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thesis entitled

SYNTHESIS AND CHEMICAL STUDIES OF SOME LANTHANIDE CRYPTATES

presented by

David Jerome Pruett

has been accepted towards fulfillment of the requirements for

Ph.D. degree in Chemistry

Major professor

Date September 18, 1978

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OF SOME LANTHANIDE CRYPTATES

By

David Jerome Pruett

arried out.

[Ln(2:2:1) CA DISSERTATION

in situ dehydrati Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

Analysis of the inf 1978

## obtained show a shift ABSTRACT tretching frequency of

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OF SOME LANTHANIDE CRYPTATES

By

David Jerome Pruett

Literature methods were modified and applied to the synthesis of 2:2:1 and 2:2:2 cryptand. A systematic survey of the ability of these ligands to coordinate the tripositive lanthanide ions (except Pm and Tm) was carried out.

It was found that 2:2:1 cryptand would react stoichiometrically to form 1:1 inclusion complexes, [Ln(2:2:1)]Cl<sub>3</sub> (Ln = La, Ce, Pr, Nd, Sm, Eu, or Gd) or [Ln(2:2:1)](NO<sub>3</sub>)<sub>3</sub> (Ln = La, Ce, Pr, Nd, or Sm) in acetonitrile solution using trimethyl orthoformate as an <u>in situ</u> dehydrating agent. The heavier lanthanides yielded mixtures of [Ln(2:2:1)]X<sub>3</sub> and uncoordinated LnX<sub>3</sub> under the same conditions.

2:2:2 cryptand reacted stoichiometrically only with the lightest members of the lanthanide series to form  $[Ln(2:2:2)]Cl_3$  (Ln = La, Ce, Pr, or Nd) or  $[Ln(2:2:2)](NO_3)_3$  (Ln = La, Ce, or Pr). The remaining members of the series again produced non-stoichiometric mixtures of  $[Ln(2:2:2)]X_3$  and  $LnX_3$ .

Analysis of the infrared spectra of the compounds

obtained show a shift in the stretching frequency of the the ether linkage from about 1125 cm<sup>-1</sup> in the free ligands to 1075 cm<sup>-1</sup> in the [Ln(2:2:1)]X<sub>3</sub> or [Ln(2:2:2)]X<sub>3</sub> complexes. The nitrate complexes contain both free any nitrate and nitrate coordinated to the lanthanide ion as a bidentate ligand. Perchlorate complexes contain only uncoordinated  $ClO_4^-$  ions.

conf It was found that encryptation had little or no effect on the electronic absorption or emission spectra of the Ln<sup>3+</sup> species.

Cyclic voltammograms for the  $[Eu(2:2:1)]^{3+}$ , and  $[Yb(2:2:1)]^{3+}$  species were recorded. Attempts to measure similar potentials for the 1 in the definition  $[Yb(2:2:2)]^{3+}$ ,  $[Sm(2:2:1)]^{3+}$ , and  $[Sm(2:2:2)]^{3+}$  species at were unsuccessful.

Stability constants for the formation of 1:1 and 2:1 complexes between fluoride ion and various [Ln(2:2:1)]<sup>3+</sup> species (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy) were determined titrimetrically by the use of a fluoride ion selective electrode.

Analysis of the proton nmr spectrum of  $[La(2:2:1)](NO_3)_3$  and consideration of the approximate symmetry of the ligand lead to the conclusion that there are eight types of magnetically non-equivalent protons in the complex, and four protons of each type. A simple AMXY pattern was observed for all four of the -N-CH<sub>2</sub>CH<sub>2</sub>-O

fragments of the  $-N-O-CH_2CH_2-O-CH_2CH_2-N$ - residues of the molecule. This implies that both of these residues have the same rigid conformation, or that only one such conformation is highly favored thermodynamically among many rapidly interconverting conformations. The spectrum of the  $[Lu(2:2:1)]^{3+}$  species was found to be very similar to its La analog, indicating only small changes in the conformation of the molecule upon substitution of the smaller ion.

The paramagnetic  $[Ln(2:2:1)]^{3+}$  cryptates (Ln = Ce). Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, and Yb) produce an nmr spectrum with eight broad lines, the pattern of which varies only in sign and magnitude as the central lanthanide ion is varied. A combination of line width data, chemical shifts, and approximate metal-proton radial distances obtained by using the crystal structure of the [Na(2:2:1)]SCN cryptate were used to assign the resonances observed in these spectra to the various types of protons in the complex. The chemical shifts were found to be almost entirely pseudocontact in origin and were used to determine that the conformation of the  $[Ln(2:2:1)]^{3+}$ complex remained constant across the series. Nmr spectra of the 2:2:2 complexes were obtained only for Ln = La, Ce, Pr, Nd, and Sm. It was found that the dissociation of the [Ln(2:2:2)]<sup>3+</sup> species could be followed conveniently by nmr experiments at elevated temperatures.

Dowex A-1 ion exchange resin was successfully employed to remove excess DyCl<sub>3</sub> from mixtures with [Dy(2:2:1)]Cl<sub>3</sub> cryptate, but the method was less effective for separating the heavier cryptate/metal salt mixtures.

The author gratefully acknowledges the assistance of Dr. Kelly M. Triplett, Victor Gazzanica, A. Rashid Kausar, and Timothy Peterson for providing the background information and expertise necessary to initiate this research program.

The time, effort, and assistance of the Guidance Committee, Dr. Alexander I. Popey, Dr. George E. Leroi, and especially Dr. Michael J. Weaver, who served as second reader, is reconsisted with appreciation.

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INTRODUCTION AND BACKGROUND

A. INTRODUCTION AND STATEMENT OF PROBLEM

'In recent years, the ability of mecrocyclic "crown" polyethers<sup>1</sup> (Figure 1) and polyoxadiazamacrobicyclic "cryptabde"<sup>2</sup> (Figure 2) to form remerkable stable coordin

#### CHAPTER I

## INTRODUCTION AND BACKGROUND

media. Thermodynamic and kinetic stabilities of these complexes were found to be dependent upon both the ratio of the ionic radius to the size of the ligand cavity, and the charge on the ion.<sup>2</sup> For example, Na<sup>+</sup> and Ca<sup>+</sup> have similar ionic radii (near 1 Å), and both form stable complexes with the 2:2:2 cryptand. While the (Ca(2:2:2))<sup>2+</sup> complex is only slightly more of the there dynamically ( $K_{\pm} = 4.4$  versus 3.9 for [Na(2:2:2))<sup>2+</sup> it insociates are 10; times more slowly in aqueous modes are 0.21 s<sup>-1</sup> tor [Na(2:2:2)]<sup>2</sup>

These puscentions led damage and co-workers" to suggest that the tripositive lanthanide ions should form cryptate complexes whose thermodynamic and kinetic stabilities would be even greater than those of the corresponding mono- and dipositive species. Further, since the ionic radii of the lanthanide ions decrease regularly with increasing atomic number, the kinetic and thermodynamic stability of their complexes with a given macrocyclic ligand might wary systematically as well.

