# COMPLEXES OF LANTHANIDE(III) NITRATES WITH A TETRAOXADIAZA MACROCYCLE

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Abstract- The 1:1 complexes of the complete series of lanthanide nitrates with a diazatetraova 18-membered macrocycle have been synthesized under anhydrous conditions. The complexes were characterized by elemental analysis, conductometric and spectral data. It is established that the macrocycle adopts a non-planar conformation and that the nitrate ions are bonded differently in the heavier (La-Sm) and lighter (Gd-Yh) lanthanide complexes. The coordinating abilities relative to the rare earths of the macrocycle and of dibenzo-18-crown-6 are discussed.

## INTRODUCTION

Macrocycles such as the crown ethers[1] and the cryptates[2] have received considerable attention in recent years due to their unusual complexing properties which directly depend upon the size of their internal cavity[3]. Most studies have been devoted to complexes formed between alkali or alkaline earth cations and a wide variety of macrocyclic ligands containing N. O or S donor atoms. A highly selective complexation of alkali ions has been achieved with macrocycles of suitable size[3] and various attempts to apply this selectivity to separations by liquid–liquid extraction have recently been described [4, 5].

In the alkali ion complex species, all the donor atoms of the cycle are involved in the coordination which is essentially induced by electrostatic (ion-dipole) forces. The lanthanide ions, because of the effective shielding of their 4f valence electrons, participate in largely electrostatic, non-directional bonds similar to the ligandalkali ion bonds. It is thus expected that the rare earth salts can form adducts with various macrocycles. This assumption is supported by recent descriptions[6,7] of 1:1 complexes of some lanthanide nitrates with the macrocyclic polyether dibenzo-18-crown-6 (I; 2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16-hexaoxacyclooctadeca-2,11diene). Although at variance with some earlier results[6], King and Heckley[7] reported that I forms 1:1 complexes with the lighter lanthanides only (La-Nd). A smaller. 15-membered cyclic polyether is able to form solvated complexes with all the rare earths.



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The present paper reports the preparation and spectroscopic properties of new lanthanide complexes with the polyoxapolyaza macrocycle II (1, 7, 10, 16-tetraoxa-4,13-diazacyclooctadecane). It is shown that minor changes in the nature of the donor atoms and in the rigidity of a macrocycle can significantly alter the complexing properties relative to the lanthanide ions even if the size of the internal cavity is approximately maintained. The data reported in this paper are directly relevant to the development of new chemical systems for the separation of rare earths.

#### **EXPERIMENTAL**

Proton NMR spectra were determined on a Varian T60 or a Bruker HFX-90 spectrometer at probe temperature. All NMR solutions were handled in an inert atmosphere dry box. The complex species with II are sparingly soluble in most deuterated solvents except  $d_3$ -nitromethane. The IR spectra were recorded using a Perkin-Elmer model 125 spectrophotometer. As ligand II reacts with the alkali halide materials used for IR spectroscopy, the spectra were recorded for samples as Nujol or hexachloro-1,3-butadiene mulls. The Raman spectra of solid samples were determined by Dr. B. Gilbert on a Cary model 81 spectrometer equipped with an argon laser. The conductivities of the complexes were obtained using a Methrom conductivity bridge E527 at 20°C with a measuring cell in a dry box.

### Preparation of ligand II (Scheme 1)

(a) 3.6-Dioxaoctane-1.8-diamine. The diamine obtained in step (3) was synthesized according to the general procedure of Fleischer *et al.*[8]. Step (2) is carried out by these authors in diethyleneglycol in which NaN<sub>3</sub> is soluble at the boiling point. This solvent is inappropriate to the present case as it is not easily separated from the bisazido compound. The following modified procedure was adopted for step (2).

Under a nitrogen atmosphere, 15 g (33 mmole) of the histosylate (step 1) were dissolved in 100 ml of anhydrous acetone and mixed with 7.5 g (0.1 mole) of NaN<sub>3</sub> and 13 g (60 mmole) of anhydrous Et<sub>x</sub>NBr. The mixture was refluxed for 32 hr. After cooling, the solution was filtered and evaporated. The residue was dissolved in diethyl ether, dried over Na<sub>2</sub>SO<sub>4</sub> and treated with activated charcoal. After evaporation of the solvent, the colorless oil weighted 6.0 g (yield 93%).

