 179 (1987).

8) M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **62**, 424 (1989).

9) "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

10) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp, 72, 150.

11) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, where $w=1/[\{\sigma(|F_o|)\}^2+(F_w \times F_o)^2]$, $F_w=0.02$ for **2**, and 0.025 for **3**. (F_w values were tried to move between 0.015 and 0.04, and the used values were found to be the best ones, respectively).

12) The final atomic positional, equivalent isotropic and anisotropic thermal parameters, final F_o-F_c tables of the complex, the perspective drawings of the complex around the Nd(2) atom and of the unit cell, and some bond lengths and bond angles data are deposited as Document No. 8885 at the Office of the Editors of *Bull. Chem. Soc. Jpn.*

13) F. Matsumoto, N. Matsumura, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **62**, 1809 (1989).