The first successful synthesis of insthanide cryptates

A. INTRODUCTION AND STATEMENT OF PROBLEM

In recent years, the ability of macrocyclic "crown" polyethers<sup>1</sup> (Figure 1) and polyoxadiazamacrobicyclic "cryptands"<sup>2</sup> (Figure 2) to form remarkably stable coordination complexes with alkali and alkaline earth cations has been extensively investigated in both aqueous and non-aqueous media. Thermodynamic and kinetic stabilities of these complexes were found to be dependent upon both the ratio of the ionic radius to the size of the ligand cavity, and the charge on the ion.<sup>2</sup> For example, Na<sup>+</sup> and Ca<sup>2+</sup> have similar ionic radii (near 1 Å), and both form stable complexes with the 2:2:2 cryptand. While the [Ca(2:2:2)]<sup>2+</sup> complex is only slightly more stable thermodynamically (K<sub>f</sub> = 4.4 versus 3.9 for [Na(2:2:2)]<sup>+</sup>),<sup>2</sup> it dissociates some 100 times more slowly in aqueous media (k = 0.21 s<sup>-1</sup> versus 27.0 s<sup>-1</sup> for [Na(2:2:2)]<sup>+</sup>),<sup>2</sup>

These observations led Gansow and co-workers<sup>3</sup> to suggest that the tripositive lanthanide ions should form cryptate complexes whose thermodynamic and kinetic stabilities would be even greater than those of the corresponding mono- and dipositive species. Further, since the ionic radii of the lanthanide ions decrease regularly with increasing atomic number, the kinetic and thermodynamic stability of their complexes with a given macrocyclic ligand might vary systematically as well.

The first successful synthesis of lanthanide cryptates



2 18-crown-6



1 16-crown-4



3 benzo-18-crown-5

0-(CH2 CH2 0)m 0-(CH2 CH20)

1	m=n=2:	Dibenzo-[18]-crown-6							
5	m=2; n=3:	Dibenzo-[21]-crown-7							
5	m=n=3:	Dibenzo-[24]-crown-8							
7	m=n=4:	Dibenzo-[30]-crown-10							





8 di-cyclohexyl-18-crown-6 9 benzo-18-crown-6

Figure 1. Crown Ethers

was recently reported, along with some of their chemical properties and applications.<sup>3</sup> The macrobicyclic cryptands



Ν

10 2:1:1

11 2:2:1

<u>12</u> 2:2:2

13 2<sub>B</sub>:2:2

Figure 2. Cryptands

produced in an effort to identify a type of initial operation of the lanthanite operation of the lanthanite operation of the lanthanite of the destruction of the Eu. Th, and Sh 2(2) and

#### B. LANTHANIDE CHEMISTRY

was recently reported, along with some of their chemical properties and applications.<sup>3</sup> The macrobicyclic cryptands were chosen as ligands rather than the monocyclic crowns because of their generally superior coordinating ability. However, the scarcity, high cost, and arduous synthetic techniques required to produce the ligand necessitated the development of less expensive and more efficient methods of synthesis.<sup>4</sup>

On the basis of results that had been obtained for rough the limited number of lanthanide cryptates already reported,<sup>3</sup> this research project was designed to systemmatically study the synthesis and properties of these compounds. Specifically the following goals were defined for this purpose: (1) to synthesize the 2:2:1 and 2:2:2 cryptands, and improve on the synthetic methods where possible; (2) to develop a synthetic method to produce as many lanthanide 2:2:1 and 2:2:2 cryptates as possible, and apply the method to most of the lanthanide nitrate and chloride salts; (3) to obtain and interpret the infrared, visible, and nmr spectra of the lanthanide cryptates produced in an effort to identify a true inclusion complex between each of the lanthanide ions studied and the 2:2:1 and 2:2:2 cryptates; (4) to obtain the cyclic voltammograms of the Eu, Yb, and Sm 2:2:1 and 2:2:2 cryptates; (5) to determine stability constants for the association of fluoride ion to lanthanide cryptates.

B. LANTHANIDE CHEMISTRY

line earths, alkali metals, and d-orbital transition ele-

Until the development of ion-exchange chromatography in the 1940's made it economically possible to obtain appreciable quantities of purified lanthanide salts, progress in the study of lanthanide chemistry was slow and had produced only a few publications. Since that time the interest and number of publications in the field have grown at an exponential rate. A review published in 1953 cited some 60 references. A similar review covering the literature through 1963 cited over 500 references.<sup>6</sup> A partial review of the literature between 1963 and 1965 listed nearly 300 references. 7 Currently The Specialists Periodical Reports of Transition Element Chemistry reviews nearly 200 articles per year, and that is only a portion of the many papers published each month which report investigations of lanthanide chemistry. Such a rapid publication rate makes it impossible to review or summarize all of the literature in the field. Only specific aspects of lanthanide coordination chemistry directly related to this thesis will be included here. Several texts and review articles are available to those generally interested in rare earth chemistry, 8,9 rare earth coordination chemistry, 6,7,10-14 electrochemistry, 15,16 and nuclear magnetic resonance spectroscopy. 17-22

1. Coordination Chemistry

In summarizing the coordination chemistry of the lanthanides it is convenient and instructive to compare and

contrast it with the coordination chemistry of the alkaline earths, alkali metals, and d-orbital transition elements. Critical examination of the literature shows that the lanthanides are more closely related to the alkali elements than to the d-orbital transition elements in their coordination chemistry. While the coordination number and geometry of the d-orbital transition elements are dictated almost exclusively by coordinate covalent bonds formed via d-orbital hybridization, alkaline earth, alkali metal, and lanthanide complexes result from almost purely ionic interactions. Although there is a wealth of data on many thousands of d-element complexes with many different types of ligands, relatively few Group IA, IIA, or lanthanide complexes are known. Moreover, the number and type of ligands which will coordinate with this latter group of elements is limited. The thermodynamic and kinetic stabilities of the d-transition element complexes cover an enormous range, from extremely stable and inert to extremely unstable and labile. Alkali metal and lanthanide ion complexes are almost always labile, and generally of a lower thermodynamic stability than the d-orbital transition metal complexes.

The major factors influencing the relative paucity of lanthanide coordination chemistry may be summarized as follows:

a.) <u>Electronic configuration</u>. Like the alkaline earth and alkali metal ions, the lanthanide ions present a spherical charge distribution and filled valence shell orbitals

to their environment. The 4f electrons, which could potentially be expected to form covalent bonds with appropriate ligands and which might be expected to provide stability and directional character to complexes, are largely or completely isolated by shielding from the filled 5s and 5p orbitals. Thus, only higher energy orbitals are available for covalent interactions. This may be contrasted to the d-block elements whose d-orbitals are available for direct participation in covalent linkages. Ligand field stabilization energies for the lanthanides are only on the order of 1 kcal/mole, but may exceed 100 kcal/mole for the d-block elements.

b.) <u>Ionic size</u>. Lanthanide ions are almost always found in the trivalent state (exceptions will be discussed in a later section). However, the ions are relatively large, and their charge/size ratio is closer to that of the divalent alkaline earths than to that of other characteristically tripositive ions such as those of the Group IIIA elements. Thus, the polarizing power of the ions is minimized and the strength of electrostatic interactions is reduced.

c.) Ligand lability. Lanthanide complexes are almost invariably labile, precluding the possibility of geometrical or optical isomerism and limiting the number of complexes that can be readily isolated in pure form. It is often found that a complex isolated in the solid state will decompose upon dissolution. With simple ligands, exchange rates are so rapid that relaxation techniques must be used

for their study.<sup>23</sup> Chelates and more complex ligands sometimes exchange slowly enough that stop flow, 24 tracer, 25 and spectral methods<sup>24</sup> may be used to follow these reactions in acidic solution; rate constants generally increase as pH decreases and decrease as ionic radius decreases. 11 d.) Competition by water and hydroxide ion. Water is a particularly effective ligand for lanthanide ions, so only very strong ligands (e.g., EDTA) can successfully compete for coordination sites in aqueous solutions. In alkaline solution, OH coordinates even more strongly than water. The extremely insoluble lanthanide hydroxides precipitate upon addition of most strongly basic ligands that might otherwise be expected to form stable complexes. coorde.) Donor atoms. The rare earth ions, like the Group IA and IIA ions, are classified as "type A" or "hard" cations.<sup>10</sup> Hence, most complexes isolated from aqueous solution involve hard anions such as F or OH, or chelates with oxygen or mixed oxygen-nitrogen donor sites (e.g., acetate, EDTA, acetylacetonate). X-ray crystallographic and infrared studies have shown halide, nitrate, oxide, and thiocyanate ions coordinated to lanthanide ions. 26-31,51 Pure nitrogen donors can form strong complexes with Ln<sup>3+</sup> ions only when competition with oxygen is eliminated by using an appropriate non-aqueous solvent such as acetonitrile.<sup>26-30</sup> Complexes with softer donor atoms (e.g., As, S, P) are essentially unknown.

