

then chemically reduced by immersion in a concentrated solution of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. This was followed by rinsings with distilled water and acetonitrile. The electrode was then immediately transferred to the drybox and ready for use. Current-potential curves on electrodes which were treated in this manner showed very low background current from +2.5 to -3.0 V.

A three-compartment cell was designed so that controlled potential electrolysis could be carried out on a sample in approximately 5 min. The central compartment contained a perforated platinum-foil working electrode, the auxiliary compartment a coiled platinum wire. The reference electrode used was a chloride-coated silver wire. This electrode was found to have a potential of +0.30 V vs. $\text{Ag}|\text{Ag}^+$ (0.1 M). Although this electrode showed no sensible deviation from this value over typical time periods of weeks, the precise potential needed for electrolyzing a particular complex was determined by recording its CV each time, immediately prior to electrolysis.

Coulometric n values were determined by electronically integrating the current-time curves obtained during a controlled potential electrolysis.

Spectroquality acetonitrile, obtained from Eastman Kodak, was purified by passing the degassed liquid through freshly activated alumina as previously described¹⁴ and in some cases by distillation over P_2O_5 and CaH_2 . No difference in electrochemical behavior was found in solvents prepared by the two different methods. In each case, further removal of oxygen was accomplished by repeated vacuum line pumping on solidified solvent. Tetra-*n*-butylammonium tetrafluoroborate and tetraethylammonium perchlorate, obtained from Southwestern Analytical, were used as supporting electrolytes. Removal of water from tetraethylammonium perchlorate was accomplished as previously described. The tetra-*n*-butylammonium tetrafluoroborate salt was heated *in vacuo* at 80° for 48 hr prior to use. Again, no difference in electrochemical behavior for the complexes was observed with the two different supporting electrolytes.

Procedure for Combined Controlled Potential Coulometry-Esr Measurements. A precise quantity of complex was weighed out and diluted to volume in a 10-ml volumetric flask. Five milliliters of this solution was transferred to the central compartment of the coulometric cell (Figure 5) and a cyclic voltammogram of the starting material was recorded under N_2 . Highly prepurified nitrogen was then purged into the central compartment and served as a stirring mechanism during the electrolysis. Alternatively, the entire electrolysis could be carried out in a Vacuum Atmospheres Dri-Lab. Both of these procedures were used. Some of the Ni(I) species were also conveniently generated by reduction of the corresponding Ni(II) complexes with sodium amalgam. After the electrolysis of a particular complex was complete, a portion of the coulometrically analyzed sample was transferred in the absence of oxygen to an esr cell. The contents of the esr cell were immediately solidified at liquid nitrogen temperature, and the esr spectrum was recorded.

The esr spectra were recorded on a Varian V-4500 spectrometer operating at 9500 MHz and equipped with a dual cavity. A small sample of DPPH was placed in the reference cavity. Two spectra were recorded for each sample, the field being swept in opposite directions and the average of the g values taken. The g values were calculated by the approximate method of Kneubühl.⁵³ The g_{\parallel} values are accurate to ± 0.005 and the g_{\perp} values to ± 0.01 . The sample tube was placed in a small dewar flask filled with liquid N_2 and designed so that it would fit in the sample cavity of the esr spectrometer.

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Lanthanide Nitrate Complexes of Some Macrocyclic Polyethers¹

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Abstract: The macrocyclic polyether benzo-15-crown-5 reacts with the hydrated lanthanide(III) nitrates in acetone solution to form complexes of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ ($\text{Ln} = \text{La, Ce, Pr, Nd, and Sm}$) with the lighter (*i.e.*, larger) lanthanides and of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ ($\text{Ln} = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu}$) with the heavier (*i.e.*, smaller) lanthanides. The macrocyclic polyether dibenzo-18-crown-6 forms similar complexes of the type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ ($\text{Ln} = \text{La, Ce, Pr, and Nd}$) in acetonitrile solution with the lighter lanthanides but fails to form stoichiometric complexes under these conditions with the heavier lanthanides. The following three principles seem to determine the lanthanide(III) nitrate coordination chemistry of these macrocyclic polyethers: (a) dibenzo-18-crown-6 forms less stable lanthanide(III) nitrate complexes than benzo-15-crown-5; (b) the thermal stabilities of the unsolvated macrocyclic polyether complexes of the lanthanide(III) nitrates decrease upon increasing atomic number of the lanthanide; (c) the tendencies of the metal ions in the macrocyclic polyether complexes of the lanthanide(III) nitrates to complex with other ligands such as water and acetone increase upon increasing atomic number of the lanthanide. The isotropic nmr shifts of the coordinated macrocyclic polyether and water protons arising from the lanthanides in the complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ ($\text{Ln} = \text{Sm, Eu, Tm, and Yb}$) correlate well with previous observations on tris(dipivaloylmethanato) lanthanide paramagnetic shift reagents. Partial separation of erbium and praseodymium by chromatography of the mixed nitrates on a column of dibenzo-18-crown-6 has been demonstrated.

