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LANTHANOID CHLORIDE COMPLEXES WITH POLYETHYLENE GLYCOLS AND GLYMES

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Lanthanoid chlorides formed the 1:1 complexes with triethylene glycol, tetraethylene glycol, pentaethylene glycol, tetraglyme, and pentaglyme. All the complexes were deliquescent. The yield of the solid complex with tetraethylene glycol decreased with the increase of the atomic number of the lanthanoid.

Several macrocyclic polyethers, so-called crown ethers and so on, have been reported to form complexes with lanthanoids.[1-4] King and Heckley suggested the possibility of separation of lanthanoids using a crown ether.[1] It was reported by the present authors that some noncyclic polyethers, polyethylene glycols and glymes, formed solid complexes with lanthanoid nitrates, too.[5] According to the structure analyses of the complexes, the glycols assume the ring-like structures similar to those of the crown ethers.[6,7] In each of the complexes of triethylene glycol(EO3) and tetraethylene glycol(EO4) a nitrate group takes part in the formation of the ring-like structure. It is interesting to see if the solid complexes are formed also for the lanthanoid salts other than the nitrates, and if the compositions of the complexes are analogous to those of the nitrate complexes. This letter reports the preparation and some properties of the complexes of lanthanoid chlorides($LnCl_3$) with some polyethylene glycols ($HO(CH_2CH_2O)_nH$, EOn) and glymes($CH_3O(CH_2CH_2O)_nCH_3$).

The solid complexes were prepared by mixing the solutions of the respective hydrated lanthanoid chloride and a ligand(EOn or glyme) in ethanol or the mixture of ethanol and ethyl acetate. The concentration of each solution was 0.02-0.1 mol dm^{-3}. Each solution was dehydrated by refluxing through a molecular sieves layer before mixing. The mixed solution was allowed to stand for a day or longer. The complex deposited from the solution was filtered off, then washed with a small amount of the mixture of ethanol and ethyl acetate, and dried in vacuo at about 110°C, except for $NdCl_3$-EO5 complex which was dried at 70°C because it appeared to melt or decompose at about 100°C. The solid complexes isolated in this investigation are listed in Table 1. All the complexes were 1:1 complexes. The compositions were analogous to those of the nitrate complexes except for the complexes with pentaglyme.[5,8] All the complexes were deliquescent but less hygroscopic than the nitrate complexes. The infrared absorption bands of the ligand(EOn or glyme) in the 1150-1000 cm^{-1} region became sharper in the complexes than those in the pure ligand. The changes are attributed to the variations in the conformations in the ligand molecule accompanying complexation with the lanthanoids. The yield of the EO4 complex of a lanthanoid chloride decreased with the increase of the atomic number of the lanthanoid. The yield ranged from 94.7%(for La) to 0%(for Tb and the lanthanoids of higher atomic numbers) at 24 hours after the mixing of two different ethanolic solutions of $LnCl_3$ and EO4($[LnCl_3] = [EO4] = 50$ mmol dm^{-3}). This result is analogous to that observed for the nitrate complexes.[9] The preliminary results of the X-ray analysis of the neodymium chloride complex with EO4 showed that its molecular structure is analogous to that of the nitrate complex. The similarity of the trend of the variation of the yield may be related to the resemblance of the structure. The detailed study on the structure is now in progress by the authors.

Table 1. Lanthanoid chloride complexes

Ligand	Composition	Ln
EO3	$LnCl_3 \cdot HO(CH_2CH_2O)_3H$	La-Lu,Y
EO4	$LnCl_3 \cdot HO(CH_2CH_2O)_4H$	La-Lu,Y
EO5	$LnCl_3 \cdot HO(CH_2CH_2O)_5H$	La-Lu,Y
Tetraglyme	$LnCl_3 \cdot CH_3O(CH_2CH_2O)_4CH_3$	La-Ho
Pentaglyme	$LnCl_3 \cdot CH_3O(CH_2CH_2O)_5CH_3$	La,Pr

Table 2. Analytical data of some selected complexes

Complex	Found%(calcd%)			
	C	H	Cl	Ln
$SmCl_3 \cdot$EO3	17.46(17.71)	3.76(3.47)	25.87(26.14)	36.2(37.0)
$SmCl_3 \cdot$EO4	21.24(21.31)	4.08(4.02)	23.42(23.58)	33.2(33.4)
$SmCl_3 \cdot$EO5	24.67(24.27)	4.43(4.48)	20.64(21.49)	30.6(30.4)
$SmCl_3 \cdot$tetraglyme	24.59(25.40)	4.61(4.69)	22.15(22.49)	31.0(31.4)
$SmCl_3 \cdot$pentaglyme	28.06(28.06)	5.70(5.10)	21.07(21.71)	27.1(27.4)

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