NOTES *Bull. Chem. Soc. Jpn.*, **54**, *1567—1568 (1981)*

Structure of the Complex of Neodymium Nitrate with Pentaethylene Glycol

Yoshiyuki HIRASHIMA,* Koji KANETSUKI, Jiro SHIOKAWA, and Nobuo TANAKA**
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka 565
***Institute for Protein Research, Osaka University, Yamada-kami, Suita, Osaka 565*

(Received September 12, 1980)

Synopsis. Crystals of the complex, $Nd(NO_3)_3$–HO-$(CH_2CH_2O)_5H$, are monoclinic. The Nd atom is coordinated by ten oxygen atoms, four from two bidentate nitrate ions and six from a pentaethylene glycol. The pentaethylene glycol forms a ring-like structure similar to that of crown compounds.

The preparation of the solid complexes of lanthanoid ions with macrocyclic polyethers was reported,[1–4] some structures being determined by X-ray crystallography.[5–7] It was found that some noncyclic polyethers form solid complexes with lanthanoid nitrates, their stability appearing to decrease with increasing atomic number of the lanthanoid in contrast to the lanthanoid complexes of most ligands.[8] This behavior is similar to that of the complexes of 18-crown-6,[9] and might be related to the structures of the complexes. X-Ray diffraction studies were carried out on the structure of the complex of pentaethylene glycol (denoted by EO5) with neodymium nitrate, the results of which are given in this report.

Crystals suitable for X-ray study were obtained by adding a dilute ethyl acetate solution of neodymium nitrate to an ethyl acetate solution of EO5 and then standing the resulting solution for crystal deposit.

Crystal data: $Nd(NO_3)_3\cdot(C_{10}H_{22}O_6)$, F.W.=568.5, monoclinic, space group $P2_1/n$, $a=8.220(2)$ Å, $b=15.072(3)$ Å, $c=17.089(4)$ Å, $\beta=110.80(2)°$, $V=1979.2(6)$ Å^3, $D_{calcd}=1.91$ g cm^{-3} for $Z=4$, $D_{obsd}=1.90$ g cm^{-3}, μ(Mo $K\alpha$)$=27.2$ cm^{-1}.

A crystal was sealed in a 1 mm diam. glass capillary because of its deliquescence. Intensity data were collected with a Rigaku automated four-circle diffractometer using β-filtered Mo $K\alpha$ radiation. The 2θ-ω scan technique was employed with a scan speed 4°/min on 2θ. A scan range of 1.4° plus θ-dependent dispersion term was used. A total of 4189 reflections were obtained. Net intensities of 1354 reflections were observed as zero. Lorentz and polarization corrections, but no absorption correction, were made.

The structure was solved by the heavy atom method, the atomic parameters except for the hydrogen atoms being refined by the block diagonal least squares method.[10] The weighting scheme applied was as follows, $w=1$ if $|F_o|>2.5$; $w=0.3$ if $|F_o|<2.5$. After several cycles of the calculation with anisotropic temperature factors, the R factor was converged to 0.11.

Figure 1 shows the structure of the complex $Nd(NO_3)_3\cdot HO(CH_2CH_2O)_5H$. The bond lengths and bond angles are given in Table 1.[†]

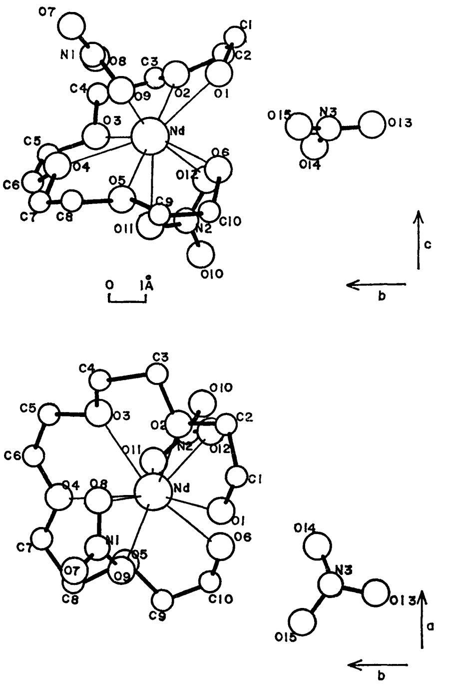

Fig. 1. Structure of $Nd(NO_3)_3\cdot$EO5.
Top: Projection along [001]. Bottom: Projection onto [001].