The use of macrocyclic polyethers as a class of complexing agents has been investigated extensively during the past several years.^{3,4} This class of com-

plexing agents has exhibited potential significance not only in coordination chemistry but also in biological

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(2) Graduate student and research assistant, 1970-1974.

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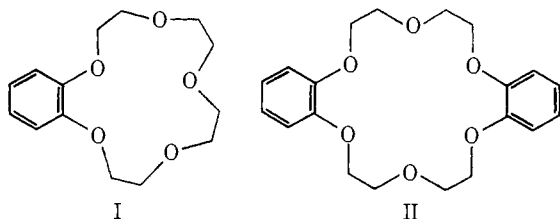
(4) J. J. Christensen, J. O. Hill, and R. M. Izatt, *Science*, **174**, 459 (1971).

systems, particularly with respect to ion transport and antibiotics, as well as in organic synthesis and catalysis.^{3,4}

Complexes of the macrocyclic polyethers with the alkali and alkaline earth metal cations have received particular attention. The interaction between the metal cation and the macrocyclic polyether appears to be electrostatic. The stoichiometries, structures, and relative stabilities of these complexes can best be understood by consideration of the size of the internal cavity of the macrocyclic polyether relative to the ionic radius and the charge density of the metal cation residing within this central cavity.

The similarities of the ionic radii and the electropositivities of the trivalent lanthanide ions relative to several of the alkali and alkaline earth metal cations suggested that the tripositive lanthanides might form stable complexes with at least some of the macrocyclic polyethers. Furthermore, the complexing properties of a class of rigid ligands such as the smaller macrocyclic polyethers might be unusually sensitive to the size of the lanthanide ion to which they are bonded since the structure is governed primarily by electrostatic and steric effects. We felt that such a sensitivity of the macrocyclic polyethers to metal cation size in complex formation could provide not only unusual coordination possibilities but also a basis for a novel method of lanthanide separation.

This paper presents the results obtained in our laboratory on the synthesis and characterization of the new complexes formed in the reactions between the hydrated lanthanide nitrates and the two macrocyclic polyethers benzo-15-crown-5 (I: cavity size 1.7–2.2 Å; systematic name, 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadeca-2-ene) and dibenzo-18-crown-6 (II: cavity size 2.6–3.2 Å; systematic name, 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene). This work has provided some evidence for significant differences in the complexing behavior of the macrocyclic polyethers I and II with the different lanthanides.



This paper also presents some preliminary evidence that this differential complexing behavior can be exploited for the separation of praseodymium and erbium on a column of the macrocyclic polyether dibenzo-18-crown-6 (II).

After the original version of this manuscript was submitted, a communication by Cassol, Seminario, and De Paoli⁵ appeared on lanthanide nitrate and thiocyanate complexes of the macrocyclic ethers I and II. Our results differ appreciably from those of Cassol, Seminario, and De Paoli.⁵ Furthermore, the present study significantly extends the observations of these authors by reporting the first solvated lanthanide nitrate complexes, the first nmr studies on lanthanide macrocyclic poly-

ether complexes, and the first experiments on the use of macrocyclic polyethers for lanthanide separations.

Experimental Section

Reactions were routinely performed under a nitrogen atmosphere even though the systems appear to be stable to air and moisture. All solvents were stored over 4A molecular sieves and used without further purification.

The macrocyclic polyethers benzo-15-crown-5 (I) and dibenzo-18-crown-6 (II) were prepared by methods reported in the literature.⁶ The hydrated lanthanide nitrates were purchased from the Rare Earth Division, American Potash and Chemical Corp., and used without further purification.

Analytical data on the complexes are given in Table I. The carbon, hydrogen, and nitrogen analyses were performed within the Chemistry Department of the University of Georgia under the supervision of Mr. W. Swanson using a Perkin-Elmer Model 240 elemental analyzer. The lanthanide metals were determined by ethylenediaminetetraacetic acid titrations using Xylenol Orange as an indicator.⁷ Decomposition temperatures (Table I) were determined in capillaries and are uncorrected.