All of these factors contribute to the relative scarcity

of lanthanide ion coordination chemistry when compared to

The lanthanide ions exhibit a wide range of coordination numbers (commonly 6-12) and geometries.<sup>31</sup> This is due to the lack of f-orbital interactions, large ionic radii, and spherical charge distributions described previously. From these physical properties of the lanthanide ions it follows that the coordination number and geometry of a complex with a given lanthanide ion will be dictated by the geometrical, conformational, and binding site requirements of the available ligands. This stands in marked contrast to the d-transition metal complexes, where it is the participation of the d-orbitals of the ions that determines coordination number and geometry in most cases.

The interpretation of the thermodynamics of lanthanide complex formation remains a topic of much debate. Several types of non-linearity are observed when free energies, enthalpies, or entropies of formation are plotted as a function of the reciprocal of ionic radius. A change in slope generally, but not always, occurs near  $Gd^{3+}$  and this has become known as the "gadolinium break".<sup>32</sup> A number of explanations have been proposed,  $^{33-37}$  but none are entirely satisfactory. There is some evidence that a change in coordination number is an important factor,  $^{37}$  but the lability of most complexes as well as disagreement among experimentalists about coordination number values make accurate studies and reliable interpretations difficult.

## 2. Nmr Spectrometry

In recent years lanthanide ions have found wide application as shift reagents<sup>19</sup> and relaxation agents<sup>19,38</sup> in a variety of nmr experiments. The large chemical shifts observed in paramagnetic lanthanide complexes (compared to the corresponding diamagnetic lanthanum complex) are composed of two contributions generally referred to as contact (or scalar) and dipolar (or pseudo-contact) shifts 19-21 Dipolar (through space) shifts arise from the magnetic anisotropy around the central lanthanide ion due to the partially filled f-orbitals. When the f-orbitals are empty (La<sup>3+</sup>), half full (Gd<sup>3+</sup>, Eu<sup>2+</sup>), or full (Lu<sup>3+</sup>, Yb<sup>2+</sup>). the contribution of this term will be zero. The contact (through bond) shift is due to a weak covalent interaction between the lanthanide 6s orbital and the molecular orbitals of the ligand. This term is usually, but not always, small in comparison to the dipolar term since covalent interactions in lanthanide complexes are generally weak or nonexistent. The total chemical shift for an axially symmetric complex may be expressed for a given nucleus i as:27

 $\delta_{i} = \lambda_{i}(S_{z}) + D(3\cos^{2}\theta_{i} - 1)r_{i}^{-3}$ (1)

 $(3\cos^2\theta_1 - 1)r_1^{-3}$  are constant along a sector of mappinger, contributions due to the two forms are in analy repareted. Simple rearrangement of Equation (1) sector

where: /s = A + 13cos 9, - 11r, 0/s

- $S_z$  = projection of the lanthanide total electron spin magnetization in the direction of the external magnetic field.
- r; = distance from the lanthanide nucleus to nucleus i.
- $\theta$  = angle r, makes with the principle symmetry axis.
- Color D = constant for a given lanthanide ion and temperature as well as a function of the anisotropy of the g value of the lanthanide ion.

The first term in this equation is the contact shift term, while the second term delineates the pseudocontact shift. Note that  $\delta_i$  is measured from the resonance frequency of the nucleus in the corresponding diamagnetic lanthanum or lutetium compound. In cases where contact shifts are negligible, it can be seen that the chemical shift will depend only on the geometry of the molecule. Thus, the chemical shift can be used to determine geometry in solution,<sup>39</sup> or, if the geometry is known, the chemical shift can be predicted.<sup>40</sup>

Procedures for determining the contact shift in cases where it cannot be neglected have recently appeared in the literature<sup>41</sup> along with examples of their successful application to structural problems in solution.<sup>41,42</sup> If  $A_i$  and  $(3\cos^2 e_i - 1)r_i^{-3}$  are constant along a series of complexes, contributions due to the two terms can be readily separated. Simple rearrangement of Equation (1) yields:

$$\delta_{i}/s_{z} = A_{i} + (3\cos^{2}\theta_{i} - 1)r_{i}^{-3}D/s_{z}$$
 (2)

Tabulated values of  $S_z^{64}$  and D,<sup>43</sup> can be used to construct a linear plot of  $\delta_i/S_z$  versus D/S<sub>z</sub>. Any deviation from the model should be immediately apparent in such a plot, within the limits of the accuracy of the D values, which have been calculated from an arbitrary set of crystal field parameters.

The sign and magnitude of the isotropic shift of a given nucleus will also depend on the number of bonds separating it from the lanthanide ion, and on which lanthanide ion is present in the complex. In this work only hydrogen nuclei separated from the paramagnetic center by at least two bonds are considered. Table 1 and Figure 3 show the variation in the chemical shift of protons in some specific compounds as a function of lanthanide ion. Note that the value of δ; changes sign three times: positive at Ce<sup>3+</sup>, negative at Eu<sup>3+</sup>, back to positive at Tb<sup>3+</sup>, and going negative once more at Er<sup>3+</sup>. The reasons for this alternation in sign are not clearly understood though several explanations have been proposed.<sup>19</sup> The result may be caused by variations in relative contributions from the contact and pseudocontact terms. Bleaney has described a theory that successfully predicts the relative sign and magnitude of the isotropic shift for a number of complexes across the entire lanthanide series. 43,65 These results are shown in Table 2.

The T1 relaxation effects of the paramagnetic lanthanide

Table 1. <sup>+</sup> H Nmr shifts in	ppm of organometallic lanthani	de complexes (C <sub>5</sub> H <sub>5</sub> ) LnB <sup>a</sup> . 19	61
Ln	(C <sub>5</sub> H <sub>5</sub> )	(H- ŷ)	
Ceb	- 2.07	+4.19	
Prb	- 9.13	+6.23	
Ndb	+ 3.20	~ +2.90	
Smb	- 6.69	+1.14 to +2.53	
Eub	- 10.46	-11.04; -11.60	
Gd <sup>b</sup> , c	Signals not	detectable <sup>d</sup>	
du	-159	+28.8; +32.4	
Dy <sup>b</sup>	-215	+56.6; +58.8	
qон	-137	+36.9	
Er <sup>b</sup>	Signal not detectable <sup>d</sup>	-4.26	
2 <sup>mg</sup>	+ 55.1	-16.4	
Ybc	+ 51.1	-12.9	
			1
a. In toluene-d <sub>8</sub> at room	temperature.		
D. FOT $B = CNC_{c}H_{1}$ ,			

FOR  $B = CNC_{6H_{11}}$ 

For  $B = P(n - C_4H_9)_3$ . с. d.

Most probably due to extremely pronounced line broadening.