(b) Cyclisation procedure. Step (4) was carried out as suggested by Stetter and Mayer[9]. The di (p-toluenesulfonyl) derivative of cycle II was synthesized (step 5) according to the method of Richman and Atkins[10] with some modifications. Under a nitrogen atmosphere, 9g (0.13 mole) of sodium ethovide were added to a suspension of 29.7g (65 mmole) of the di(p-toluene-sulfonyl) derivative of 3,6-dioxaoctane-1.8-diamine in

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boiling ethanol. The mixture was maintained at boiling for 10 min and the solvent was distilled off under vacuum. To the white solid residue were added 500 ml of DMF and the mixture was heated to 100°C. A solution of the bis *p*-toluenesulfonate of triethyleneglycol (29.8 g, 65 mmole) in 250 ml of DMF was then added dropwise over a period of 3 hr. After cooling, the solvent was evaporated to near dryness and the remaining slurry was stirred with 250 ml of water until the product solidified. The white material was filtrated, washed with water and recrystallized from toluene (yield 82%, molecular weight by osmometry: Calcd, 570.7; Found: 572.1).

(c) Macrocycle II. The hydrolysis (step 6) of the disulfonamide derivative of cycle II was performed according to the general procedure of Closson et al. [11]. A solution of 0.07 equiv. of sodium naphtalenide in 1,2-dimethoxyethane (DME) was added to a suspension of 0.01 equiv. of the disulfonamide in DME. The reaction mixture was stirred for 1 hr and then quenched with water. The solvent was eliminated by vacuum distillation and water was added to the remaining solid. Naphtalene was then isolated by filtration and thoroughly washed with water. The aqueous filtrates were made slightly acidic with nitric acid and were evaporated to dryness. The nitrate salt of cycle II was isolated by two extractions of the solid white residue with 200 ml of hot anhydrous ethanol. The solvent was removed by distillation. A solution of the nitrate salt in water was then treated with an excess of an aqueous solution of tetramethylammonium hydroxyde. Water was eliminated by stirring with refluxing benzene and collecting the azeotrope in a Dean-Stark trap. After filtration, benzene was stripped off on a rotatory evaporator. The residual yellowish oil was distilled in a Kugelrohr (150°C, 0.2 mm). Anal. Caled.: C, 54.94; H, 9.99; N, 10.68. Found: C, 54.99; H, 10.20; N, 10.78. m.p.: 115-116°C[2]. Exchange in D<sub>2</sub>O leads to a macrocycle deuterated in the NH positions as verified by NMR.

## Syntheses and analyses of complex species

Macrocycle II is a strong base; the synthesis of its lanthanide complexes from hydrated nitrate salts is hampered by partial hydrolysis of the metal ions. All syntheses had to be carried out under nitrogen in a controlled atmosphere dry box.

Anhydrous acetonitrile solutions of lanthanide nitrates were easily obtained by refluxing the hydrated solutions through a Soxhlet extractor packed with molecular sieves [12]. A 24 hr refluxing time with 50 g of molecular sieves is sufficient to prepare 50 ml of an anhydrous  $2 \times 10^{-1}$  M solution as verified by

Karl Fischer titration. This method appears to be of wide applicability[13] and successfully replaces more involved techniques[14, 15] for the preparation of anhydrous solutions of lanthanide salts. The complexes were prepared by addition of a 5 ml acetonitrile solution containing 1 mmole of anhydrous lanthanide nitrate to 1 mmole of neat macrocycle II. The precipitate formed immediately and the suspension was refluxed for 1 hr. After cooling, the complex species were filtered, washed with acetonitrile and held overnight in vacuum at 80°C (yield around 80%).

Elemental carbon, hydrogen and nitrogen analyses were performed within the chemistry department of the University. The lanthanide analyses were carried out by titration with ethylenediamine-tetraacetic acid in an acetate buffer using Xylenol Orange as an indicator[16]. The complexes were directly dissolved in dilute nitric acid prior to the titration and the pH was adjusted with pyridine.

# RESULTS AND DISCUSSION

## Preparation of the complexes

The tetraoxadiaza macrocycle II was synthesized according to Scheme 1 from inexpensive starting materials. This synthesis involves a minimum number of steps and does not require high dilution techniques (2) to achieve the internal condensation into a large ring.