(a) **Preparation of $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ (Ln = La, Ce, Pr, and Nd).** A solution of 7 mmol of the hydrated lanthanide nitrate in 10 ml of acetone was stirred vigorously with a solution of 7–10 mmol of benzo-15-crown-5 (I) in 10 ml of acetone at room temperature. A crystalline precipitate formed almost immediately. After standing for 1 hr at room temperature, this precipitate was filtered, washed with two 10-ml portions of acetone, and dried at 20° (35 mm) for 1–2 hr. Additional product was recovered from the acetone filtrates by concentrating the solution under vacuum, carefully adding hexane, and cooling at 0°. The final products may contain traces of water and/or acetone which can be removed by drying at 130–150° (0.5 mm) for 18 hr. The total yields of $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ (Ln = La, Ce, Pr, and Nd) were nearly quantitative (>90%).

Analytically pure samples were prepared by recrystallization from saturated boiling acetone solutions by slowly cooling to room temperature and allowing to stand overnight.

(b) **Preparation of $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu).** A solution of 7 mmol of the hydrated lanthanide nitrate in 10 ml of acetone was stirred vigorously with a solution of 10 mmol of benzo-15-crown-5 in 10 ml of acetone at room temperature. A clear solution was obtained which failed to give a precipitate after 1 hr of stirring in contrast to the experiments with the corresponding derivatives of the lighter lanthanides discussed above in (a). Acetone was distilled from the reaction mixture until the volume was reduced to about one-third of the original volume. Hexane was then added dropwise to the hot solution with stirring until the first traces of permanent turbidity resulted. The reaction mixture was then cooled to room temperature and allowed to stand overnight. The crystalline precipitate was filtered, washed with two 10-ml portions of hexane, and dried at 25° (35 mm) for 1–2 hr. Additional product could be isolated by cooling the filtrate to –78°. The solvated complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ were isolated in 70–90% yields.

If the hexane is added too rapidly to the acetone solution during the crystallization of the products, viscous oils rather than crystalline products may be obtained, particularly with the europium and gadolinium derivatives. If such oils are obtained, they can be crystallized by repetition of the crystallization process with more careful addition of the hexane.

Analytically pure samples were obtained from 1:1 acetone–hexane solutions by spontaneous evaporation of solvents at room temperature.

The water and acetone from the $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ complexes may be removed by drying at 70–90° (0.1–0.5 mm) for 48–72 hr. However, the unsolvated complexes are amorphous glassy solids which do not analyze for pure $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ complexes.

(c) **Reaction of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with Benzo-15-crown-5.** Numerous reactions of hydrated samarium(III) nitrate with benzo-15-crown-5 have been carried out using the general procedure outlined in (b) above. However, different products of stoichiometries ranging from the solvent-free $\text{Sm}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ to the solvated

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Table I. Lanthanide Complexes of the Macrocyclic Polyethers

