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X-RAY STRUCTURE ANALYSIS OF NEODYMIUM NITRATE COMPLEX WITH TRIETHYLENE GLYCOL

Yoshiyuki HIRASHIMA,* Toshiyuki TSUTSUI, and Jiro SHIOKAWA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamada-oka, Suita, Osaka 565

Neodymium atom is decacoordinated with oxygen atoms in the title complex, where triethylene glycol forms a ring-like structure with a bidentate nitrate. The distances between a neodymium atom and the coordinated oxygen atoms are somewhat shorter than those in the complexes with tetraethylene glycol and pentaethylene glycol.

It has been reported that some polyethylene glycols (noncyclic polyethers) form solid complexes with lanthanoid nitrates.$^{1)}$ According to the X-ray structure analyses of the complex of neodymium nitrate with tetraethylene glycol(EO4) and that with pentaethylene glycol(EO5),$^{2,3)}$ both polyethylene glycols form ring-like structures with their oxygen atoms inside, coordinating to the neodymium atoms as multi-dentate ligands. The ring-like structures are similar to those of crown compounds.$^{4-7)}$ The coordination number of neodymium is ten in both complexes in spite of the difference of the number of oxygen atoms between EO4 and EO5. It is interesting to investigate the structure of the complexes of lanthanoid nitrates with triethylene glycol(EO3) in order to see if a ring-like structure is likewise formed in the complex of EO3 which has only four oxygen atoms. This letter reports the results of the X-ray structure analysis of the complex of neodymium nitrate with triethylene glycol.

Single crystals were prepared by the following procedure: an ethyl acetate solution of hydrated neodymium nitrate(50 mmol/dm^3) was mixed with an equal volume of ethyl acetate solution of EO3(50 mmol/dm^3). The resulting solution was dehydrated partially by refluxing through a molecular sieves layer until the deposition of a few crystals was observed, and then allowed to stand. The single crystal used for X-ray analysis was a hexagonal prism with the edges of about 0.13 mm. The crystal was placed in a 0.7 mm diameter glass capillary. Crystal data; $Nd(NO_3)_3 \cdot HO(CH_2CH_2O)_3H$, F.W. = 480.46, monoclinic, space group $P2_1/n$, $a = 14.815(5)$, $b = 9.371(2)$, $c = 12.389(3)$ Å, $\beta = 117.27(2)°$, $V = 1528.8(6)$ Å^3, $d_{obsd} = 2.08$ g cm^{-3}, $d_{calcd} = 2.09$ g cm^{-3} for $Z = 4$, $\mu(MoK\alpha) = 33.31$ cm^{-1}. Intensity data were collected on a Rigaku automated diffractometer with graphite monochromated MoKα radiation using an ω-2θ scan technique with 8°/min in 2θ, 2θ range being 0-50°. The intensities of three standard reflections were monitored every 61 reflections and no significant deviation was observed (less than 1.5%). A total of 2700 unique reflections were obtained, of which 2163 were $|F_o|>0$. Lorentz and polarization corrections were applied, but no absorption one was made. The structure was solved by the heavy atom method, and refined by the block-diagonal least-squares method with HBLS-V program.8) The final R value is 0.095 for the intensities with $|F_o|>0$.

The molecular structure of the neodymium nitrate-triethylene glycol complex is shown in Fig. 1 with atomic numbering.9) A neodymium atom is coordinated with a triethylene glycol(EO3) and three nitrate groups. The three nitrates are all bidentate. The neodymium atom is coordinated with ten oxygen atoms, four from the EO3 and six from three nitrates. The EO3 molecule forms a ring-like structure together with the bidentate nitrate($N(3)O_3$) situated at the open side of the EO3 chain. The neodymium atom lies slightly above the mean plane(<0.05Å) formed by the six coordinated oxygen atoms of the EO3 and the nitrate. Two other nitrates are located above and below the mean plane. The coordination polyhedron is similar to that based on a dodecahedron as in the EO4 and the EO5 complexes of neodymium nitrate.2,3) Two axial nitrates above and below the mean plane, or the ring-like structure, are bidentate in any one of the complexes of neodymium nitrate with EO3, EO4, and EO5, while the other one is bidentate in the EO3 complex, unidentate in the EO4 complex,3) and noncoordinated in the EO5 complex.2) Consequently neodymium atom remains decacoordinated in all the three different complexes in spite of the difference of the number of the coordinating oxygen atoms of the three glycols.