Macrocycle II forms complexes with all the rare earths if the syntheses are performed under strictly anhydrous conditions. In the presence of hydration water, the lanthanum adduct with II is the only complex which can be prepared analytically pure. Heavier lanthanides tend to form hydroxy compounds and gadolinium and all the following rare earths are entirely precipitated as hydroxydes. The elemental analyses of various complexes are reported in Table 1. All products are crystalline powders of color characteristic of the coordinated ion. They appear to be relatively stable to air and moisture although they undergo rapid hydrolytic decomposition if added to water. Under our operative conditions, no pure dibenzo-18-crown-6 (I) complexes of lanthanide ions heavier than Nd could be prepared. This observation is in agreement with the data reported by King and Heckley [7] who used hydrated rare earth solutions for their syntheses but it is at variance with earlier work by Cassol et al. [6]. These authors described the synthesis of the complete series of lanthanide complexes with macrocycle I.

## Spectroscopic studies

(a) *IR spectra*. IR spectroscopy affords evidences for the complexation of lanthanide nitrates by macrocycle II. The C-O-C and C-N-C absorption bands are found at  $1105-1135 \text{ cm}^{-1}$  in the spectrum of the free ligand and at  $1070-1100 \text{ cm}^{-1}$  in the spectrum of the coordinated species. Similar shifts have been reported for the rare earth complexes of I[7].

Coordination also alters the position of the NH bands. In the spectrum of the free ligand, the NH wagging band  $\delta_{\rm NH}$  occurs near 780 cm<sup>-1</sup> and is relatively broad and intense. In the complex species La-Sm, this band is displaced to 805 cm<sup>-1</sup> and becomes considerably narrower. As  $\delta_{\rm NH}$  partially overlaps with the  $\nu_3(B_1)$  nitrate band, its spectral assignment was checked by deuteration of the ligand in the NH position. The new ND band is found at 752 cm<sup>-1</sup>. The free ligand also gives rise to a weak NH stretching vibration  $\nu_{\rm NH}$  at 3335 cm<sup>-1</sup>. In the La-Sm complexes, two narrow and greatly intensified bands appear at 3285 cm<sup>-1</sup> and 3275 cm<sup>-1</sup> (two  $\nu_{\rm ND}$  bands are observed at 2445 and 2435 cm<sup>-1</sup> for the deuterated

Table 1. Analytical data for Ln(NO<sub>4</sub>), II

	C (%)		H (%)		N (%)		Ln (%)	
	Calcd	Found	Caled	Found	Calcd	Found	Caled	Found
La	24.54	24.58	4.46	4.54	11.92	11.67	23.65	23.36
Pr	24.46	24.62	4.45	4.51	11.88	11.73	23.91	23.87
Nd	24.32	24.41	4.42	4.51	11.82	11.87	24.34	24.33
Sm	24.07	24.13	4.38	4.27	11.70	11.73	25.11	25.08
Eu	24.01	24.09	4.36	4.32	11.67	11.62	25.31	25.43
Gd	23.80	23.68	4.33	4.28	11.56	11.49	25.96	25.91
Τh	23.73	23.62	4.31	4.39	11.53	11.48	26.17	26.21
Dv	23.59	23.69	4.29	4.37	11.46	11.35	26.60	26.73
Но	23.50	23.38	4.27	4.08	11.42	11.40	26.89	26.72
Er	23.41	23.56	4.26	4.32	11.37	11.42	27.17	27.19
Tm	23.35	23.47	4.24	4.22	11.34	11.27	27.37	27.41
Ϋ́h	23.19	23.06	4.22	4.18	11.27	11.37	27.84	27.60

species). The shift toward frequencies as well as the intensity enhancement upon complexation have been reported for many other metal-amine complexes[17]. These alterations of the spectra are attributed to an attraction of the free electron pairs of the amine groups by the metal ion and to the resulting increase in polarity of the NH bonds. Moreover Weiss et al. [18, 19] have shown in their crystallographic analysis of the solid state structure of free macrocycle II that the NH bonds are pointing toward the center of the internal cavity and could be involved in weak hydrogen bondings with some heterocyclic oxygen atoms. On the contrary, in the 1:1 KSCN complex, the NH bonds are directed outwards and the nitrogen free electron pairs are coordinated to the alkali ion[19]. Similar structural modifications could be partially responsible for the important alterations of the  $\nu_{\rm NH}$  band of the lanthanide complexes.