The Nd atom is coordinated by ten oxygen atoms, four from two nitrate ions and six from a pentaethylene glycol (EO5). The coordination polyhedron is similar to that based on bicapped-dodecahedron,[11] though it is irregular. The pentaethylene glycol acts as a hexadentate ligand forming a ring-like structure with its oxygen atoms. The ring-like structure is similar to the structure of so-called crown compounds. The six oxygen atoms of EO5 are not quite coplanar, their shifts from the mean plane being in the range 0.03—0.83 Å. The Nd atom is located near the center of the hexagon of the oxygen atoms of EO5. The angles of O_i–Nd–O_{i+1} ($i=1$—5) are close to 60° (60—63°), while the angle of O_1–Nd–O_6 is 67° a little higher than the others. This can be attributed to the large shifts of the two terminal oxygen atoms from the mean plane (0.64 and 0.83 Å). Above and below this mean plane two nitrate ions coordinate to a Nd atom as a bidentate ligands. The angle of N_1–Nd–N_2 is 169°, the bi-capped units being slightly distorted from the ideal form. A third nitrate ion does not coordinate to a Nd atom (the nearest Nd–O distance: 4.6 Å).

The average Nd–O bond length is 2.54 Å, which is between the bond lengths of La–O and Tb–O (2.6

[†] The complete F_o-F_c data and the table of atomic parameters are deposited as Document No. 8122 at the Chemical Society of Japan.

TABLE 1. BOND LENGTHS(l/Å) AND ANGLES(θ/°) IN THE $Nd(NO_3)_3$·EO5 COMPLEX

Nd-O bond		N-O bond		C-C or C-O bond		C-C-O or C-O-C angle		O-N-O angle	
Nd-O (1)	2.49(1)	N (1)-O (7)	1.21(2)	C (1)-C (2)	1.46(5)	O (1)-C (1)-C (2)	113(3)	O (7)-N (1)-O (8)	123(2)
Nd-O (2)	2.55(2)	N (1)-O (8)	1.23(2)	C (3)-C (4)	1.57(4)	C (1)-C (2)-O (2)	108(3)	O (7)-N (1)-O (9)	121(2)
Nd-O (3)	2.58(2)	N (1)-O (9)	1.28(2)	C (5)-C (6)	1.36(6)	O (2)-C (3)-C (4)	105(2)	O (8)-N (1)-O (9)	116(2)
Nd-O (4)	2.62(2)	N (2)-O (10)	1.20(3)	C (7)-C (8)	1.38(5)	C (3)-C (4)-O (3)	108(2)	O (10)-N (2)-O (11)	123(2)
Nd-O (5)	2.62(2)	N (2)-O (11)	1.23(2)	C (9)-C (10)	1.43(4)	O (3)-C (5)-C (6)	118(4)	O (10)-N (2)-O (12)	122(2)
Nd-O (6)	2.48(2)	N (2)-O (12)	1.26(2)			C (5)-C (6)-O (4)	114(4)	O (11)-N (2)-O (12)	115(2)
Nd-O (8)	2.55(2)	N (3)-O (13)	1.23(3)	O (1)-C (1)	1.41(4)	O (4)-C (7)-C (8)	114(3)	O (13)-N (3)-O (14)	123(2)
Nd-O (9)	2.47(1)	N (3)-O (14)	1.22(3)	C (2)-O (2)	1.36(4)	C (7)-C (8)-O (5)	109(3)	O (13)-N (3)-O (15)	117(2)
Nd-O (11)	2.52(2)	N (3)-O (15)	1.25(3)	O (2)-C (3)	1.48(4)	O (5)-C (9)-C (10)	114(3)	O (14)-N (3)-O (15)	121(2)
Nd-O (12)	2.52(2)			C (4)-O (3)	1.41(4)	C (9)-C (10)-O (6)	114(2)		
				O (3)-C (5)	1.38(5)				
				C (6)-O (4)	1.35(5)	C (2)-O (2)-C (3)	114(2)		
				O (4)-C (7)	1.45(4)	C (4)-O (3)-C (5)	109(2)		
				C (8)-O (5)	1.41(4)	C (6)-O (4)-C (7)	109(3)		
				O (5)-C (9)	1.43(4)	C (8)-O (5)-C (9)	116(2)		
				C (10)-O (6)	1.43(3)				

