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X-RAY CRYSTAL STRUCTURE OF NEODYMIUM NITRATE COMPLEX WITH TETRAETHYLENE GLYCOL

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Neodymium atom is decacoordinated with oxygen atoms in the title complex, where tetraethylene glycol acts as a pentadentate ligand, forming a ring-like structure together with a unidentate nitrate. Two bidentate nitrates coordinate to neodymium atom from above and below the plane formed by tetraethylene glycol.

Preparation of lanthanoid complexes with macrocyclic polyethers, crown compounds, has been reported,$^{1-6)}$ and some structures were determined.$^{7-10)}$ It has been reported that some polyethylene glycols(noncyclic polyethers) form solid complexes with lanthanoids, too.$^{11)}$ The structure of the complex of neodymium nitrate with pentaethylene glycol was determined by X-ray crystal analysis.$^{12)}$ In the complex pentaethylene glycol has a ring-like structure, coordinating to the neodymium atom as a hexadentate ligand. It is interesting to investigate the structures of the lanthanoid complexes with polyethylene glycols other than pentaethylene glycol. This letter reports the results of the X-ray analysis of the complex, $Nd(NO_3)_3 \cdot HO(CH_2CH_2O)_4H$.

The crystals for X-ray analysis were prepared by mixing 5 ml of 5 mM ethyl acetate solution of hydrated neodymium nitrate and an equal volume of 5 mM ethyl acetate solution of tetraethylene glycol, and then by allowing the resulting solution to stand. A 0.2×0.13×0.13 mm^3 crystal was placed in a 0.7 mm diameter glass capillary because of its deliquescence. Crystal data: $Nd(NO_3)_3 \cdot HO(CH_2CH_2O)_4H$, F.W. = 524.52, monoclinic, space group $P2_1/n$, a = 8.125(1) Å, b = 16.808 Å, c = 12.742(1) Å, β = 101.02(1)°, V = 1708.2(4) Å^3, d_{obsd} = 2.03 gcm^{-3}, d_{calcd} = 2.04 gcm^{-3} for Z = 4, μ(MoKα) = 31.40 cm^{-1}. Intensity data were collected on a Rigaku automated diffractometer with graphite monochromated MoKα radiation using an ω-2θ scan technique with 4°/min along the 2θ axis, 2θ range being 0°-55°. The intensities of three standard reflections were monitored after every 63 reflections and no significant deviation was observed (less than 1.5%). A total of 2932 unique reflections were obtained, of which 1857 reflections were $F_o > 3\sigma(F_o)$. 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.$^{13)}$ The final R value is 0.047 for the data with $F_o > 3\sigma(F_o)$.

A view of the neodymium nitrate-tetraethylene glycol complex is shown in

Fig. 1 with atomic numbering.[14] Neodymium atom is decacoordinated with five oxygen atoms of a tetraethylene glycol (denoted by EO4 hereafter) and five oxygen atoms of two bidentate nitrates and a unidentate nitrate. The coordination polyhedron is similar to that based on a bicapped dodecahedron[15] as in the pentaethylene glycol (denoted by EO5 hereafter) complex.[12] Three nitrates are all bonded to neodymium atom in the EO4 complex, while one of three nitrates is not bonded in the EO5 complex as was reported.[12] Two bidentate nitrates coordinate to neodymium atom from above and below the plane formed by EO4 molecule. Third nitrate coordinates to neodymium atom from the open side of the EO4 chain, acting as a unidentate ligand. EO4 molecule acts as a pentadentate ligand, forming a ring-like structure similar to that in the EO5 complex, though a coordinated oxygen of the unidentate nitrate is situated in a corner of the hexagon formed by the oxygen atoms. The coordination of the third, unidentate nitrate results in the formation of the coordination polyhedron similar to that of EO5 complex in spite of the difference of the number of oxygen atoms between EO4 and EO5.

