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Lanthanoid Nitrate Complexes with Some Polyethylene Glycols and Glymes

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Lanthanoid nitrates($Ln(NO_3)_3$) formed solid complexes with several polyethylene glycols and glymes. The compositions of the complexes were 1:1 (Ln:ligand) for triethylene glycol(EO3), tetraethylene glycol(EO4), pentaethylene glycol(EO5), and tetraglyme, 1:2 (Ln:ligand) for diethylene glycol, 2:1 for heptaethylene glycol, and 4:3 for pentaglyme and hexaglyme. Solid complexes were deposited also for hexaethylene glycol, but their compositions were not definitely determined. The solid complexes obtained here were all deliquescent. The deposition of the complexes was generally interfered with by water in the solution, and was not observed for some heavier lanthanoids when a small amount of water was present in the solution. The solubilities of the solid complexes with EO4 and EO5 increased with an increase in the atomic number of the lanthanoid, a fact suggesting a unique selectivity of the glycols. The infrared absorption bands of polyethylene glycols or glymes in the 1000—1150 cm^{-1} region became sharper upon the complexing of the glycols or glymes with lanthanoids; this sharpening can be explained by the change in the conformations in the ligand molecules.

Macrocyclic polyethers, so-called crown ethers, have been reported to form complexes with several cations.[1—4] The lanthanoid complexes of crown ethers have been reported, too.[5—8] King and Heckley suggested the possibility of the separation of lanthanoids by using crown ethers.[6] On the other hand, Yanagida *et al.* have reported the complexation of alkali and alkaline earth metals with noncyclic polyethers, polyethylene glycols and glymes.[9—11] Vögtle *et al.* have investigated the complexes of several noncyclic poly(oxyethylene) derivatives, which they call noncyclic crown ethers.[12—15] The lanthanoid complexes of polyethylene glycols have been reported by the present authors;[16] X-ray structure analyses indicate that polyethylene glycol molecules in the complexes assume ring-like structures similar to those of crown ethers,[17—19] suggesting that polyethylene glycols may have unique selectivities. The separation of lanthanoids with tetraethylene glycol by means of a fractional precipitation has been attempted on the basis of the fact that the yield of the lanthanoid complexes decreases as the atomic number of the lanthanoid increases.[20] Thus, polyethylene glycols may be promising reagents for the separation of lanthanoids. In the present work, lanthanoid complexes with several polyethylene glycols and glymes were isolated, and their properties were investigated.

Experimental

Materials. The lanthanoid nitrates were prepared by dissolving the corresponding oxides(>99.9% purity, Shin-Etsu Chemical Industry Co., Ltd.) into an excess of nitric acid. The solutions were concentrated on sand baths and then allowed to stand until the salts were deposited. The salts were dried at about 70 °C *in vacuo* for 6 h. The numbers of the hydrating water were 5—7.

The polyethylene glycols($HO(CH_2CH_2O)_nH$, EO*n*) and polyethylene glycol dimethyl ethers($CH_3O(CH_2CH_2O)_nCH_3$, glymes) used in this investigation were as follows: diethylene glycol (EO2, Wako Pure Chemicals Industries, Ltd.); triethylene glycol (EO3, Wako Pure Chemicals Industries, Ltd.); tetraethylene glycol(EO4, Tokyo Kasei Kogyo Co., Ltd.), and tetraethylene glycol dimethyl ether(tetraglyme, MeEO4Me, Tokyo Kasei Kogyo Co., Ltd.). They were all used after distillation. The penta-, hexa-, and hepta-ethylene glycols(EO5, EO6, and EO7) were offered by the Okahara Lab. (Department of Appled Chemistry of this Faculty). The pentaglyme and hexaglyme(MeEO5Me and MeEO6Me) were prepared by the method reported by Yanagida *et al.*[9]