19 e



Figure 3. Variation of the chemical shift of some specific nuclei in substrate molecules combined with  $\ln(\text{DPM})_3$  systems. ( $\Delta$ ) n-hexanol:  $\alpha$  -methylene proton; ( $\nabla$ ) 4-picoline-N-oxide; and ( $\bigcirc$ ) 4-vinylpiridine 2 proton.<sup>19</sup>

in co	mental <sup>a</sup> , <sup>b</sup>	$Ln(cmp)^{2+}$ $Ln(dpm)_{3}^{P}$	0 0	- 8.2 + 20	- 3.0 + 9.5	- 0.2 + 2.4	+ 5.1 - 10	q	- 50 + 91	-100 +100	- 42 + 71	+ 16 - 27	+ 10 - 70	+ 12 - 33		
bound to lanthan	Experi	Ln (oda) <mark>+</mark>	0	- 14.9	- 5.6	- 0.7	+ 13.4	not observe	- 92	-100	- 30	+ 38	+ 61	+ 26		
lifts of ligands	N. 1. 3	Ln (dpa) <sub>3</sub>	0	- 13	- 7.6	- 1.3	+ 12		- 92	-100	- 51	+ 31	+ 64	+ 23		+8
Relative nmr sh	Theory		oult	- 11.0	- 4.2	- 0.7	+ 4.0	0	- 86	-100	- 39	+ 33	+ 53	+ 22	0	
Table 2.	a j	Ln <sup>3+</sup>	La	Pr	PN	Sm	Eu	Gd	Tb	Dy	Ho	Er	HT	qх	Γu	

p.a.

ions lead to broad spectral lines in which little spinspin coupling information is retained. In the extreme case of  $\mathrm{Gd}^{3+}$ , the lines are often broadened to the point of being unobservable. This may occasionally happen with other ions as well. Table 3 shows typical line widths at half maximum for some homologous  $\mathrm{Ln}^{3+}$  systems.

Relaxation effects can also be used to determine structural information. For a rapidly tumbling lanthanide complex where the electron spin relaxation time  $T_{le}$  is short compared to the rotational reorientation time, electronnuclear dipolar interactions are the dominant relaxation mechanism. It can be shown that:<sup>66</sup>

$$1/T_{1} = 1/T_{2} = (4/3) \mathscr{V}_{N}^{2} g_{N}^{2} \beta^{2} J (J + 1) T_{1e} r^{-6}$$
(3)

where:

 $T_{1} = \text{longitudinal relaxation time}$   $T_{2} = \text{transverse relaxation time}$   $\gamma_{N} = \text{nuclear magnetogyric ratio}$   $g_{N} = \text{Lande' g factor}$   $\beta = \text{Bohr magneton}$  J = resultant electron spin angular momentum  $T_{1e} = \text{electron spin-lattice relaxation time}$ 

In a paramagnetic lanthanide complex where there is no exchange between free and coordinated ligands and line widths in the nmr spectra of the diamagnetic La and Lu complexes are
	idth	mailer than those in the paramegnetic complexes $T_2 \rightarrow T_2$ is directly obtainable from the of the resonance signed at half height as follows:	
ems	De	23 4.0 23 20 20 20 20 20 20 20 20 20 20 20 20 20	
syst	ombin.	ing Equations (3) and (4), we can write, fos any pa	
logous Ln	Cd		
e homo	ecall.	the or can be determine a terming of contact shift is	
mals of som	BG	200 10 10 10 170 130 130 130 130 240 240 240 240 240 240 230 FPM	
I nmr sig	ince l eters or val	M is dip in cc1 <sub>4</sub> ( in cc1 <sub>4</sub> ( in cc1 <sub>4</sub> ( protom	
Iths of T	quand	40 16 15 15 15 15 255 255 40 40 40 40 40 3 10 11 (DPM) 3 Ln(DPM) 3 Ln(DPM) 3 Ln(DPM) 3 Ln(DPM) 3 Ln(DPM) 3 Ln(DPM) 4 Ln(DPM) 4 Ln(DPM) 4 Ln(DPM) 2	
e 3. Half wid	Ln <sup>3+</sup> ions	Ce Pr Pr Pr Sm Sm Sm Sm Sm Sm Sm Sm Sm Sm	
Table		е. с. с. с. с. г.	

 $(\underline{i.e.}, T_{2_{dia}})$ ,  $T_{2_{aia}}$ ),  $T_{2_{aia}}$  ),  $T_{2_{aia}}$  ),  $T_{2_{aia}}$  ),  $T_{2_{aia}}$ ,  $T_{2_{aia}}$ , T

$$\mathcal{V}_{\frac{1}{2}} = \frac{1}{\Pi^{r} T_{2}} \qquad (4)$$

Combining Equations (3) and (4), we can write, for any pair of nuclei A and B:

$$\frac{\mathbf{T}_{1}^{A}}{\mathbf{T}_{2}^{B}} = \frac{\mathbf{T}_{2}^{B}}{\mathcal{V}_{4}^{B}} = \frac{\mathbf{v}_{4}^{B}}{\mathbf{v}_{4}^{A}} = \frac{\mathbf{r}_{6}^{6}}{\mathbf{r}_{8}^{B}} \text{ for respective observations}$$
(5)

Recalling Equation (1), and assuming the contact shift is negligible or can be determined, then:

$$\frac{\delta_{A}}{\delta_{B}} = \left(\frac{3\cos^{2}\theta_{A} - 1}{3\cos^{2}\theta_{B} - 1}\right) \left(\frac{r_{A}^{-3}}{r_{B}^{-3}}\right) \text{ for each other production (6)}$$

Since both  $\int$  and  $\mathcal{V}$  are experimentally obtainable parameters, Equations (5) and (6) may be solved simultaneously for values of  $r_A/r_B$ , and  $(3\cos^2\theta_A - 1)/(3\cos^2\theta_B - 1)$ . Computer analysis is sometimes used to determine values for  $r_i$  and  $\theta_i$  by simply varying the two parameters until Equations (1), (5), and/or (6) are satisfied.<sup>123</sup>

## 3. Infrared Spectroscopy

Infrared data has proven to be extremely useful in determining whether or not coordination between a ligand

and a lanthanide ion has occured and in identifying binding sites on the ligand. It is also useful in distinguishing coordinated from non-coordinated anions. Examples of the first two applications include: (1) establishing oxygen as the donor atom in triphenylphosphine oxide, <sup>44</sup> methylethylenephosphate, <sup>46</sup> and hexamethylphosphoramide<sup>45,47</sup> by observing the displacement of the P=0 stretch; (2) similar observations of the As=0 stretch in triphenyl- and tribenzylarsine oxides; <sup>44,48</sup> (3) corresponding observations of the C=0 stretching frequency in pyramidone<sup>49</sup> and N,N-dimethylacetamide; <sup>50</sup> and (4) monitoring the C-O-C stretch of lanthanide crown ether complexes, <sup>51</sup>

Infrared data is especially useful in distinguishing coordinated and non-coordinated nitrate and perchlorate anions since coordination changes the symmetry and thus the number and frequency of infrared active bands for these groups. The uncoordinated nitrate group, for example, has  $D_{3h}$  symmetry and four infrared bands. Two of these bands, occuring at about 1340 cm<sup>-1</sup> ( $\mathcal{Y}_3$ ) and 825 cm<sup>-1</sup> ( $\mathcal{Y}_2$ ), are usually identifiable. Coordination (either mono- or bidentate) reduces the symmetry to  $C_{2v}$ , displacing the four original bands and resulting in the appearance of two more. Of these, bands at 1315 cm<sup>-1</sup> ( $\mathcal{Y}_1$ ), 1490 cm<sup>-1</sup> ( $\mathcal{Y}_4$ ), 820 cm<sup>-1</sup> 810 cm<sup>-1</sup> ( $\mathcal{Y}_6$ ), and 740 cm<sup>-1</sup> and 730 cm<sup>-1</sup> ( $\mathcal{Y}_3$ ) are analytically useful.<sup>11,14,26,29,52</sup>

When the  $ClO_4^-$  ion (T<sub>d</sub> symmetry) is coordinated its symmetry is lowered to  $C_{3v}$ , causing an infrared band at

llll cm<sup>-1</sup> to split and intensifying the band around 927 cm<sup>-1</sup>. In lanthanide trimethylphosphonate<sup>46</sup> and hexamethylphosphoramide<sup>47</sup> perchlorate complexes the presence of both ionic and coordinated perchlorate has been shown. However, in other complexes such as  $\text{Ln}(\text{en})_4(\text{ClO}_4)_3$ ,<sup>26</sup>  $\text{Ln}(\text{pn})_4(\text{ClO}_4)_3$ ,<sup>29</sup> and  $\text{Ln}(\text{phen})_4(\text{ClO}_4)_3$ <sup>28</sup> (en = ethylenediamine, pn = 1,2-propanediamine, phen = 1,10-phenanthroline), all perchlorate groups are uncoordinated. Similar results are obtained for the thiocyanate group where both coordinated and ionic thiocyanate are found in Yb(phen)\_2(SCN)\_3, but only ionic SCN<sup>-</sup> is found in  $\text{Ln}(\text{phen})_3(\text{SCN})_3$ .