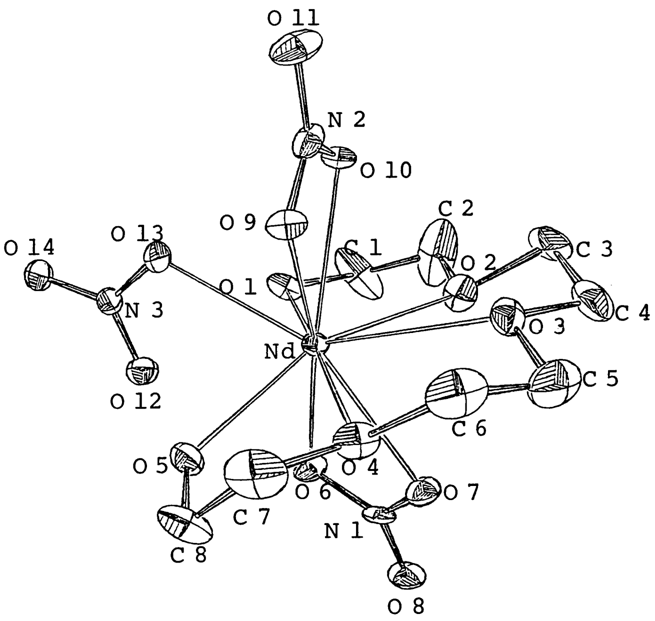

Fig. 1 An ORTEP view of $Nd(NO_3)_3 \cdot EO4$ with atomic numbering

The bond lengths and bond angles are listed in Table 1. The distances between oxygen atoms and neodymium atom range from 2.48 to 2.70 Å, the mean value being 2.57 Å. The distance is slightly longer than that in the EO5 complex (2.47-2.62 Å, mean 2.54 Å). The mean Nd-O distance is shorter for the terminal, hydroxyl oxygens than that for the ethereal oxygens (2.51 Å as compared with 2.65 Å) probably due to the higher electron density on the hydroxyl oxygens. The distance between Nd and O_{12}, one of uncoordinated oxygen atoms of a unidentate nitrate, is rather short compared with those between neodymium and the other uncoordinated oxygen atoms, though it is too long for coordination. Each of three nitrates is nearly planar: the shifts of the atoms of each nitrate from the mean plane are less than 0.008 Å. In the infrared spectrum of the present complex, the absorption band of free nitrate ($\sim$1380 cm^{-1}) was not observed and its splitting into two bands (1290 cm^{-1} and 1510 cm^{-1}) was observed. Only two combination bands (1745 cm^{-1} and 1780 cm^{-1}) were observed in the region from 1700 to 1800 cm^{-1} though four combination bands are expected to be observed when both bidentate and unidentate nitrates are present.[16] These results indicate the presence of coordinated nitrates and the absence of free nitrate, being in coincidence with the determined structure above described, however affords no evidence for distinguishing between two distinct types of nitrates, bidentate and unidentate ones. Table 1 shows that each bidentate nitrate has the feature of C_{2v} symmetry, that is, the N-O bond distance to the uncoordinated oxygen is shorter and the angle O-N-O involving both coordinated oxygens is smaller than 120°. The unidentate nitrate has a similar feature, as if it were a bidentate nitrate. It may be related to the rather short distance between Nd and O_{12}. These results are in agreement with infrared spectrum, showing no evidence of the presence of both bidentate and unidentate nitrates.

The EO4 molecule forms a ring-like structure with its oxygen atoms inside. Five oxygen atoms of EO4 are not quite coplanar, but their shifts from the least square plane of themselves are smaller than 0.34 Å. Neodymium atom lies out of this plane by 0.29 Å. The angles O-C-C and C-O-C are in the range of 107-116°, being close to the regular tetrahedral angle. The average bond length of C-C is 1.40(4) Å, being rather short for the bond length of single bond C-C, especially C1-C2 distance is abnormally short. The thermal vibrational parameters of C1 and C2 atoms are rather large. Probably the presence of a partial disorder and/or thermal vibration cause the apparent shortening of the bond length. Similar bond shortening has been observed and discussed for several complexes of crown compounds and for a polyethylene glycol complex.[17-20] The tortion angles in the EO4 chain are listed in Table 2. The *trans* and *gauche* conformations were reported to be most stable ones for C-O and C-C bonds, respectively, in the complexes of polyoxyethylene compounds.[21] In the present complex the tortion angles around the C-O bonds are all close to 180°, indicating that those bonds are

Table 1. Interatomic distances(l/Å) and bond angles(θ/°) in the complex

Nd - O1	2.547(9)	O1 - C1	1.47(2)	N1 - O6	1.265(13)	O1 - C1 - C2	116(2)
Nd - O2	2.607(10)	C1 - C2	1.32(3)	N1 - O7	1.255(13)	C1 - C2 - O2	115(2)
Nd - O3	2.645(9)	C2 - O2	1.39(3)	N1 - O8	1.214(14)	C2 - O2 - C3	109(2)
Nd - O4	2.696(9)	O2 - C3	1.45(2)			O2 - C3 - C4	107(1)
Nd - O5	2.481(9)	C3 - C4	1.44(3)	N2 - O9	1.262(13)	C3 - C4 - O3	110(1)
		C4 - O3	1.41(2)	N2 - O10	1.266(13)	C4 - O3 - C5	110(1)
Nd - N1	3.000(10)	O3 - C5	1.47(2)	N2 - O11	1.204(14)	O3 - C5 - C6	107(2)
Nd - O6	2.576(8)	C5 - C6	1.42(3)			C5 - C6 - O4	108(2)
Nd - O7	2.538(9)	C6 - O4	1.45(2)	N3 - O12	1.264(13)	C6 - O4 - C7	113(1)
		O4 - C7	1.42(2)	N3 - O13	1.262(13)	O4 - C7 - C8	109(1)
Nd - N3	3.164(10)	C7 - C8	1.43(2)	N3 - O14	1.208(13)	C7 - C8 - O5	108(1)
Nd - O12	2.905(9)	C8 - O5	1.48(2)				
Nd - O13	2.525(8)					O6 - N1 - O7	115(1)
						O7 - N1 - O8	123(1)
						O6 - N1 - O8	122(1)
						O9 - N2 - O10	117(1)
						O10 - N2 - O11	121(1)
						O9 - N2 - O11	122(1)
						O12 - N3 - O13	116(1)
						O13 - N3 - O14	121(1)
						O12 - N3 - O14	123(1)

Table 2 Totion angles(ϕ/°) for EO4 molecule

O1 - C1 - C2 - O2	35.8	C1 - C2 - O2 - C3	194.6
O2 - C3 - C4 - O3	55.1	C2 - O2 - C3 - C4	188.1
O3 - C5 - C6 - O4	58.8	C3 - C4 - O3 - C5	181.8
O4 - C7 - C8 - O5	45.5	C4 - O3 - C5 - C6	175.5
		C5 - O6 - O4 - C7	170.2
		C6 - O4 - C7 - C8	186.7

nearly *trans*. The angles around C3-C4 and C5-C6 bonds are close to 60°, indicating that those bonds are approximately *gauche*, while the angles around C1-C2 and C7-C8 bonds are rather small. The deviation is attributed to the repulsion between the terminal hydroxyl groups and the monodentate nitrate.

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