Isolation of Solid Complexes of Lanthanoid Nitrates with Polyethylene Glycols and Glymes. A typical procedure for the preparation of solid complexes was as follows. About 1 mmol of a hydrous lanthanoid nitrate($Ln(NO_3)_3 \cdot nH_2O$, $n=$ 5—7) in 10 cm^3 of ethyl acetate was mixed with about 1 mmol of a polyethylene glycol or a glyme in 10 cm^3 of ethyl acetate, after which the resulting solution was allowed to stand for a day. The solid complex deposited from the solution was filtered off, washed several times with 2 cm^3 of ethyl acetate, and then dried at about 60 °C *in vacuo* for 8 h. Each solution was dehydrated before mixing for the systems in which no solid complex was deposited, or in which the yield of the complex was low, by means of the method described above. The dehydration was carried out by refluxing each solution through a molecular-sieve layer. The composition of the solid complex deposited was not affected by dehydration. For the preparation of lanthanoid complexes with EO5, a solution of the lanthanoid nitrate was added to the EO5 solution under the conditions where there was always an excess of EO5.

Measurements of Infrared Spectra and Conductance. The infrared spectra were recorded on a Hitachi 260-10 spectrometer. The conductances of the solutions of the complexes were measured at 25.0±0.1 °C with a Yokogawa-Hewlett Packard Universal Bridge.

Measurements of Solubility. A flask containing 30 cm^3 of ethyl acetate and an appropriate amount of a solid complex was shaken in a water bath thermostatted at 25.0±0.1 °C for 24 h or longer. The solid complex remaining undissolved was filtered off, and the concentration of the lanthanoid in the filtrate was determined by means of EDTA titration, with Xylenol Orange as an indicator.

X-Ray Powder Diffraction Analysis. The X-ray powder diffraction analysis was performed with a Rigaku Rotaflex diffractometer with a scintilation detector and Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å).

Results and Discussion

Isolation of Solid Complexes. The solid complexes of lanthanoid nitrates and yttrium nitrate with several polyethylene glycols and glymes were isolated in this investigation. The well-defined complexes are listed in Tables 1—8, along with their analytical data. The solid complexes were deposited also for EO6, though they are not given in the tables because their compositions were not determined definitely. The solid complexes obtained here were all deliquescent. The deposition of the solid complexes was interfered with by water in the solution, and generally the solid complexes were not deposited for the heavier lanthanoids when the dehydration procedure was not carried out.

Table 1. Elemental analyses of $Ln(NO_3)_3\cdot(EO2)_2$ complexes

Ln	Color	Found(Calcd)(%)			
		C	H	N	Ln
Pr	Pale green	17.69	3.78	7.84	26.0
		(17.82)	(3.74)	(7.79)	(26.1)
Nd	Pale pink	17.45	3.75	7.70	26.6
		(17.71)	(3.72)	(7.75)	(26.6)
Sm	White	17.57	3.75	7.72	27.2
		(17.51)	(3.67)	(7.66)	(27.4)
Eu	White	17.61	3.79	7.45	27.4
		(17.46)	(3.66)	(7.64)	(27.6)

Table 2. Elemental analyses of $Ln(NO_3)_3\cdot EO3$ complexes

Ln	Color	Found(Calcd)(%)			
		C	H	N	Ln
La	White	14.99	2.70	8.84	28.7
		(15.17)	(2.97)	(8.84)	(29.2)
Ce	White	14.93	2.77	8.67	29.2
		(15.13)	(2.99)	(8.82)	(29.4)
Pr	Pale green	15.09	2.85	8.69	29.4
		(15.11)	(2.96)	(8.81)	(29.5)
Nd	Pale pink	14.80	2.99	8.79	30.0
		(15.00)	(2.94)	(8.75)	(30.0)
Sm	White	14.75	2.91	8.79	30.9
		(14.81)	(2.90)	(8.64)	(30.9)
Eu	White	14.67	2.85	8.41	31.2
		(14.76)	(2.89)	(8.61)	(31.1)
Gd	White	14.62	2.91	8.52	31.8
		(14.61)	(2.86)	(8.52)	(31.9)
Tb	White	14.36	2.82	8.51	32.1
		(14.56)	(2.85)	(8.49)	(32.1)
Dy	White	14.38	2.91	8.25	32.6
		(14.45)	(2.83)	(8.43)	(32.6)
Ho	Pale orange	14.50	2.82	8.11	32.8
		(14.38)	(2.82)	(8.39)	(32.9)
Er	Pale pink	14.80	2.86	7.80	33.5
		(14.31)	(2.80)	(8.35)	(33.2)
Tm	White	14.24	2.77	8.30	33.1
		(14.26)	(2.79)	(8.25)	(33.4)
Yb	White	14.26	2.78	8.35	34.4
		(14.15)	(2.77)	(8.25)	(34.0)
Lu	White	13.92	2.81	8.07	34.1
		(14.10)	(2.77)	(8.22)	(34.2)
Y	White	17.00	3.12	10.14	20.9
		(16.95)	(3.33)	(9.88)	(20.9)