Relative intensities of the various bands may be used to measure relative amounts of coordinated and free anions;<sup>53</sup> but infrared alone cannot distinguish between unidentate, bidentate, or bridging nitrate groups, all three of which may occur. Raman polarization techniques can be used to identify unidentate nitrate groups as was illustrated by showing that the No<sub>3</sub><sup>-</sup> ion in  $Ln(TBP)_3(NO_3)_3$  must be either bidentate or bridging.<sup>54</sup>

#### 4. Electronic Spectra

All of the Ln<sup>3+</sup> ions except La, Ce, Yb, and Yb have characteristically narrow, line-like electronic spectra arising from Laporte forbidden 4f-4f transitions. Molar absorptivities are generally small (0.03 - 12 l/mole-cm.), but have proven useful in analysis of rare earth mixtures.<sup>55</sup> The absorptions are very sharp and require high resolution instruments to accurately measure absorbance maxima and <sup>10</sup> molar absorptivities.<sup>56</sup>

In general, coordination of a lanthanide ion produces little or no change in the electronic spectra. This is due to the shielding of the 4f electrons by the 5s and 5p orbitals mentioned earlier. However, there are certain bands which are more susceptible to small shifts in wavelength, splitting, and absorptivity.<sup>6</sup> While these changes are of interest to those studying spectroscopic states, and perhaps of use in determining symmetries of the complex species in solution, they are of little utility in determining more generally useful physical properties (<u>e.g.</u>, stability constants, rates of formation, purity, etc.).

In contrast to the available thermodynamic data, the electronic spectra are well understood<sup>57</sup> and detailed explanations of small crystal field effects, <sup>58</sup> the nephelauxetic effect, <sup>62</sup> and hypersensitivity<sup>59</sup> are available. These visible transitions, especially of europium, have been used with some success in lasers.<sup>60</sup>

#### 5. Electrochemistry

The electrochemistry of the lanthanide elements is very limited compared to that of the d-transition elements, since the tripositive ions are uniformly the most common and stable oxidation state for each of these elements. Notable exceptions include the Ce<sup>4+</sup> ion which has numerous applications as a strong oxidant in redox reactions<sup>61</sup> although it is

stable only in acidic solutions.  $Eu^{2+}$ ,  $Yb^{2+}$ , and perhaps  $Sm^{2+}$  exist, but their stability decreases in the order listed.<sup>15</sup> A few stability constants have been measured,<sup>63</sup> and attempts have been made to measure reduction potentials for some Ce, Eu, and Yb complexes.<sup>15</sup> Electrochemical studies of the  $Eu^{3+}$ -  $Eu^{2+}$  couple in water produced the expected result that chelation of the tripositive ion shifted the reduction potential of the couple to more negative values relative to that of the uncomplexed aquated species.

special emphasis on the known contrast de and actinide compounds.

#### 1: Crown Ether

Figure 1 shows a moder of the second size from ethers Those containing of matter points first at the second size of benzo groups increases. The consumity are marrially insoluble in water, and only slightly mixing is alrohola and other common volvents. They discolve ready, however, in methylene chloride and chloroform.

In contrast, the alightstic crows are lighted or fee maiting solids that dissolve in a rewarker is weigh of solvents from water to patroleum winer.

Aromatic crowns exhibit the characteristics care for absorption near 275 nm in the ulterviolet fractor of the spectrum, with moler absorptivities on the same of C. OMACROCYCLIC POLYETHERS AND THEIR COMPLEXES

Though topologically more complex polycyclic ligands are being developed,<sup>2</sup> the major research emphasis remains on exploring the properties of the monocyclic crown complexes and bicyclic cryptate complexes. In this section, a brief discussion of crown ethers and their complexes will be presented to serve as a background for the development of cryptand chemistry. These two summaries will be followed by a review of transition metal macrocyclic complexes, with special emphasis on the known lanthanide and actinide compounds.

# 1. Crown Ethers other botal tons of the graatest stability

Figure 1 shows a number of representative crown ethers. Those containing aromatic side rings are colorless, crystalline compounds whose melting points rise as the number of benzo groups increases. The compounds are essentially insoluble in water, and only slightly soluble in alcohols and other common solvents. They dissolve freely, however, in methylene chloride and chloroform.<sup>68</sup>

In contrast, the aliphatic crowns are liquids or low melting solids that dissolve in a remarkable range of solvents from water to petroleum ether.<sup>68</sup>

Aromatic crowns exhibit the characteristic catechol absorption near 275 nm in the ultraviolet region of the spectrum, with molar absorptivities on the order of

2200 l mole<sup>-1</sup> cm<sup>-1</sup> per benzene ring. In the infrared, both the aliphatic and aromatic crowns show a large, characteristic infrared band near 1100 cm<sup>-1</sup> due to the aliphatic ether linkage.<sup>68</sup> Changes in these spectral properties are of great utility in identifying crown complexes.

from oxygen at high temperatures. The aromatic crowns react like anisole, and may be halogenated, nitrated, or condensed into resins with formaldehyde.

Macrocyclic complex chemistry began in 1967, when Pederson first observed the formation of stable coordination complexes between crown ethers and the alkali, alkaline earth, and a few other metal ions.<sup>1</sup> The greatest stability was found when each of the oxygen bonding sites was separated by a two carbon bridge as shown in Figure 1. Ligands with one or more oxygen atoms replaced by N or S atoms have also been studied.<sup>68</sup> but generally form less stable complexes with the alkaline earth and alkali metal ions. The -O-C-C-Olinkages are sufficiently flexible to allow the ligand to wrap its central, two dimensional cavity around the metal ion to maximize complex stability. For example, when the small polyether 4 (Figure 1) coordinates to the large Rb<sup>+</sup> ion, it sits on the metal as a crown, 69,70 accounting for the common name of this class of ligands. However, when the large ligand 7 coordinates to the smaller  $K^+$  ion, it folds around the metal to create a three dimensional cavity. 71

When ions of different sizes are chelated, a given ligand may assume a number of conformations. The nine complexes of benzo-18-crown-5 that have been studied by X-ray crystallography show seven different conformations for the ligand.<sup>72</sup> In some cases a second ligand molecule may be able to coordinate to a given metal ion, as in the potassium benzo-18crown-6 complex.<sup>73</sup> In still other instances a solvent molecule (sodium benzo-18-crown-6  $\cdot$  H<sub>2</sub>O)<sup>74</sup> or an anion (La(<u>syn-di-(cis-cyclohexyl)-18-crown-6)</u> (NO<sub>3</sub>)<sub>3</sub>)<sup>75</sup> may coordinate to the metal ion in addition to the macrocyclic ligand.