Metal	Color	Dec temp, °C	Analyses, %				Metal
			C	H	N		
(A) Benzo-15-crown-5 Complexes of the Type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$							
La	White	280-285	Calcd	28.3	3.4	7.1	23.4
			Found	28.3	3.4	6.8	23.5
Ce	White	235-245	Calcd	28.3	3.4	7.1	23.6
			Found	28.3	3.4	7.1	23.3
Pr	Pale green	275-276	Calcd	28.2	3.4	7.1	23.7
			Found	27.8	3.4	6.8	23.8
Nd	Pale pink	270	Calcd	28.1	3.4	7.0	24.1
			Found	27.9	3.2	6.4	24.2
Sm	Off white	232-235	Calcd	27.9	3.3	6.9	24.8
			Found	28.2	3.4	6.3	24.6
(B) Benzo-15-crown-5 Complexes of the Type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$							
Sm	White	85-100	Calcd	28.5	4.5	5.9	21.0
			Found	28.8	4.5	6.0	20.9
Eu	Pale yellow-green	104-108	Calcd	28.4	4.5	5.9	21.2
			Found	28.4	4.5	5.9	21.3
Gd	White	105-110	Calcd	28.2	4.5	5.8	21.7
			Found	28.0	4.2	5.6	21.9
Tb	White	118-121	Calcd	28.1	4.4	5.8	21.9
			Found	27.9	4.4	6.0	22.3
Dy	White	118-123	Calcd	28.0	4.4	5.8	22.3
			Found	28.0	4.0	5.9	22.5
Ho	White	120-123	Calcd	27.9	4.4	5.8	22.6
			Found	28.2	4.1	5.8	22.7
Er	White	138-141	Calcd	27.8	4.4	5.7	22.8
			Found	28.2	4.2	5.5	23.1
Tm	White	136-140	Calcd	27.8	4.4	5.7	23.0
			Found	27.8	4.4	5.8	23.3
Yb	Very pale yellow	138-142	Calcd	27.7	4.4	5.7	23.4
			Found	27.6	4.4	5.7	23.5
Lu	White	126-136	Calcd	27.6	4.4	5.7	23.6
			Found	27.6	4.3	5.8	23.8
(C) Dibenz-18-crown-6 Complexes of the Type $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$							
La	Off white	280-285	Calcd	35.0	3.5	6.1	20.3
			Found	35.0	3.5	5.7	20.2
Ce	Off white	220-225	Calcd	35.0	3.5	6.1	20.4
			Found	35.1	3.5	6.1	20.2
Pr	Very pale green	270-275	Calcd	35.0	3.5	6.1	20.5
			Found	34.7	3.6	5.6	20.5
Nd	Very pale pink	247-248	Calcd	34.8	3.5	6.1	20.9
			Found	34.6	3.6	5.9	20.6

$\text{Sm}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ have been obtained in different experiments. The solvated complex $\text{Sm}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ appears to be the favored product when the crystallization step is carried out very slowly by allowing the solvents to evaporate spontaneously at room temperature for 1-2 days.

Preparation of $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ (Ln = La, Ce, Pr, and Nd). A mixture of 2 mmol of the hydrated lanthanide nitrate, 3 mmol of dibenzo-18-crown-6 (II), and 35-55 ml of acetonitrile was boiled under reflux for 30 min with vigorous stirring. After cooling to room temperature, the precipitate was filtered, washed with two 10-ml portions of dichloromethane, and dried at 25° (35 mm) for 1-2 hr. Additional product was recovered from the filtrate by adding excess dichloromethane or diethyl ether and cooling. Nearly quantitative yields (>90%) of the $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ derivatives were obtained. Traces of water and/or acetonitrile in the product can be removed by drying at 130-150° (0.1 mm) for ~16 hr.

An analogous preparative procedure for the lanthanides samarium through terbium gave clear solutions from which only nonstoichiometric materials $\text{Ln}(\text{NO}_3)_3 \cdot x\text{C}_{20}\text{H}_{24}\text{O}_6$ ($x = 0.4-0.8$) could be isolated. An analogous procedure for the lanthanides dysprosium through ytterbium gave no new products; crystallization of these reaction mixtures gave only a physical mixture of the lanthanide nitrate and dibenzo-18-crown-6 as indicated by infrared data.

Separation of Praseodymium and Erbium on a Dibenz-18-crown-6 Column. A 4×45 cm column of solid dibenzo-18-crown-6 (II) was prepared using the general procedure for preparing chromatography columns and using hexane (in which dibenzo-18-crown-6 is essentially insoluble) as a solvent. A solution of 1.0745 g (2.47 mmol) of praseodymium(III) nitrate hexahydrate and 1.1065 g (2.49 mmol) of erbium(III) nitrate pentahydrate in 10 ml of acetone was placed on the dibenzo-18-crown-6 column. The column was

then eluted with a 1:2 mixture of acetone and hexane at a rate of about 2.7 ml/min. Successive 25.0-ml fractions were collected and analyzed through their visible spectra (8000-3600 Å). The initial 100 ml of eluate contained only small amounts of dibenzo-18-crown-6 which had been dissolved out of the column. The following 350 ml of eluate contained 50% of the initial amount of erbium(III) ions and approximately 15% of the initial amount of praseodymium(III) ions present. The next 300 ml of eluate contained 40% of the initial amount of erbium(III) ions and 30% of the initial amount of praseodymium(III) ions present (*i.e.*, after 750 ml of eluate collected, 90% of the Er(III) and only 45% of the Pr(III) ions had been recovered). The remaining erbium(III) and praseodymium(III) ions were slowly eluted in following fractions. The eluate was highly enriched in praseodymium(III) as the amount of erbium decreased steadily to zero. The final fractions of eluate contained only praseodymium(III) ions.