The Complexes with Diethylene Glycol(EO2): The solid complexes of $Ln(NO_3)_3\cdot(EO2)_2$ (Ln; Pr, Nd, Sm, and Eu) were obtained as is shown in Table 1. Solid complexes were deposited also for the other lanthanoids and yttrium, but their compositions were not definitely determined. The ratios of metal/EO2 in such complexes ranged from 1/2 to 1/3.

The Complexes with Triethylene Glycol(EO3): Table 2 shows that EO3 formed 1:1 complexes with all the lanthanoids investigated and with yttrium. All the complexes were formulated as $Ln(NO_3)_3\cdot EO3$, as is shown in Table 2, when the solid complexes were dried *in vacuo* at 80 °C. When the complexes were dried at room temperature (about 20 °C), however, the complex of lanthanum nitrate contained water and ethyl acetate, though the complexes of the other lanthanoid nitrates contained neither water nor ethyl acetate. The X-ray analysis of the complex of neodymium nitrate[19] has also indicated the absence of solvating water or a solvent. The deposition of the solid complexes seems to require the presence of a small amount of water in the solution. No solid complexes were obtained when the solutions were thoroughly dehydrated, and the deposition of the complexes was observed when a small amount of water was present. However, the presence of a large amount of water inhibited the deposition, as in the other EOn

Table 3. Elemental analyses of $Ln(NO_3)_3\cdot EO4$ complexes

Ln	Color	Found(Calcd)(%)			
		C	H	N	Ln
La	White	18.37	3.55	7.89	26.6
		(18.51)	(3.49)	(8.09)	(26.8)
Ce	White	18.75	3.65	8.22	26.8
		(18.47)	(3.49)	(8.08)	(26.9)
Pr	Pale green	18.50	3.38	8.16	26.9
		(18.44)	(3.48)	(8.06)	(27.0)
Nd	Pale pink	18.13	3.40	8.05	27.3
		(18.32)	(3.46)	(8.01)	(27.5)
Sm	White	17.98	3.26	7.94	28.3
		(18.11)	(3.42)	(7.92)	(28.3)
Eu	White	17.96	3.41	7.82	28.3
		(18.05)	(3.41)	(7.90)	(28.6)
Gd	White	17.64	3.21	7.72	29.0
		(17.88)	(3.38)	(7.82)	(29.3)
Tb	White	17.70	3.04	7.85	29.4
		(17.82)	(3.37)	(7.79)	(29.5)
Dy	Pale yellow	17.74	3.21	7.60	29.7
		(17.70)	(3.34)	(7.74)	(29.9)
Ho	Pale orange	17.63	3.32	7.65	30.0
		(17.62)	(3.33)	(7.71)	(30.3)
Er	Pale pink	17.68	3.29	7.50	30.4
		(17.55)	(3.31)	(7.67)	(30.5)
Tm	White	17.81	3.28	7.75	31.1
		(17.50)	(3.30)	(7.65)	(30.8)
Yb	White	17.49	3.03	7.83	31.3
		(17.36)	(3.29)	(7.59)	(31.3)
Lu	White	17.77	3.62	7.69	31.8
		(17.30)	(3.27)	(7.57)	(31.5)
Y	White	20.37	3.96	8.73	18.9
		(20.48)	(3.87)	(8.96)	(18.7)

complexes. These results suggest that water plays a part in the deposition of the complexes, but no further investigation was carried out.