Solution structures of crown complexes have been studied less and are less conclusive than X-ray studies. Some infrared studies provide evidence that conformations of free and complexed ligands are not the same  $^{76,77,79}$  as may be expected from solid state structures. A recent high field proton nmr analysis  $^{78}$  has shown that complexes of  $\underline{4}$  and  $\underline{9}$ have the same structure in a number of solvents as the sodium complex of  $\underline{4}$  in the solid state. This structure is conformationally different from that of the pure ligand in the solid state. Complexes of  $K^+$ ,  $Cs^+$ , and  $Ba^+$  with dibenzo-30-crown-10 were found to be the same in both solution and solid. Rotation of the ether linkages was seen to be rapid in both free and complexed ligands.

Stability constants are a convenient method for measuring the strength of complexation in solution. Techniques used for their measurement include calorimetric titration, <sup>80</sup>

potentiometric titration with ion-selective electrodes. 81 and spectroscopic methods. 82 Representative stability constants for several polyether-cation complexes are collected in Table 4. Because crowns have been found to increase the permeability of artificial membranes to ion transport, 83,84 considerable attention has been devoted to understanding the relative selectivity of polyether complexation with various ions. Comprehensive reviews of the factors influencing cation selectivity and complex stabilities are available 2,68,83,84 As expected, bonding is largely electrostatic in alkali metal or alkaline earth-polyether complexes. Selectivity and stability are chiefly a function of the relative size of the polyether cavity and the metal ion, and the charge on the ion. Competition between ligand and solvent is important, and stability is usually increased greatly non-aqueous solvents. 68

While it might be expected that macrocyclic complexes would exhibit the well known chelate effect, it can be seen from the data in Table 4 that crowns 2, 4, and 8 form considerably more stable complexes than the analagous acyclic compound 14, included in the table. This same observation has been made with certain naturally occuring macrocycles,<sup>86</sup> and has been variously called the "macrocyclic effect"<sup>87</sup> or "multiple juxtapositional fixedness".<sup>86</sup> This effect is thought to be enthalpic in origin, and to be due to differences in solvation of the donor atoms in each type of ligand.

Compound <sup>a</sup>	Solvent	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	A9 <sup>+</sup>	Ph2+
Compound <sup>a</sup>	Solvent	Li <sup>+</sup>	Na <sup>+</sup>	+*	Rb+	Cs <sup>+</sup>
18-crown-6 <sup>2</sup>	HOT IST					
.8-crown-6 <sup>2</sup>	CH <sub>3</sub> OH	1	4.3	6.1		4.6
libenzo-18-crown-6 <sup>97</sup>	CH <sub>3</sub> OH	1	4.4	5.0	5 16	3.6 <sup>b</sup>
licyclohexyl-18-crown-6	H <sub>2</sub> O	0.6	1.7	2.2	1.5	1.2 <sup>b</sup>
(isomer A) <sup>127</sup>	CH3OH	1	4.1	6.0	-	4.6
penzo-18-crown-5 <sup>127</sup>	H <sub>2</sub> O	<1.0	<0.3	0.6	1	1
penzo-18-crown-5 <sup>127</sup>	CH <sup>3</sup> OH	1	3.7	3.6 <sup>b</sup>		2.8 <sup>b</sup>
libenzo-24-crown-8 <sup>127</sup>	СН3ОН	1	1	3.5		3.8
1.1 <sup>97</sup>	H <sub>2</sub> O	5.5	3.2	42	42	<b>&lt;</b> 2
::2:197	H <sub>2</sub> O	2.5	5.4	3.95	2.55	٢2
::2:29/	H <sub>2</sub> O	42	3.9	5.4	4.35	42
::2:2 <sup>97</sup>	CH <sub>3</sub> OH/H <sub>2</sub> O	1.8	7.21	9.75	8.40	3.54

Stability constants of some cations with various ligands Table 4.

Data taken from references shown in superscripts on returns а.

Data for complexes containing 2:1 ligand to cation ratios. b.

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Compound <sup>a</sup>	Solvent	Ca <sup>2+</sup>	$sr^{2+}$	Ba <sup>2+</sup>	Ag+	Pb <sup>2+</sup>
18-crown-6 <sup>2</sup>	сн <sub>3</sub> он	8	1	1	8	
dibenzo-18-crown-6 <sup>97</sup>	сн <sub>з</sub> он	   	1	1	1 1 1	   
dicyclohexyl-18-crown-6	H <sub>2</sub> 0	1	3.2 <sup>b</sup>	3.6 <sup>b</sup>	2.36	5.0
(isomer A) <sup>127</sup>	CH <sub>3</sub> OH	8 8 8	1	8 1 1	-	1 1 1
benzo-18-crown-512/	H <sub>2</sub> 0	   	! ! !	   	9 10 10	 
benzo-18-crown-5 <sup>12/</sup>	сн <sub>3</sub> он	   	1	   	 	1 1 1
dibenzo-24-crown-8 <sup>127</sup>	СН3ОН	8	   	1	8	8
2:1:1 <sup>97</sup>	H <sub>2</sub> O	2.5	<b>k</b> 2	<b>۲</b> 2	1	1 1 1
2:2:1 <sup>97</sup>	н <sub>2</sub> 0	6.95	7.35	6.3	10.6	   
2:2:2 <sup>97</sup>	H <sub>2</sub> 0	4.4	8.0	9.5	9.6	12.0
2:2:2 <sup>97</sup>	сн <sub>3</sub> он/н <sub>2</sub> о	7.6	11.5	12	   	 

Data taken from references shown in superscripts. a.

Data for complexes containing 2:1 ligand to cation ratios. þ.

In macrocycles, the relatively rigid cyclic structure does not allow the donor atoms to be as extensively solvated as in the less hindered acyclic compounds, therefore, complexation of the macrocycle requires less desolvation energy than the acyclic species. Further, the macrocycles have their binding site repulsion energies overcome during synthesis, but this requirement must be satisfied for the acyclic species during complexation. Finally, the macrocycles often enter into complexation with their binding sites already in a sterically favorable spatial arrangement, where the binding sites of an acyclic compound would be moving more randomly through solution.

The data in Table 3, along with that in Tables 4 and 5, also make it clear that the stability of a complex increases as the charge on the metal ion increases and as the size of the ion approaches the size of the cavity. The former effect is undoubtedly the result of increased electrostatic attraction between ligand and ion. There is also a greater entropy increase to be realized in the desolvation of the more highly charged ion, but this will be less significant in nonaqueous media where solvation is generally less extensive than in water. An exhaustive treatment of all the factors influencing the stability and selectivity of crown ethers may be found in the literature.<sup>2</sup>

Rates of formation of alkali metal ion-crown complexes have been found to be extremely fast, nearly diffusion

ion	radius	ion	radius	ion	radius
Li <sup>+</sup>	0.78	Be <sup>2+</sup>	0.34		0.62
Na <sup>+</sup>	0.98	Mg <sup>2+</sup>	0.78	In <sup>3+</sup>	0.92
к+	1.33	Ca <sup>2+</sup>	1.06	ч <sup>3+</sup>	1.06
Rb <sup>+</sup>	1.49	Sr <sup>2+</sup>	1.27	La <sup>3+</sup>	1.22
Cs <sup>+</sup>	1.65	Ba <sup>2+</sup>	1.43	Eu <sup>3+</sup>	1.12
Ag <sup>+</sup>	1.13	Pb <sup>2+</sup>	1.20	Lu <sup>3+</sup>	0.99

Table 5. Ionic radii (Å) for selected cations<sup>1</sup>

Table 6. Estimated<sup>2</sup> cavity radii (Å) for some ligands

ligand	radius
di-cyclohexyl-18-crown-6 (isomer A)	1.3 - 1.6
2:1:1	0.8
2:2:1	1.1
2:2:2	1.4

controlled, and can only be studied with  $nmr^{88-92}$  and relaxation<sup>93</sup> techniques. Fast ligand conformational rearrangement often accompanies complex formation.