The composition of the 1:2 acetone-hexane solvent used to separate praseodymium and erbium in the above experiment is somewhat critical. In repeat experiments using 1:3 and 2:3 acetone-hexane mixtures, no separation of praseodymium and erbium was observed. The 1:3 acetone-hexane mixture was too nonpolar to elute the lanthanides from the column at an appreciable rate. The 2:3 acetone-hexane mixture was so polar that it eluted the lanthanides from the column at a rate too fast to achieve detectable separation.

The rate of elution is also important since for 1:2 acetone-hexane the separation of Er(III) and Pr(III) is markedly enhanced by a slower elution rate.

Infrared Spectra. Infrared spectra of the new complexes were recorded using a Perkin-Elmer 621 spectrometer with grating optics. Spectra were recorded in the region 650-4000 cm^{-1} as Nujol and

Table II. Proton Nmr Spectra of Benzo-15-crown-5 and Its Lanthanide Complexes

Compound	Proton nmr spectrum, ^a τ					Isotropic H-2 shift of Ln(dmp) ₃ in 4-vinylpyridine ^d
	Benzo-15-crown-5			Other ligands		
	C ₆ H ₄	CH ₂ ^b	CH ₂ ^c	H ₂ O	(CH ₃) ₂ CO	
C ₁₄ H ₂₀ O ₅	3.23	6.13	6.39			
Sm(NO ₃) ₃ ·C ₁₄ H ₂₀ O ₅ ·3H ₂ O·(CH ₃) ₂ CO	3.31	6.13	6.40	5.32	7.98	+0.8
Eu(NO ₃) ₃ ·C ₁₄ H ₂₀ O ₅ ·3H ₂ O·(CH ₃) ₂ CO	3.19	6.03	6.42	2.16	7.86	-3.5
Tm(NO ₃) ₃ ·C ₁₄ H ₂₀ O ₅ ·3H ₂ O·(CH ₃) ₂ CO	3.47	6.98	7.72	<i>e</i>	7.91	-23.6
Yb(NO ₃) ₃ ·C ₁₄ H ₂₀ O ₅ ·3H ₂ O·(CH ₃) ₂ CO	3.23	6.35	6.88	<i>e</i>	7.89	-11.0
Lu(NO ₃) ₃ ·C ₁₄ H ₂₀ O ₅ ·3H ₂ O·(CH ₃) ₂ CO	3.31	6.18	6.42	5.03	7.96	<i>f</i>

^a The proton nmr spectra of the complexes Ln(NO₃)₃·C₁₄H₂₀O₅·3H₂O·(CH₃)₂CO (Ln = Gd, Tb, Dy, Ho, and Er) were so severely broadened that unequivocal peak assignments could not be made. ^b This resonance may be assigned to the four protons of the two methylene groups bonded to oxygen atoms also bonded to the benzene ring. ^c This resonance may be assigned to the 12 protons of the six methylene groups bonded to oxygen atoms only bonded to methylene groups. ^d These data were taken directly from Table II of W. DeW. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971). ^e Not observed. ^f Lutetium(III) is diamagnetic and thus would have no isotropic shift.

Fluorolube mulls between sodium chloride plates and in the region 200–650 cm⁻¹ as Nujol mulls between polyethylene plates. The nitrate combination modes in the 1700–1800 cm⁻¹ region were very weak requiring much more concentrated Nujol mulls for this region than for the remainder of the infrared spectrum.

Proton Nmr Spectra (Table II). Proton nmr spectra were recorded on a Hitachi Perkin-Elmer Model R-20 spectrometer at 60 MHz using acetone-*d*₆ solutions with tetramethylsilane as an internal standard.

Conductance Measurements. Conductances were determined in 0.001 *M* acetonitrile solutions at room temperature (~25°) using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. The molar conductances of the benzo-15-crown-5 complexes Ln(NO₃)₃·C₁₄H₂₀O₅ (Ln = La, Ce, Pr, and Nd) and Ln(NO₃)₃·C₁₄H₂₀O₅·3H₂O·(CH₃)₂CO (Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) fell in the range 3–10 cm² ohm⁻¹ mol⁻¹. The molar conductances of the dibenzo-18-crown-6 complexes Ln(NO₃)₃·C₂₀H₂₄O₆ were in the range 15 ± 2 cm² ohm⁻¹ mol⁻¹. These values contrast with a molar conductance of 170 cm² ohm⁻¹ mol⁻¹ found for tetraethylammonium chloride under the same conditions.