The Complexes with Tetraethylene Glycol(EO4): Tetraethylene glycol(EO4) always formed a solid complex with the composition of $Ln(NO_3)_3 \cdot EO4$, irrespective of the mixing ratio or the mixing method of the solutions of the lanthanoid nitrate and EO4 (Table 3). The EO4 complexes were the least deliquescent of the complexes isolated in this investigation. These phenomena may be attributed to the fact that the chain length of EO4 is suitable for the 1:1 complex without any pronounced strain.[18]

The Complexes with Pentaethylene Glycol(EO5): Table 4 shows that the composition of well-defined complexes of EO5 are $Ln(NO_3)_3 \cdot EO5$. The 1:1 complex was deposited when there was an excess of EO5, while the ratio of Ln/EO5 in the complexes deposited was often larger than 1, ranging from 1.0 to 1.5 when the EO5 solution was added to the lanthanoid solution or when the mixing ratio of Ln/EO5 was larger than 1. However, only lanthanum nitrate always formed the 1:1 complex, regardless of the mixing conditions. This fact may be related to the fact that the ionic radius of lanthanum is the largest in the lanthanoids. The solid complexes were all hygroscopic; those of the heavier lanthanoids were more hygroscopic than those of the lighter lanthanoids, that of lutetium nitrate especially being so hygroscopic that the determination of the contents of C, H, and N was unsuccessful in the present method.

TABLE 4. ELEMENTAL ANALYSES OF $Ln(NO_3)_3 \cdot EO5$ COMPLEXES

Ln	Color	Found(Calcd)(%)			
		C	H	N	Ln
La	White	21.02 (21.33)	3.84 (3.94)	7.43 (7.46)	24.7 (24.7)
Ce	White	21.08 (21.28)	3.86 (3.93)	7.57 (7.44)	24.8 (24.8)
Pr	Pale green	21.41 (21.25)	3.90 (3.92)	7.46 (7.43)	24.9 (24.9)
Nd	Plale pink	20.96 (21.13)	3.85 (3.90)	7.37 (7.39)	25.2 (25.4)
Sm	White	20.60 (20.90)	3.63 (3.86)	7.19 (7.31)	26.0 (26.2)
Eu	White	20.60 (20.84)	3.85 (3.85)	7.17 (7.29)	26.4 (26.4)
Gd	White	20.49 (20.65)	3.85 (3.81)	7.20 (7.23)	26.9 (27.0)
Tb	White	20.57 (20.57)	3.79 (3.81)	7.23 (7.21)	27.3 (27.3)
Dy	Pale yellow	20.48 (20.45)	3.77 (3.79)	7.10 (7.16)	27.6 (27.7)
Ho	Pale orange	20.38 (20.12)	3.66 (3.77)	7.11 (7.13)	28.3 (28.0)
Er	Pale pink	20.30 (20.08)	3.76 (3.69)	7.11 (7.10)	28.3 (28.3)
Tm	White	20.17 (20.25)	3.74 (3.74)	7.21 (7.08)	28.7 (28.5)
Yb	White	20.04 (20.10)	3.65 (3.72)	7.03 (7.03)	29.0 (29.0)
Lu	White	—[a] (20.04)	—[a] (3.70)	—[a] (7.01)	29.2 (28.1)

a) The contents of C, H, and N could not be determined because of great hygroscopy.

The Complexes with Heptaethylene Glycol(EO7): The 2:1 complexes were deposited for lanthanum and cerium. Table 5 shows the analytical data. For the other lanthanoids, the composition of the complex was not definitely determined or no solid complex was deposited. A heptaethylene glycol is considered to be bonded to two lanthanoid atoms because its chain length is too long to wrap around only one lanthanoid atom. The structures of the complexes prepared here are supposed to be similar to that of the 2:1 complex of merculy(II) chloride with hexaethylene glycol dimethyl ether reported by Iwamoto.[21]