## 2. Cryptands

Based on the results obtained with the monocyclic crown complexes, Lehn began to extend the development of synthetic macrocyclic ligands to bicyclic, tricyclic and other topologically more complex macrocycles with the goal of designing still more potent organic complexing agents for the alkali and alkaline earth cations.<sup>2,95</sup> The bicyclic cryptands (Figure 2) have been most extensively studied, and are most relevant to the work presented here. Lehn reasoned that the complexation process is not a result of energetic considerations alone, (i.e., thermodynamic and kinetic stabilities), but also of an overall intermolecular recognition process which includes topological, binding site, and other considerations. Hence, the selectivity of a ligand for a specific ion may be increased by matching the size of the ligand, and the type and number of binding sites to maximize what Lehn has called the "complementarity" between the ion and ligand. From this point of view the ability of crown ethers to coordinate to the spherical alkali and alkaline earth cations is a result of the "complementarity" between the ligand's cyclic cavity of hard, electronegative binding sites with the hard, electropositive spherical cation. Further, he

suggested that a spherical cavity containing similar binding sites would be an even more effective complexing agent. Lehn accomplished the synthesis of these ligands,<sup>93</sup> and reported their superior coordinating ability.<sup>94</sup>

Many properties of the crown ethers may be directly extrapolated to the cryptands. The saturated cryptands are liquids or low melting solids at room temperature. The benzo cryptands are higher melting, and their solubilities are lower in most solvents. Both types are stable to heat, but may react with oxygen at elevated temperatures. Their spectroscopic properties are similar to those of the crown ethers.<sup>2,93</sup>

Structurally, the (-O-CH<sub>2</sub>-CH<sub>2</sub>-) bridge produces the most stable complexes, and substitution of N or S for O yields less stable alkaline earth or alkali metal complexes, but more stable d-transition metal complexes.<sup>83</sup> This behavior is readily understood in terms of polariza-bility or hard and soft acid-base arguments.<sup>83</sup>

The conformation of the cavity in a bicyclic ligand is more rigid than that in a monocycle, but it can undergo certain well characterized deformations. The way in which the cavity configuration varies to accommodate ions of different size has been systematically studied for the 2:2:2 complexes of Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> iodides. The results may be understood by viewing the molecule along its threefold axis<sup>32</sup> as shown in Figure 4. The six oxygen atoms



a) View of oxygen atoms along the three-fold axis.



b) Possible conformations of the nitrogen lone pairs.Figure 4. Conformational variations of the 2:2:2 cryptand

are arranged in two triangular faces that are twisted off center from each other by an angle  $\Theta$ . As the radius of the metal ion increases from Na<sup>+</sup>, to K<sup>+</sup>, to Rb<sup>+</sup>,  $\Theta$ decreases from 45° to 21° to 15°. The maximum cavity size is reached at  $\Theta = 15^{\circ}$ . Complexation of the still larger Cs<sup>+</sup> ion does not alter the angle further.

A second manner in which the cavity configuration may vary is also illustrated in Figure 4. The lone pairs of the bridgehead nitrogens may be directed out of (exo-exo) or into (endo-endo) the cavity, or one may be in an endo conformation while the other is in an exo conformation. Obviously the lone pair can coordinate most effectively to a cation within the cavity only in the endo conformation, and in all cases analyzed to date, the ligand has assumed an endo-endo conformation in coordination complexes. The ligand may be frozen into an endo-exo or exo-exo configuration by forming the mono- or diborane adduct.<sup>95</sup> Nmr studies of the pure ligands<sup>91-96</sup> have always shown the molecules in the most highly symmetric conformation possible. Spectral patterns characteristic of exo-exo, endo-endo, or endo-exo configurations have never been observed, even at very low temperatures. 94,96

Stability constants of cryptate complexes have been obtained by the same calorimetric, potentiometric, and spectroscopic methods used for the corresponding crown complexes. A few representative stability constants are

listed in Table 4. With the crown complexes, stability may be increased by increasing the charge on the cation, or by selecting a cation whose radius most closely matches that of the cryptand cavity. Enthalpies and entropies of complexation have also been measured and discussed.<sup>98,99</sup>

Analysis of that thermodynamic data reveals the existence of a "cryptate effect" that is analogous to and of greater magnitude than the corresponding macrocyclic effect discussed earlier. Figure 5 shows a comparison of these two effects for K<sup>+</sup> complexes in a methanol/water (95:5) mixture. Note that the cryptate complex is more stable than its macrocyclic counterpart by a factor of about  $10^5$ , while the macrocyclic compound is more stable than its acyclic counterpart by a factor of about  $10^4$ . Like the macrocyclic effect, the cryptate effect is enthalpic in origin, due to the strong interaction of the cations with the weakly solvated ligands. Entropies of cryptate formation may be positive or negative, due to variation in the structure making and breaking ability of the bulky organic cations that are formed.<sup>98</sup>

Most kinetic data for dissociation and formation of cryptate complexes has been obtained by using  ${}^{1}$ H,  ${}^{13}$ C, and alkali cation nmr. ${}^{96,100,101}$  Conductimetric ${}^{103}$  and spectral  ${}^{102}$  changes have been used in stopped-flow experiments to provide additional information. Representative values of some formation and dissociation rate constants



stability; the values given are the stability constants log K of the K<sup>+</sup> complex in methanol (top) and methanol/water (95:5) (bottom). Figure 5. The macrocyclic and macrobicyclic effects (  $\Delta$  ) on complex

are listed in Table 7. A number of important conclusions can be drawn from these investigations:<sup>2,95</sup> (1) the dissociation rates of cryptate complexes are more than 10<sup>3</sup> times slower than corresponding crown complexes; (2) dissociation rates decrease as stability constants increase; (3) dissociation rates of alkaline earth cryptates are  $10^2$ to  $10^6$  times slower than for the alkali metals; (4) formation rates are approximately one hundred times slower than water exchange rates for Group IA elements and approximately 10<sup>4</sup> times slower than for Group IIA elements; (5) the transition state resembles the free ion and ligand more than the complex; (6) exchange rates are fastest when cation solvation is low, ligand flexibility is high, and complex stability is low; (7) dissociation may occur along an acid catalyzed path at low pH.<sup>103</sup>

Like the macrocyclic polyethers, cryptands solubilize the alkali metals in various solvents, and, in addition, may produce appreciable concentrations of solvated electrons.<sup>104,105</sup> Perhaps the most remarkable demonstration of the effect has been the isolation of the first salts containing alkali metal anions.<sup>105-107</sup> [Na(2:2:2)]<sup>+</sup> Na<sup>-</sup>, [Na(2:2:2)]<sup>+</sup> e<sup>-</sup> and [K(2:2:2)]<sup>+</sup> K<sup>-</sup> have all been observed.