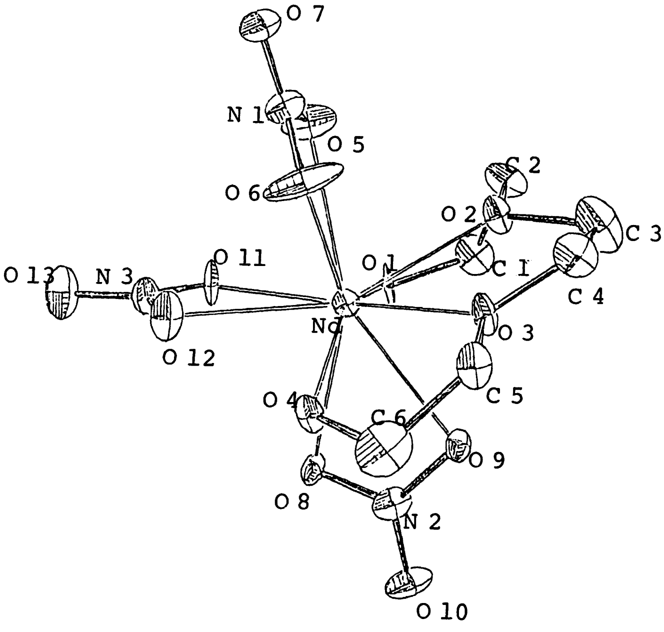

Fig. 1 An ORTEP view of $Nd(NO_3)_3{\cdot}EO3$ complex with atomic numbering

The bond lengths and bond angles are listed in Table 1. The average value of bond lengths between the neodymium atom and the coordinated oxygen atoms is 2.53 Å, being slightly shorter than those in the EO4 and the EO5 complexes (2.57 and 2.54 Å, respectively). The Nd-O distances for the coordinated oxygen atoms (O5, O6, O8, and O9) of the axial nitrates (the mean value : 2.56 Å) are not only longer than those for the oxygen atoms(O1-O4, O11, and O12) which form a hexagon in the present complex (the mean value : 2.51 Å), but also longer than those for the coordinated oxygen atoms of the axial nitrates in the EO4 and the EO5 complexes(2.55 and 2.52 Å, respectively) although the average value of the Nd-O distances for all the coordinated oxygen atoms is shorter in the EO3 complex than in the EO4 and the EO5 complexes. On the other hand the mean values of the Nd-O distances for the oxygen atoms forming hexagons in the complexes with EO3, EO4, and EO5 are 2.51 Å, 2.59 Å, and 2.57 Å, respectively, the difference between them being larger than that for all the coordinated oxygen atoms above described. The shortening of the Nd-O distance in the present complex compared with those in the EO4 and the EO5 complexes may be attributed to the fact that two oxygen atoms of a nitrate take part in forming a hexagon in the complex. The distance between the two coordinated oxygen atoms of the nitrate is 2.13 Å, being rather shorter than those between the other couples of adjacent oxygen atoms(2.6-2.8 Å). This fact makes it possible for the oxygen atoms forming the hexagon to be situated closer to a neodymium atom in the EO3 complex than in the EO4 and the EO5 complexes without causing appreciable strain in the EOn chain.