The Complexes with Glymes: The 1:1 (Ln:glyme) complexes were deposited for tetraglyme (MeEO4Me), just as for EO3, EO4, and EO5, while the 4:3 complexes were deposited for pentaglyme (MeEO5Me) and hexaglyme (MeEO6Me). Tables 6, 7, and 8 show the complexes isolated in this investigation, together with the analytical data. The solid complexes of pentaglyme were deposited also for the lanthanoids which are not listed in Table 7, but their compositions were not defined well. Although there is a possibility that the 4:3 complexes prepared here were mixtures of the complexes with simple compositions, such as the 1:1 and 2:1 complexes, the 4:3 complex was always deposited for the system of praseodymium nitrate with pentaglyme, even when the mixing ratio of the nitrate to the glyme was varied from 1/4 to 4/1. Correspondingly, the possibility of the deposition of the mixture may well be neglected. The 4:3 complexes

TABLE 5. ELEMENTAL ANALYSES OF $[Ln(NO_3)_3]_2 \cdot EO7$ COMPLEXES

La	Color	Found(Calcd)(%)			
		C	H	N	Ln
La	White	17.19 (17.23)	2.83 (3.10)	8.72 (8.61)	28.05 (28.46)
Ce	White	16.99 (17.20)	3.09 (3.09)	8.52 (8.60)	28.44 (28.63)

TABLE 6. ELEMENTAL ANALYSES OF $Ln(NO_3)_3 \cdot$ MeEO4Me COMPLEXES

Ln	Color	Found(Calcd)(%)			
		C	H	N	Ln
La	White	21.75 (21.95)	4.10 (4.05)	7.55 (7.68)	25.0 (25.4)
Ce	White	21.68 (21.90)	4.06 (4.04)	7.52 (7.66)	25.1 (25.6)
Pr	Pale green	21.67 (21.87)	4.00 (4.04)	7.48 (7.65)	25.0 (25.7)
Nd	Pale pink	21.52 (21.74)	4.02 (4.01)	7.62 (7.60)	25.9 (26.1)
Sm	Pale yellow	21.35 (21.50)	3.92 (3.97)	7.35 (7.52)	26.1 (26.9)

Table 7. Elemental analyses of $[Ln(NO_3)_3]_4\cdot[MeEO5Me]_3$ complexes

Ln	Color	Found(Calcd)(%) C	H	N	Ln
La	White	19.63 (20.60)	3.77 (3.75)	7.51 (8.01)	26.0 (26.5)
Ce	White	20.32 (20.56)	3.66 (3.74)	7.89 (7.99)	26.4 (26.6)
Pr	Pale green	20.42 (20.52)	3.67 (3.73)	7.78 (7.98)	26.6 (26.8)
Nd	Pale pink	20.19 (20.42)	3.58 (3.71)	7.81 (7.93)	27.0 (27.2)
Sm	Pale yellow	20.13 (20.16)	3.74 (3.67)	7.78 (7.84)	27.8 (28.1)

Table 8. Elemental analyses of $[Ln(NO_3)_3]_4\cdot[MeEO6Me]_3$ complexes

Ln	Color	Found(Calcd)(%) C	H	N	Ln
La	White	22.24 (22.61)	3.83 (4.07)	7.22 (7.53)	24.9 (24.9)
Ce	White	22.19 (22.56)	4.07 (4.06)	7.47 (7.52)	25.0 (25.1)
Pr	Pale green	22.33 (22.53)	3.99 (4.05)	7.46 (7.51)	25.2 (25.2)
Nd	Pale pink	21.93 (22.40)	4.03 (4.03)	7.59 (7.46)	25.3 (25.6)