TABLE 2. TORSION ANGLES(ϕ/°) IN THE PENTAETHYLENE GLYCOL

O (1)-C (1)-C (2)-O (2)	47	C (1)-C (2)-O (2)-C (3)	160	C (2)-O (2)-C (3)-C (4)	−172
O (2)-C (3)-C (4)-O (3)	−51	C (3)-C (4)-O (3)-C (5)	−170	C (4)-O (3)-C (5)-C (6)	−154
O (3)-C (5)-C (6)-O (4)	27	C (5)-C (6)-O (4)-C (7)	−174	C (6)-O (4)-C (7)-C (8)	165
O (4)-C (7)-C (8)-O (5)	−43	C (7)-C (8)-O (5)-C (9)	−160	C (8)-O (5)-C (9)-C (10)	−179
O (5)-C (9)-C (10)-O (6)	33				

and 2.47 Å, respectively) reported for bis(bipyridyl)-trinitratolanthanoids which are decacoordinate complexes.[11,12] The sequence of the bond lengths is reasonable in view of the expected contraction in radius for the lanthanoid series.

The tortion angles in EO5 are given in Table 2. The conformation around the CH_2–CH_2 bonds are all nearly gauche, while those around the CH_2–O bonds are all approximately trans. The conformation for CH_2–CH_2–O–CH_2–CH_2–O–CH_2 is GTT$\overline{\text{G}}$TT, which was reported by Iwamoto[13] to be the most stable conformation, where T, G, $\overline{\text{G}}$ denote trans, gauche, and minus gauche, respectively. Some of the angles around the CH_2–CH_2 bonds are considerably lower than 60°. The deviation can be attributed to the deformation of the EO5 molecule from the ideal form in order to maintain the Nd–O distances at suitable lengths for coordination.

References

1) R. B. King and P. R. Heckley, *J. Am. Chem. Soc.*, **96**, 3118 (1974).

2) M. Ciampolini and N. Nardi, *Inorg. Chim. Acta*, **32**, L9 (1979).

3) A. Cassol, A. Seminaro, and G. De Paoli, *Inorg. Nucl. Chem. Lett.*, **9**, 1163 (1973).

4) J.-C. G. Bünzli and D. Wessner, *Helv. Chim. Acta*, **61**, 1454 (1978).

5) M. E. Harman, F. A. Hart, M. B. Hursthouse, G. P. Moss, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, **1976**, 396.

6) M. Ciampolini, P. Dapporto, and N. Nardi, *J. Chem. Soc., Dalton Trans.*, **1979**, 974.

7) J.-C. G. Bünzli, B. Klein, and D. Wessner, *Inorg. Chim. Acta*, **44**, L147 (1980).

8) Y. Hirashima and J. Shiokawa, *Chem. Lett.*, **1979**, 463.

9) R. M. Izatt, J. D. Lamb, and J. J. Christensen, *J. Am. Chem. Soc.*, **99**, 8344 (1977).

10) T. Ashida, "The Universal Crystallographic Computing System-Osaka," The computation Center, Osaka University (1973), p. 55.

11) A. R. Al-Karaghouli and J. S. Wood, *Inorg. Chem.*, **11**, 2293 (1972).

12) D. S. Moss and S. P. Sinha, *Z. Phys. Chem.*, **63**, 391 (1969).

13) R. Iwamoto, *Bull. Chem. Soc. Jpn.*, **46**, 1144 (1973).