From the splitting of the  $\nu_{\rm NH}$  band, it is concluded that two non-equivalent amino groups are present in the La-Sm complexes. For the heavier rare earths (Eu-Yb), the  $\nu_{\rm NH}$  stretching vibration becomes much larger and is shifted further to low frequencies by 90 cm<sup>-1</sup>. This new modification of the spectra could be induced by hydrogen bonding, presumably between the NH groups and the nitrate ions. The absorption bands of the latter are indeed altered when the shape and position of the NH band are modified. Assignments of the nitrate absorptions based upon the  $C_{2i}$  symmetry of the coordinated nitrate ion are reported in Table 2. For purposes of clarity, we adopted the notations used by King and Heckley [7] in the description of the complexes with dibenzo-18-crown-6 (1). For the rare earths La-Sm, the two valence vibrations  $v_1$  and  $v_4$  are separated by 180 cm<sup>-1</sup> in agreement with data reported for complexes containing bidentate nitrate ions. Furthermore the separation between the two weak combination peaks  $\nu_2$  +  $v_s$  and  $v_s + v_a$  is at the lower end of the 20-66 cm<sup>-1</sup> range proposed by Lever *et al.*[20] as indicative of bidentate nitrate groups. Finally, the presence of only one type of coordinated nitrate ion is confirmed by the Raman spectra in which the  $\nu_5$  band is single and intense. The nitrate absorption bands are more complex in the IR spectra of the heavier lanthanides Eu-Yb. Five to six combination bands are observed in the 1700-1800 cm region. The  $\nu_1$ ,  $\nu_4$  and  $\nu_2$  absorption bands are divided into several peaks but no bands could be assigned to ionic nitrate groups. Three inequivalently bonded nitrate ions are apparently present in these complex species as three intense  $\nu_2$  peaks are observed in the Raman spectra. The IR spectra are too complex to allow a distinction between monodentate and bidentate nitrate groups but the former are probably present in these complexes.

It should be pointed out that all the complexes with macrocycle II are non-ionic. The molar conductivities of 0.001 M solutions in acetonitrile are in the range 15–22 cm<sup>2</sup>  $\Omega$  <sup>4</sup> mole <sup>4</sup> which is indicative of non-electrolyte behaviour (tetraethylammonium chloride has a molar conductance of 175 cm<sup>2</sup>  $\Omega$  <sup>4</sup> mol <sup>4</sup>[15]). The nitrate ions are thus directly bonded to the metal ion in agreement with the IR data. Finally the ligand absorptions in the 900–1200 cm <sup>4</sup> region are quite different in the IR spectra of macrocycle II and of its complexes with rare earths La-Sm and Eu-Yb, thus suggesting several conformations of the coordinated ligand.

Thus, macrocycle II appears to form complexes with the rare earths of two distinct types. None of these is symmetrical as either different NH groups, either different NO<sub>4</sub> anions (or both) are observed in the IR or Raman spectra.

(b) *NMR spectra*. The NMR spectra afford a further indication of the low symmetry of the lanthanide complexes with macrocycle II. Rare earth ions induce proton paramagnetic shifts which are essentially dipolar in origin[22, 23]. The dipolar shift of a ligand nucleus is a

Table 2. Assignment of bands in regions of nitrate absorptions (cm. ')

	$v_i(A_2)$	$\nu_4(B_2)$	$v_2(A_1)$	$\nu_3(B_1)$	P.	P <sub>e</sub>	rs+rs	$v_{s} \leq v_{t}$
(La-Sm)(NO3) eH (Gd-Yb)(NO3) eH	1490 1525–1500	1310 1270–1290	1050† 1025‡ 1035 1045	815 810	735 735	710§ 710§	1785 five pe 1720	1730 to six aks =1770

"Single and intense in IR and Raman spectra.

Three intense bands in the Raman spectra.