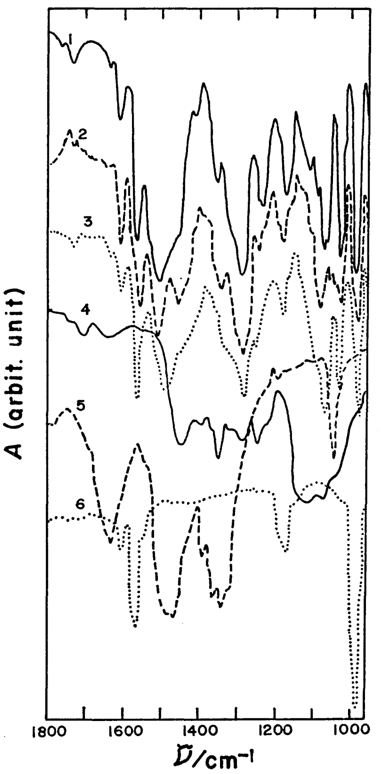

Fig. 1. IR spectra of neodymium nitrate, its complexes, EO4, and hexachlorobutadiene(HCB).
1: $Nd(NO_3)_3\cdot EO3$ (HCB mull), 2: $Nd(NO_3)_3\cdot EO4$ (HCB mull), 3: $Nd(NO_3)_3\cdot EO5$ (HCB mull), 4: EO4 (liquid); 5: $Nd(NO_3)_3\cdot 6H_2O$ (KBr pellet), 6: HCB (liquid).

of the lanthanoid nitrates have been reported also for crown compounds,[22] and the structure of the 4:3 complex of neodymium nitrate with 18-crown-6 ether has previously been reported;[23] *i.e.*, two different complex ions, the 1:1 complex cation $[Nd(NO_3)_2\cdot 18\text{-crown-}6]^+$ and the complex anion containing no crown ether $[Nd(NO_3)_6]^{3-}$, are included in it.

Infrared Spectra of the Complexes. The infrared spectra of the solid complexes were similar to each other. In particular, there is little difference in the spectra among the complexes of individual lanthanoids with a given ligand (polyethylene glycol or glyme). The spectra of neodymium nitrate complexes with EO3, EO4, and EO5 are shown in Fig. 1 as typical examples, together with those of pure EO4, neodymium nitrate, and hexachlorobutadiene. Remarkable differences were observed between the complexes and the pure ligands in the 1000—1150 cm^{-1} region. The bands of the pure ligand (EO4 in Fig. 1) were broad in this region, while the bands became sharper in the case of the complexes. This change can be explained as follows: the ligand molecule can assume various conformations in a pure ligand; consequently, many bands appear in the spectra, overlapping each other, and resulting in broad bands, while the ligand molecule assumes a definite conformation in the complex. Accordingly, only the absorption bands corresponding to the conformation are observed, and the bands become sharp as a whole. A detailed discussion of similar phenomena in the merculy(II) chloride complexes has been reported by Iwamoto.[24] The absorption bands assigned to the coordinated nitrates were observed at about 1500 cm^{-1} and at about 1300 cm^{-1} for the complexes. There was no absorption band assigned to free nitrates at about 1380 cm^{-1} in the spectra of any of the complexes. According to the X-ray analyses of the neodymium nitrate complexes[17—19] three nitrates are all coordinated to a neodymium atom in the EO3 and EO4 complexes, while one nitrate is not coordinated in the EO5 complex. The results of the X-ray analyses are in agreement with the infrared spectra for the EO3 and EO4 complexes, but appear to be in conflict with that for the EO5 complex. According to the X-ray analyis, the uncoordinated nitrate in the EO5 complex assumes a C_{2v} symmetry rather than the D_{3h} one characteristic of a free nitrate. This fact explains the absence of the absorption band at about 1380 cm^{-1} in spite of the presence of the uncoordinated nitrate in the EO5 complexes.

Powder X-Ray Diffraction. The structures of neodymium nitrate complexes with EO3, EO4, and EO5 have been determined by the X-ray analyses of the single crystals.[17—19] The powder X-ray diffractions were measured for the complexes of the other lanthanoids as well as those of neodymium. Figure 2 shows some typical diffraction patterns. The diffraction patterns for the complexes of most of the lanthanoids with EO3, EO4, and EO5 were similar to those of the complexes of neodymium with the cor-