Results and Discussion

(A) Preparation of the Complexes. The nature of the complexes obtained from the lanthanide(III) nitrates and macrocyclic polyethers appears to be quite dependent on the reaction conditions employed. Cassol, Seminario, and De Paoli⁵ have reported the syntheses of the two complete series of unsolvated 1:1 complexes Ln(NO₃)₃·(polyether) (Ln = all lanthanides except Pm; polyether = benzo-15-crown-5 (I) or dibenzo-18-crown-6 (II) by slow crystallization from concentrated acetonitrile solutions. No reference was made by these authors⁵ concerning the existence of any solvated complexes. In our laboratory unsolvated 1:1 complexes were obtained only for the lighter (*i.e.*, larger) lanthanides (La, Ce, Pr, and Nd) with both macrocyclic polyethers I and II. The smaller polyether I yielded only the solvated complexes Ln(NO₃)₃·C₁₄H₂₀O₅·3H₂O·(CH₃)₂CO with the heavier (*i.e.*, smaller) lanthanides (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). These solvated complexes could not be thermally desolvated under vacuum without decomposition. Under our reaction conditions the larger polyether II gave no isolable stoichiometric species with any of the heavier lanthanides.

(B) Thermal Stability Observations. The solvent-free complexes Ln(NO₃)₃·C₁₄H₂₀O₅ (Ln = La, Ce, Pr, Nd, and Sm) and Ln(NO₃)₃·C₂₀H₂₄O₆ (Ln = La, Ce, Pr, and Nd) are relatively thermally stable since they only de-

compose at temperatures well above 200°. The decomposition temperatures of each of these two series of solvent-free complexes (Table I) decrease upon increasing atomic number of the lanthanide except for cerium. Complications involving oxidation to cerium(IV) may account for this anomaly. Thermal decomposition of the solvent-free lanthanide(III) nitrate complexes is violent with gas evolution and formation of a deep red color.

The solvated complexes Ln(NO₃)₃·C₁₄H₂₀O₅·3H₂O·(CH₃)₂CO (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are much less thermally stable than the solvent-free complexes discussed above, since the solvated complexes all decompose below 150°. The decomposition temperatures of the solvated complexes increase upon increasing atomic number of the lanthanide. Thermal decomposition of the solvated complexes appears to involve boiling off the solvating molecules (water and/or acetone) with formation of glassy residues.

(C) Spectroscopic Studies. The *f* → *f* transitions of the lanthanide(III) nitrates are unaffected by complexing with the macrocyclic polyethers I and II in the complexes described in this paper. Thus, the benzo-15-crown-5 (I) complexes of the lanthanide(III) nitrates generally exhibit the color characteristic of the parent lanthanide cation although the benzenoid ultraviolet bands tail off into the visible region with resultant muting of the characteristic colors. All of the dibenzo-18-crown-6 (II) complexes of the lanthanide(III) nitrates are off-white solids. The characteristic colors of the lanthanide ion are lost under the tailing off of the benzenoid ultraviolet bands into the visible region which is much more pronounced than in benzo-15-crown-5 (I).

The infrared spectra of the lanthanide(III) nitrate complexes of the macrocyclic polyethers I and II are quite complex and are similar but not identical with a superposition of the spectra of the lanthanide(III) nitrate and the free ligand. These subtle differences provide definite evidence that the lanthanide(III) nitrate complexes of the macrocyclic polyethers described in this paper involve chemical bond formation between the lanthanide ion and the macrocyclic polyether. The free macrocyclic polyethers I and II exhibit two different ν (C–O) bands at ~1225–1260 cm⁻¹ and at ~1120–1140 cm⁻¹. Upon complex formation these bands are shifted to lower energy by 20–40 cm⁻¹ and

Table III. Nitrate Infrared Bands in the Macrocyclic Polyether Complexes of the Lanthanide(III) Nitrates

Compound type	Nitrate ir bands, ^a cm ⁻¹					
	$\nu_1(A_1)^b$	$\nu_4(B_2)^b$	$\nu_2(A_1)$	$\nu_3(B_1)$	$\nu_2 + \nu_5^c$	$\nu_2 + \nu_6^c$
$\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$	1490	1300	1030	815	1765	1742, 1735 1728
$\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$	1500	1300	1031 1020	815	1765 1755	1730 1720
$\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$	1470	1300	1045	825	1760	1725