The angles O-Nd-O for the adjacent oxygen atoms of the hexagon are a little larger than 60° except for that between the oxygen atoms(O11 and O12) of the nitrate, which is 50°. Therefore the hexagon is somewhat distorted. The smaller angle of O11-Nd-O12 is attributed to the smaller distance between the two oxygen atoms compared with those between the other oxygen atoms. The mean values of the lengths of the C-O bonds and the C-C bonds in the EO3 chain are 1.44 Å and 1.52 Å, respectively, being reasonable ones. The angles of C-O-C and C-C-O in the EO3 chain are 110.3-115.9° and 101.5-118.1°, respectively. Both angles are close to the regular tertahedral angle. Four oxygen atoms of EO3 are not entirely coplanar, but the shift of each oxygen atom from the square mean plane is little (less than 0.22 Å). Each of three nitrates is almost planar, but they show a little departure from the idealized C_{2v} local symmetry which is expected for bidentate nitrates. The three planes formed by the nitrates are nearly perpendicular to one another : the angles between them are 84.0-106.7°. The tortion angles in the EO3 chain are listed in Table 2. The *gauche* and *trans* conformations were

Table 1. Interatomic distances(ℓ/Å) and bond angles(θ/°) in the complex $Nd(NO_3)_3 \cdot EO3$

Nd - O1	2.49(3)	O1 - C1	1.42(6)	N1 - O5	1.29(5)	O1 - C1 - C2	108(4)
Nd - O2	2.50(3)	C1 - C2	1.48(7)	N1 - O6	1.24(6)	C1 - C2 - O2	106(4)
Nd - O3	2.54(3)	C2 - O2	1.50(5)	N1 - O7	1.22(5)	C2 - O2 - C3	110(3)
Nd - O4	2.50(3)	O2 - C3	1.54(7)			O2 - C3 - C4	102(4)
		C3 - C4	1.51(8)	N2 - O8	1.22(4)	C3 - C4 - O3	118(4)
Nd - O5	2.55(4)	C4 - O3	1.43(6)	N2 - O9	1.30(4)	C4 - O3 - C5	116(3)
Nd - O6	2.57(5)	O3 - C5	1.38(5)	N2 - O10	1.20(5)	O3 - C5 - C6	113(4)
		C5 - C6	1.56(8)			C5 - C6 - O4	109(4)
Nd - O8	2.55(2)	C6 - O4	1.39(7)	N3 - O11	1.24(5)		
Nd - O9	2.57(2)			N3 - O12	1.28(5)	O5 - N1 - O6	113(4)
				N3 - O13	1.25(5)	O6 - N1 - O7	123(4)
Nd - O11	2.54(3)					O7 - N1 - O5	123(4)
Nd - O12	2.51(3)						
						O8 - N2 - O9	115(3)
				O1 - Nd - O2	63(2)	O9 - N2 - O10	122(3)
				O2 - Nd - O3	63(2)	O10 - N2 - O8	123(4)
				O3 - Nd - O4	63(2)		
				O4 - Nd - O12	69(3)	O11 - N3 - O12	116(4)
				O12 - Nd - O11	50(2)	O12 - N3 - O13	121(4)
				O11 - Nd - O1	65(3)	O13 - N3 - O11	122(4)

Table 2. Tortion angles(ϕ/°) in the EO3 molecule

O1 - C1 - C2 - O2	51	C1 - C2 - O2 - C3	114
O2 - C3 - C4 - O3	31	C2 - O2 - C3 - C4	175
O3 - C5 - C6 - O4	30	C3 - C4 - O3 - C5	165
		C4 - O3 - C5 - C6	192

reported to be the most stable ones for the C-C and C-O bonds, respectively, in the complexes of polyoxyethylene derivatives.[10] Some of the tortion angles in the EO3 chain are appreciably smaller than 60°(*gauche* angle) for the O-C-C-O bonds or smaller than 180°(***trans*** angle) for the C-O-C-C bonds. Though similar deviation is observed also for the EO4 and EO5 complexes, the deviation is more remarkable in the present complex. The enhancement of the deviation is attributed to the closer approach of the coordinated oxygen atoms to a neodymium atom in the present complex.

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