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CRYSTALLINE COMPLEXES OF POLY(OXYETHYLENE) DERIVATIVES WITH LANTHANOIDS

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The crystalline complexes of poly(oxyethylene) derivatives ($HO(CH_2CH_2O)_nH$, n=2-7; $CH_3O(CH_2CH_2O)_4CH_3$) with lanthanoid nitrates were prepared. The well-defined complexes have the composition of ligand:metal = 1:1 or 1:2. The stability of the complex seems to decrease with increasing atomic number of the lanthanoid.

Crown compounds form crystalline complexes with many salts, especially those of alkali and alkaline earth cations.1-4) The complexes of lanthanoids with crown compounds have been also isolated,5-8) and King and Heckley demonstrated the possibility of lanthanoid separation.6) Yanagida et al. reported the complexation of noncyclic poly(oxyethylene) derivatives with alkali and alkaline earth metals and the isolation of the solid complexes.9) The authors have now found that lanthanoids salts also form crystalline complexes with noncyclic poly(oxyethylene) derivatives. The complexes were prepared by mixing the ethyl acetate solutions of hydrated lanthanoid nitrates ($Ln(NO_3)_3 \cdot nH_2O$, n=2-6) with the ethyl acetate solutions of poly(oxyethylene) derivatives ($HO(CH_2CH_2O)_nH$, n=2-7; $CH_3O(CH_2CH_2O)_4CH_3$) and by allowing the mixed solutions to stand for crystal deposit. Generally, the heavier the lanthanoid is, the slower the crystallization is. As is shown in Table 1 the 1:1 complexes are obtained for triethylene glycol(EO3), tetraethylene glycol(EO4), pentaethylene glycol(EO5) and tetraethylene glycol dimethyl ether (M_2EO4). The 1:2(ligand:metal) complexes are obtained for heptaethylene glycol (EO7). The stoichiometry of the crystalline complexes of dimethylene glycol(EO2) and hexaethylene glycol(EO6) is not yet determined, because only the mixed products were deposited. The complexes are generally hygroscopic and soluble in water, methanol, ethanol and acetone with partial dissociation. The yield of the crystalline complex decreases with increasing atomic number of the lanthanoid: when the lanthanoid nitrate($Ln(NO_3)_3 \cdot 5H_2O$) and EO4 are mixed in the ratio of 1:1 (molar ratio) and left standing at 20°C for 2 hours, the yield is 98.6% for La, 14% for Gd and 0% for Tb-Lu. The difference of the yield may be explained by the fact that the stability of the complex of a crown compound decreases with the increase of the atomic number of the central lanthanoid10): this stability trend is opposite to that of most other ligands whose complexes are more stable with the lanthanoids of higher atomic number. Preliminary results of the determination of crystal structure of the complex of EO5 by X-ray diffraction indicate that the structure of the complex is similar to that of the crown compound11): the ligand molecule, EO5 molecule, has an open circular structure and the oxygen atoms are on the inner side. The lanthanoid ion is located near the center of the circular structure. The stability of the complex is expected to depend on the relative size of the lanthanoid ion and the cavity of the ligand molecule circle. The detailed study on the structure of the complex by X-ray diffraction is now in progress. The difference in the yield of crystalline complex among the lanthanoids indicates the possibility of a new lanthanoid separation by fractional crystallization using poly(oxyethylene) derivatives.

Table 1. Lanthanoid complexes of poly(oxyethylene) derivatives

Ligand		Ln	Formula of complex
$HO(CH_2CH_2O)_2H$	(EO2)	Tb-Er	a)
$HO(CH_2CH_2O)_3H$	(EO3)	La-Er	$Ln(NO_3)_3 \cdot HO(CH_2CH_2O)_3H$
$HO(CH_2CH_2O)_4H$	(EO4)	La-Tb	$Ln(NO_3)_3 \cdot HO(CH_2CH_2O)_4H$
$HO(CH_2CH_2O)_5H$	(EO5)	La-Gd	$Ln(NO_3)_3 \cdot HO(CH_2CH_2O)_5H$
$HO(CH_2CH_2O)_6H$	(EO6)	La-Eu	a)
$HO(CH_2CH_2O)_7H$	(EO7)	La,Ce	$[Ln(NO_3)_3]_2 \cdot HO(CH_2CH_2O)_7H$
$CH_3O(CH_2CH_2O)_4CH_3$	(M_2EO4)	La,Ce	$Ln(NO_3)_3 \cdot CH_3O(CH_2CH_2O)_4CH_3$

a) The stoichiometry is not yet determined.

Table 2. Typical crystalline complexes of lanthanoid with poly(oxyethylene) derivatives

Complex	Color	Decomposition Temperature(°C)	Found(Calcd)%			
			C	H	N	Metal
$Pr(NO_3)_3 \cdot$ EO3	pale green	221	15.09 (15.11)	2.85 (2.96)	8.69 (8.81)	29.37 (29.53)
$Pr(NO_3)_3 \cdot$ EO4	pale green	207-207.5	18.50 (18.44)	3.38 (3.48)	8.16 (8.06)	26.90 (27.04)
$Pr(NO_3)_3 \cdot$ EO5	pale green	155-157	21.41 (21.25)	3.90 (3.92)	7.46 (7.43)	24.94 (24.93)
$[La(NO_3)_3]_2 \cdot$EO7	white	186-187	17.19 (17.23)	2.83 (3.10)	8.72 (8.61)	28.05 (28.46)
$La(NO_3)_3 \cdot M_2$EO4	white	182.5-184.5	21.68 (21.95)	3.97 (4.05)	7.53 (7.68)	25.28 (25.35)

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