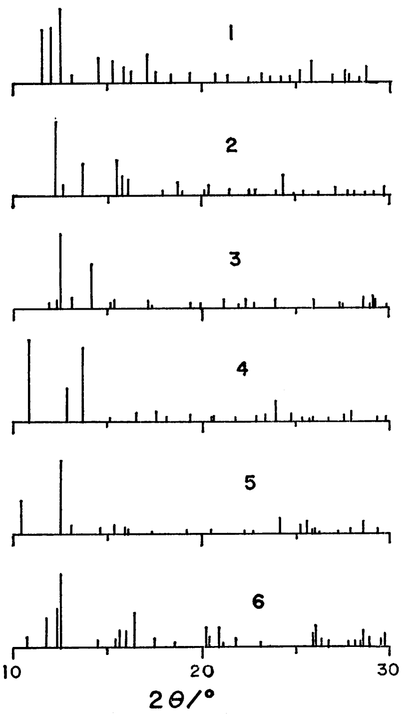

Fig. 2. X-Ray diffraction patterns of some lanthanoid complexes.
1: $La(NO_3)_3 \cdot EO3$, 2: $Nd(NO_3)_3 \cdot EO3$, 3: $Nd(NO_3)_3 \cdot EO4$, 4: $Er(NO_3)_3 \cdot EO4$, 5: $La(NO_3)_3 \cdot EO5$, 6: $Nd(NO_3)_3 \cdot EO5$.

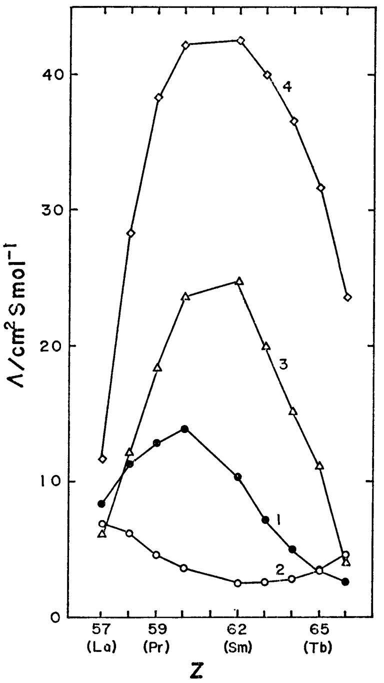

Fig. 3. Molar conductivities of lanthanoid nitrate complexes with EO3, EO4, and EO5 in acetone. Concentration: 1 mmol/dm³, temp: 25 °C.
1: $Ln(NO_3)_3 \cdot nH_2O$, 2: EO3 complexes, 3: EO4 complexes, 4: EO5 complexes.

responding ligands. The complexes are expected to have structures similar to those of the neodymium complexes. The complexes of lanthanum and cerium with EO3 and EO5, and the complexes of terbium and the heavier lanthanoids with EO4 yielded patterns different from those of the corresponding neodymium complexes. These results suggest that the structures of the complexes are dissimilar to those of the neodymium complexes. The structures of the complexes are now being studied in detail by the present authors.

Electric Conductivities of the Solutions. Figure 3 shows the molar conductivities of the acetone solutions of the lanthanoid nitrate complexes of EO3, EO4, and EO5, together with those of the parent nitrates. All the values were lower than 45 S cm² mol⁻¹, suggesting that the complexes and the nitrates were essentially nonelectrolytes or dissociated as the 1:1 electrolytes.[25] The molar conductivities increased in the following order for a given lanthanoid: EO3 complex<parent nitrate<EO4 complex<EO5 complex. The mobility of the cation can reasonably be considered to decrease by complexing with any one of the glycols because of the increase in the size of the species. Therefore, the order of the conductivities described above is attributed to the difference in the degree of ionic dissociation among the complexes. According to the X-ray structure analyses of the complexes of neodymium nitrate, all the nitrates in the EO3 complex are bidentate, while one of the nitrates in the EO4 complex is unidentate and is uncoordinated in the EO5 complex, though the other two are bidentate. The degree of the dissociation is, therefore, expected to increase in this order: EO3 complex< EO4 complex<EO5 complex, since the ease of the dissociation of nitrates increases in this order: bidentate<unidentate<noncoordinated.