Very weak IR peak, medium weak Raman peak. Several peaks. function of the principal molecular susceptibilities  $\chi_x$ ,  $\chi_y$ ,  $\chi_z$  and of the structure of the complex in solution:

$$\left(\frac{\Delta\nu}{\nu}\right)^{dip} = -\frac{D}{3N} \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle - \frac{D'}{2N} \left\langle \frac{\sin^2\theta\cos 2\Omega}{r^3} \right\rangle$$
$$D = \chi_z - \frac{1}{2}(\chi_z + \chi_y)$$
$$D' = \chi_z - \chi_y$$

where  $\theta$ ,  $\Omega$  and r are the polar coordinates of the nucleus under consideration relative to the axes of the magnetic susceptibility tensor. This equation simplifies only for axially symmetric [22, 23] complexes, which is most probably not the case for adducts with II. It is impossible to compute the shifts induced by lanthanide ions in macrocycle II as the D and D' susceptibility terms are unknown. Qualitative conclusions can however be reached on a firm basis from the NMR spectra.

Table 3 contains the mean geometric factors of the

Table 3. Mean geometric factors  $G(\theta, r) = \langle 3\cos^2 \theta - 1/r^3 \rangle$  and  $G'(\theta, \Omega, r) = \langle \sin^2 \theta \cos^2 \Omega/r^3 \rangle$  for complexes with macrocycle II

	<i>G</i>	G'				
Planar conformation <sup>+</sup>						
CH <sub>2</sub> (3, 5, 12, 14)	$-1.00 \times 10^{-2}$	$+1.03 \times 10^{-2}$				
CH <sub>2</sub> (2, 6, 11, 15)	$-1.16 \times 10^{-2}$	$+1.10 \times 10^{-3}$				
CH <sub>2</sub> (8, 9, 17, 18)	$-1.25 \times 10^{-2}$	$-1.25 \times 10^{-2}$				
Non-planar conformation <sup>‡</sup>						
$CH_2$ (3, 5)	$-3.84 \times 10^{-3}$	$+9.38 \times 10^{-3}$				
CH <sub>2</sub> (2, 6)	$-1.46 \times 10^{-3}$	$+6.82 \times 10^{-4}$				
CH <sub>2</sub> (8, 18)	$-1.32 \times 10^{-3}$	$-1.35 \times 10^{-2}$				
CH <sub>2</sub> (9, 17)	$-1.74 \times 10^{-3}$	$-1.25 \times 10^{-2}$				
CH <sub>2</sub> (11, 15)	$+6.35 \times 10^{-2}$	$-5.74 \times 10^{-3}$				
CH <sub>2</sub> (12, 14)	$+2.44 \times 10^{-2}$	$-3.68 \times 10^{-4}$				

<sup>+</sup>Mean values for KSCN·II computed[23] from crystallographic data[19]. The z axis is normal to the plane of the donor atoms. The y axis is coincident with the C<sub>2</sub> axis bissecting the C<sub>8</sub>-C<sub>9</sub> and C<sub>17</sub>-C<sub>18</sub> bonds.

‡Mean values computed for NaSCN-18-crown-6·H<sub>2</sub>O from crystallographic data[24, 25]. The oxygen atoms numbered O4 and O13 by Dunitz *et al.*[25] are replaced by N atoms, respectively N<sub>4</sub> and N<sub>13</sub>. The macrocycle is oriented with the z axis pointing at N<sub>13</sub> and the x axis pointing at N<sub>4</sub>.

dipolar equation for the various  $CH_2$  groups of macrocycle II as computed from the X-ray data reported [19] for the planar structure KSN II. The orientation of the axes specified in Table 3 is considered the most reasonable in view of the symmetry of the ligand. Three sets of geometric factors are obtained and the NMR spectra should exhibit three  $CH_2$  peaks. Inverting the axes would change the values of the geometric factors but not the number of separate peaks to be observed.