^a For the assignments and notations see R. J. Foster and D. G. Hendricker, *Inorg. Chim. Acta*, **6**, 371 (1972). ^b Broad and unresolved (± 10 cm⁻¹). ^c Very weak combination bands. A much more concentrated Nujol mull was used to determine these frequencies than the fundamental frequencies $\nu_1 - \nu_4$.

become noticeably weaker. For each of the three classes of complexes, $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ (Ln = La, Ce, Pr, Nd, and Sm), $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), and $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ (Ln = La, Ce, Pr, and Nd), the infrared spectra are independent of the lanthanide ion indicating that the metal-ether interactions are essentially identical within the limitations of the sensitivity of the infrared spectra.

In the solvated complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ the presence of the solvents is evident from bands at 1695–1698 (vs) and 1640–1635 (s) cm⁻¹ from the acetone $\nu(\text{C}=\text{O})$ and water $\delta(\text{O}-\text{H})$ frequencies, respectively. In the infrared spectra of all of the ten solvated complexes of this type, the relative intensities of the 1695–1698-cm⁻¹ (from the acetone), the 1635–1640-cm⁻¹ (from the water), and the 1595–1598-cm⁻¹ (from the macrocyclic polyether) bands are essentially constant confirming the constant 1:3:1 macrocyclic polyether:water:acetone ratios of all ten complexes indicated by the analytical data. The downward shift of only 15–20 cm⁻¹ of the acetone $\nu(\text{C}=\text{O})$ frequency in the solvated complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ relative to free acetone suggests that the interaction of the acetone with the metal ion is very weak, since coordination of a carbonyl oxygen to a lanthanide atom normally⁸ results in a reduction of the $\nu(\text{C}=\text{O})$ frequency by 80–120 cm⁻¹.

All three types of lanthanide(III) nitrate macrocyclic polyether complexes, $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$, $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$, and $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$, exhibit low conductance values in acetonitrile solution indicating that they are nonelectrolytes with no ionic nitrate groups. All three nitrates must be bonded to the lanthanide ion as monodentate, bidentate, and/or bridging ligands.

The infrared bands (Table III) attributed to the nitrate groups in the three series of lanthanide(III) nitrate macrocyclic polyether complexes support the presence of only bidentate nitrate ligands. The positions of the nitrate stretching frequencies are similar to those in other lanthanide nitrate complexes with bidentate nitrate ligands.^{9–13} More significantly the separations between the two very weak combination bands in the 1700–1800-cm⁻¹ region in the macrocyclic polyether

complexes of the lanthanide(III) nitrates are 35 ± 5 cm⁻¹ which is in the 20–66-cm⁻¹ range found¹⁴ for known bidentate nitrate complexes rather than the 5–26-cm⁻¹ range found for known monodentate nitrate complexes.

The proton nmr spectra of the macrocyclic polyether complexes of the lanthanide(III) nitrates were investigated (Table II). Unfortunately, the solvent-free complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5$ (Ln = La, Ce, Pr, Nd, and Sm) and $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{20}\text{H}_{24}\text{O}_6$ (Ln = La, Ce, Pr, and Nd) were too insoluble in $(\text{CD}_3)_2\text{CO}$ for spectra to be observed. This limited the proton nmr investigations of the macrocyclic polyether lanthanide(III) nitrate complexes to the more soluble solvated derivatives $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$. Among these compounds only five of the ten complexes gave satisfactory nmr spectra (Table II). The proton nmr spectra of the other complexes of this type exhibited resonances which were too broad to be unequivocally detected and assigned.

Our proton nmr observations on the lanthanide complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ correlate well with the observations by Horrocks and Sipe¹⁵ on the effects of the tris(dipivaloylmethanato)lanthanide(III) shift reagents on the proton nmr spectra of 4-vinylpyridine and 2-picoline. However, all of the isotropic proton nmr shifts for the lanthanide complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ were much less than those arising from the tris(dipivaloylmethanato)-europium(III) paramagnetic shift reagent.¹⁶ The lanthanide complexes $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ which exhibited too much line broadening to give tractable nmr spectra (Ln = Gd, Tb, Dy, Ho, and Er) were the same lanthanides which exhibited excessive line broadening ($\Delta\nu_{1/2} \geq 50$ Hz) in the nmr spectrum of the methyl protons of 2-picoline.¹⁵ The small isotropic shifts of the proton nmr resonances in the other $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ complexes (Ln = Sm, Eu, Tm, and Yb) correlate well with the observed¹⁵ isotropic shifts of the corresponding tris(dipivaloylmethanato)lanthanide(III) complexes on the H-2 proton of 4-vinylpyridine taking the nmr spectrum of the corresponding diamagnetic lutetium complex $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ as the reference. The shifts of the water protons in the $\text{Ln}(\text{NO}_3)_3 \cdot \text{C}_{14}\text{H}_{20}\text{O}_5 \cdot 3\text{H}_2\text{O} \cdot (\text{CH}_3)_2\text{CO}$ complexes were much larger than the shifts of the macrocyclic polyether protons in accord with the closer proximity of the water protons