Solubilities of the Complexes. In the preparation of the solid complexes, the complexes of lighter lanthanoids appeared to be deposited more easily than those of heavier lanthanoids. This phenomenum is probably related to the difference in the solubilities between the complexes. Figures 4 and 5 show the solubilities of the EO4 complexes and the EO5 complexes respectively in ethyl acetate. The solubility generally increased with the increase in the atomic number of the lanthanoid both for the EO4 complexes and for the EO5 complexes, though some exceptions were observed (the heavier lanthanoids for the EO4 complexes and the lighter lanthanoids for the EO5 complexes). The observed solubilities shown in the figures are actually apparent ones, being affected not only by the solubilities of the undissociated complexes, but also by the stabilities of the complexes, for the complexes are probably, in part, dissociated in the solutions. The trend of the solubility shown in the figures implies an increase in the solubility of the undissociated complex and/or a decrease in the stability constant of the complex with an increase in the atomic number of the lanthanoid. The stability constants of the complexes with EO4 and EO5 may be expected to decrease with the increase in the atomic number of the lanthanoid; this tendency is contrary to those of the lanthanoid complexes with most other ligands, just as the stability constant of the lanthanoid complex with 18-crown-6 ether, which is similar in

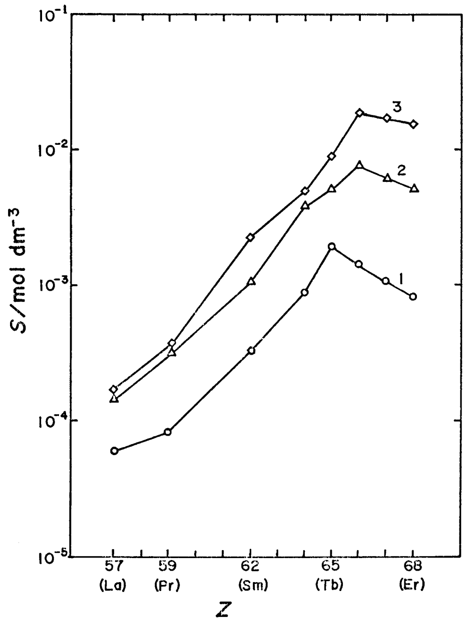

Fig. 4. Solubility(S) of $Ln(NO_3)_3 \cdot EO4$ complexes in ethyl acetate at 25 °C.
$[H_2O]$: 1. 0 mol/dm^3, 2. 0.125 mol/dm^3, 3. 0.25 mol/dm^3.

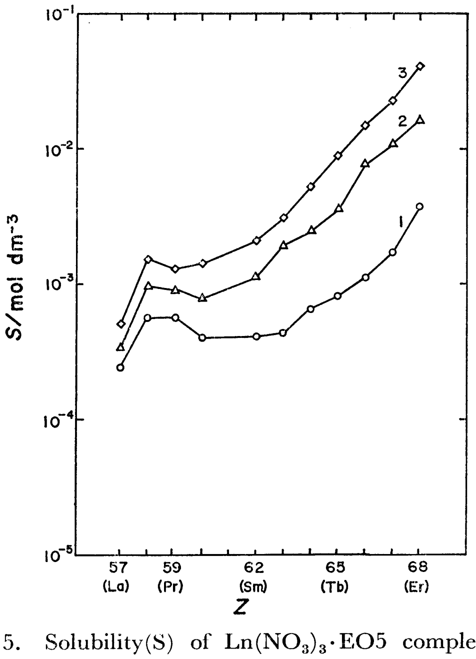

Fig. 5. Solubility(S) of $Ln(NO_3)_3 \cdot EO5$ complexes in ethyl acetate at 25 °C.
$[H_2O]$: 1. 0 mol/dm^3, 2. 0.125 mol/dm^3, 3. 0.25 mol/dm^3.

molar structure to the complexes with EO4 and EO5, has been reported to decrease with the increase in the atomic number of the lanthanoid.[26] The anomalous behavior observed for terbium–erbium in the EO4 complexes and for lanthanum–praseodymium in the EO5 complexes is probably related to the difference in the crystal structures between those complexes and the other ones, as has been described above. The solubilities were increased by the presence of water in the solution for all the complexes. This result is in accordance with the fact that the deposition of the solid complexes was interfered with by water. The difference in the solubility among the complexes of individual lanthanoids with EO4 or EO5 suggests a new method for the mutual separation of lanthanoids by means of fractional precipitation.[20]

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