The same computations were performed on a nonplanar configuration similar to the crystallographic structure reported by Dunitz et al. [24, 25] for the complex between NaSCN and the fully oxygenated analogue of II (18-crown-6, III). In this configuration the N13 atom and the two adjoining ethylene groups are out of the mean plane formed by the other donor atoms of the macrocycle. The six sets of geometric factors which are computed should give rise to six CH<sub>2</sub> peaks in the NMR spectra. The NMR spectrum of a deuterated nitromethane solution of Pr(NO<sub>3</sub>)<sub>3</sub>·II is presented in Fig. 1. The spectrum exhibits six CH<sub>2</sub> peaks considerably shifted from their diamagnetic position both towards high and low fields. Although our structural model is only a very crude approximation of the true structure of the complex species in solution, it can account for the sign of the paramagnetic shifts for a broad range of D and D'values. For instance, if D and D' are set equal, respectively, to -1000 and  $-750 \times 10^{-6}$  cgsu mole<sup>-1</sup>, the induced shifts towards high fields of the CH<sub>2</sub> peaks (3, 5), (11, 15) and (12, 14) are +2.6, +1.6 and +20.0 ppm whereas the  $CH_2$  peaks (2, 6), (9, 17) and (12, 14) would be shifted to low fields by -11.7, -19.4 and -22.2 ppm. No effort was made to reach a quantitative fit between the proposed structure and the observed spectrum as a thorough interpretation of the paramagnetic shifts is beyond the scope of the present study. The observation of six distinct NMR peaks however allows one to assign to the lanthanide complexes with II an irregular conformation similar to the structure of NaSCN-III mentioned above[24, 25].

It is noteworthy that an excess of macrocycle II does not exchange with the coordinated ligand, indicating slow intermolecular ligand exchange on the NMR time scale and high stability of the complexes.



Fig. 1. NMR spectrum of a deuterated nitromethane solution of Pr(NO<sub>3</sub>)<sub>3</sub>·II. A similar spectrum was obtained for Eu(NO<sub>3</sub>)<sub>3</sub>·II with CH<sub>2</sub> peaks at -10.85, -6.54, -5.29, -1.39, +9.30 and +11.28 ppm from TMS. The NMR spectrum of pure macrocycle II exhibits peaks at -3.60, -3.50 and -2.85 ppm.

# CONCLUSION

In our operative conditions and in agreement with the recent work of King and Heckley [7], macrocycle 1 is found to yield solid complexes of the lighter lanthanides (La-Nd) only. On the other hand, 1:1 adducts with macrocycle II are obtained with all the rare earths if the syntheses are performed in anhydrous conditions. The ability of II to complex all the lanthanides involves a rearrangement of the molecular structure. In the lighter (i.e. larger) lanthanide complex species (La-Sm), only one type of coordinated nitrate ion is observed in the Raman and IR spectra and the macrocycle adopts a non-planar conformation. In the heavier (i.e. smaller) rare earth complexes (Gd-Yb), cycle II is also non-planar and one can differentiate three types of nitrate ions: some of these are probably monodentate and possibly involved in hydrogen bonding with the amine groups.

The differences in selectivity of complexation by macrocycles I and II should not be assigned to their dimensions as they have internal cavities of approximately the same size. Moreover the decrease in oxygen basicity of dibenzo-18-crown-6 induced by the aromatic substituents is likely too small to account for the behaviour of this ligand. Probably of much greater consequence is the ability of the macrocycles to rearrange around the central metal ion.

The rare earths as well as the sodium ions are too small to fill the internal cavity of I and II. In the many crystallographic structures reported[24] for the adducts of Na' salts with I, the six oxygen atoms of the ligand adopt an approximately planar conformation despite the small size of the metal ion. A roughly planar structure has recently been reported for the lanthanum nitrate complex with the less rigid ligand, syn-di-(cis-cyclohexyl)-18-crown-6[26]. On the other hand, the unsubstituted hexaether 18-crown-6 complexed with NaSCN adopts an irregular conformation which would be considerably strained in the case of cycle I or its cyclohexyl analogue [24]. The same irregular conformation is used in this work to interpret qualitatively the paramagnetic NMR shifts. As alkali ions and rare earths are similar by their ionic size and by the nature of their coordination bonds, it is concluded that cycle I is unable to rearrange to a sufficient extent to complex all the lanthanides because of the rigidity brought about by the aromatic substituents. On the contrary, cycle II can adopt various conformations of reduced cavity size and coordinates with all the rare earths despite their radius contraction. The ability of the NH groups of II to participate in hydrogen bonding with the nitrate anions could also be of importance in the complexation. If the macrocycles are to be applied to the separation of rare earth ions, the required high selectivity will most probably be achieved only with sufficiently large and rigid ligands.

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