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to an oxygen donor. Indeed the isotropic shifts of the macrocyclic polyether protons in the samarium and europium compounds were insignificant; these two metals were among those found by Horrocks and Sipe¹⁵ to shift the H-2 protons in 4-vinylpyridine by less than 4 ppm. On the other hand, the isotropic shifts of the water protons in the thulium and ytterbium compounds were too large to be observed on the available spectrometer; these two metals were among those found by Horrocks and Sipe¹⁵ to shift the H-2 proton in 4-vinylpyridine by more than 10 ppm.

(D) Lanthanide Separation Experiments. The close similarities in the ionic radii of the different lanthanides make their chemistry very similar and hence their separation relatively difficult. The significant and systematic differences in the coordinating properties of the macrocyclic polyethers with the different lanthanides suggested that differential complexing behavior with a rigid macrocyclic polyether could be used as a basis for lanthanide separation. In order to test this possibility we chromatographed a mixture of praseodymium and erbium nitrates on a column of dibenzo-18-crown-6 (II) and analyzed the eluates by visible spectroscopy. Dibenzo-18-crown-6 (II) rather than benzo-15-crown-5 (I) was selected as a column material for this experiment for the following reasons: (1) it is more readily available than benzo-15-crown-5; (2) it is essentially insoluble in acetone whereas benzo-15-crown-5 is highly soluble in acetone; (3) it forms less stable complexes

with the lanthanides which should make the lanthanides more readily eluted from a column of dibenzo-18-crown-6 than from one of benzo-15-crown-5. We were able to find conditions in such a chromatography experiment where praseodymium was adsorbed sufficiently more strongly than erbium on a dibenzo-18-crown-6 column that not only qualitative separation between the two metals could be detected spectroscopically but also praseodymium spectroscopically free from erbium could be obtained from the latest lanthanide-containing eluates of such a chromatogram. The demonstrated weaker retention of erbium relative to praseodymium on a dibenzo-18-crown-6 column is a further indication of the previously discussed decreasing stability of lanthanide macrocyclic polyether complexes upon increasing atomic number of the lanthanide. Whether this effect can be exploited to improve the ease, efficiency, and practicality of lanthanide separation can only be determined after considerably more extensive experimentation with macrocyclic polyethers under conditions more closely approximating those currently used for lanthanide separation by ion exchange and related methods.

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Metal-Porphyrin Interactions. III. A Dissociative-Interchange Mechanism for Metal Ion Incorporation into Porphyrin Molecules¹

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Abstract: The kinetics of divalent metal ion incorporation into the monomeric tetrakis(4-*N*-methylpyridyl)porphine (TMTPyP), tetrasulfonated tetraphenylporphine (TPPS₄), and uroporphyrin I (Uro) were studied in acidic and basic solutions. The TMTPyP reactions were nitrate catalyzed if the formal charge in the activated complex was 6+ and either catalyzed or uncatalyzed pathways operate for lower charges. No anion catalysis was found in the TPPS₄ or Uro reactions. The majority of observations on the incorporation of metal ions into porphyrins can be explained with a dissociative-interchange mechanism, by taking into account porphyrin deformation.

Over the past 10 years, a number of studies² have been addressed to the question of how metal ions are incorporated into porphyrin molecules to form metalloporphyrins. While there are many elegant ways to synthesize metalloporphyrins,^{3,4} the mechanisms of

such reactions are by no means clear. The earliest kinetic studies used derivatives of protoporphyrin IX which, in combination with Fe(II), is the prosthetic group of hemoglobin.⁵ However, their free-base forms are insoluble in acids, and they appear to show extensive association in basic solution.⁶ In the presence of detergents such porphyrins and their esters are

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