Cryptands have been attached to polymeric supports and used in separation<sup>108</sup> and catalytic<sup>109</sup> processes. Separation of mixtures of alkaline earth and alkali metal ions is readily achieved,<sup>108</sup> and remarkable results for

Ligand	Cation	k <sub>d</sub> (s <sup>-1</sup> )	$k_{f} (\underline{M}^{-1}s^{-1})$
2:1:1	Li <sup>+</sup>	0.025	8 x10 <sup>3</sup>
2:1:1	Ca <sup>2+</sup>	0.820	2.6 $\times 10^2$
2:2:1	Na <sup>+</sup>	14.5	3.6 x10 <sup>6</sup>
2:2:1	Ag <sup>+</sup>	$4.5 \times 10^{-4}$	
2:2:1	Ca <sup>2+</sup>	$6.6 \times 10^{-4}$	5.9 x10 <sup>3</sup>
2:2:1	sr <sup>2+</sup>	$1.5 \times 10^{-4}$	3.3 $\times 10^4$
2:2:1	Ba <sup>2+</sup>	$6.1 \times 10^{-2}$	1.22x10 <sup>5</sup>
2:2:2	Na <sup>+</sup>	27	$2 \times 10^{5}$
2:2:2	к+	7.5	$2 \times 10^{6}$
2:2:2	Rb <sup>+</sup>	38	7.5 x10 <sup>5</sup>
2:2:2	T1 <sup>+</sup>	60	2.5 $\times 10^8$
2:2:2	Ca <sup>2+</sup>	0.21	5.5 x10 <sup>3</sup>
2:2:2	Sr <sup>2+</sup>	$7.5 \times 10^{-5}$	7.5 $\times 10^3$
2:2:2	Ba <sup>2+</sup>	1.7x10 <sup>-5</sup>	5.5 x10 <sup>4</sup>

Table 7. Kinetics of cation complexation by cryptands<sup>a,b</sup>

- a. Table contains selected data taken from references 2, 102, 103.
- b. Acid catalyzed dissociation pathways are not considered in this table.

the isotopic separation of  $^{22}$ Na and  $^{24}$ Na have been reported. $^{95}$ 

## 3. Transition Metal Complexes

While most of the research on macrocyclic polyethers has been justifiably directed toward the properties that make them unusual, namely their ability to form strong coordination complexes with the alkali metals and alkaline earths, some investigations of transition metal cryptates have also been carried out. Tables 4 and 7 contain some thermodynamic and kinetic data for Pb<sup>2+</sup>, Ag<sup>+</sup>, and Tl<sup>+</sup> crown and cryptate complexes. A crystal structure reported for the 2:2:1 complex of Co<sup>2+</sup> shows an unusual pentagonal bipyramidal structure.<sup>110</sup> Cobaltous crown complexes have also attracted come attention. 111 Electrochemical studies of Tl<sup>+</sup> cryptates have shown the usual result of more negative reduction potentials upon complexation of the ion compared to the free aquated species and of a slower rate of reduction.<sup>112</sup> Lehn has also reported that 2:2:2 cryptand displays a high selectivity to Cd<sup>2+</sup>,  $Hg^{2+}$ , and  $Pb^{2+}$  over  $Zn^{2+}$  and  $Ca^{2+}$ , and so may be useful in treating heavy metal poisoning.<sup>95</sup>

In general, the more polarizable transition metals are found to produce more stable macrocyclic complexes than the Group IA or Group IIA elements. If the oxygen binding sites on the crown or cryptand are replaced by nitrogen or sulfur, the stability and selectivity of alkali metal and

alkaline earth complexes are reduced, while those of the transition metals are increased.<sup>68,83,95</sup>

The literature concerning lanthanide and actinide crown complexes is sparse and often contradictory. The most complete studies to date have been done by Cassol, Seminaro, and Paoli,<sup>113</sup> and by King and Heckley.<sup>51</sup> Unfortunately, they report quite different results. King and Heckley isolated 1:1 complexes of lanthanide-nitrate salts and benzo-15-crown-5 and dibenzo-18-crown-6 only for the lighter lanthanides, and solvated or non-stoichiocmetric complexes for the heavier lanthanides (i.e., roughly Gd through Lu). Cassol, et. el., report 1:1 complexes for all the lanthanide nitrates and thiocyanates from La through Lu with the same two crown ethers. Experimental conditions were similar, but not identical. Recent thermodynamic measurements by a third group of research workers tend to confirm the results of King and Heckley.<sup>114</sup> It was found that the stability constants for the Ln<sup>3+</sup>-18-crown-6 complexes decreases steadily from La<sup>3+</sup> to  $Gd^{3+}$ , and drops abruptly to zero from  $Tb^{3+}$  to  $Lu^{3+}$ . As discussed previously, this "gadolinium break" is not without precedent, and the data obtained for these compounds is consistent with the hypothesis that a change in solvation number is responsible for this effect. Further studies of these complexes must be carried out before definitive conclusions can be drawn about the heavier

members of the series.

The synthesis of the lighter lanthanide crown complexes has been well documented, most powerfully by the determination of the crystal structure of the lanthanum nitrate-dicyclohexyl-18-crown-6 complex. Nmr investigations of both  $La^{3+}$  and  $Pr^{3+}$  complexes with this ligand have also been carried out very recently.<sup>40</sup>

Only one communication has been published reporting the synthesis and properties of lanthanide cryptates.<sup>3</sup> The chlorides of  $La^{3+}$ ,  $Pr^{3+}$ ,  $Gd^{3+}$ , and  $Yb^{3+}$  with 2:2:1 cryptand were prepared under anhydrous conditions in nonaqueous media. The nitrate salt of  $La^{3+}$  and 2:2:2 cryptand was also reported. These compounds exhibited a number of unusual chemical and physical properties. In contrast to most lanthanide complexes, these lanthanide cryptates were kinetically inert. In neutral or acidic solution no dissociation occurs even after several days, and even at pH greater than 10 the complexes are stable for several hours. This inertness facilitates the use of the Gd complex as a relaxation agent in  $^{13}$ C nmr studies. It was shown that the  $T_1$  relaxation times of the CH<sub>2</sub> and CO carbons in acetone were markedly reduced in the presence of the complex, while chemical shifts were effectively unchanged.

The effect of encryptation on the Eu(III)/Eu(II) redox couple is even more remarkable. The cyclic

voltammogram for 0.4 mM  $Eu^{3+}$  in 0.5 <u>M</u> NaClO<sub>4</sub> at pH 2 shows an irreversible wave with  $E_f = -625$  mV versus SCE. For 0.35 <u>M</u> [Eu(2:2:1)]<sup>3+</sup> at pH 7 in 0.5 <u>M</u> NaClO<sub>4</sub>, the separation of the cathodic and anodic peaks is a sweep rate independent 65 mV, very close to the theoretical 57 mV separation expected for an electrochemically reversible redox couple at room temperature. Further, the formal potential was shifted in a positive direction to -435 mV versus SCE. An even greater positive shift was found for  $[Eu(2_{B}:2:1]^{3+}$  and  $[Eu(2:2:2)]^{3+}$ . This is the opposite effect than is usually observed upon complexation of an ion, and indicates that the Eu(II) state is more highly stabilized by encryptation than is the Eu(III) state. This is thought to be a result of the better fit of the larger Eu(II) ion in the cryptate cavity, and of the lesser desolvation energy required for encryptation of Eu(II) versus Eu(III).

The final important property of the  $Eu^{3+}$  cryptates that was reported concerns their ability to coordinate small anions. Addition of OH<sup>-</sup> or F<sup>-</sup> ions to a solution of  $[Eu(2:2:1)]^{3+}$  produced a substantial shift of the reduction potential toward more negative values. It was found that the complex could actually be titrated with fluoride ion, and that titration followed with a fluoride specific electrode. Stability constants for the coordination of one and two fluoride ions were reported. Macrocyclic complexes of the actinides are essentially unknown. Early reports of the synthesis of uranyl complexes with 18-crown-6 have been found to be erroneous.<sup>114</sup> Thermodynamic measurement show no interaction between  $Th^{4+}$ or  $UO_2^{2+}$  and 18-crown-6 in methanol.<sup>114</sup> There is one report of actinide cryptate complexes,<sup>115</sup> but the evidence, especially for the uranyl complex, is not entirely convincing. CHAPTER II

EXPERIMENTAL

### A. CRYPTAND SYNTHESIS

Lehn and coworkers have developed and published the most widely used methods for cryptand synthesis.<sup>93</sup> The key reactions involve high dilution condensations of diacid chlorides with diamines to yield cyclic amides. After reduction with  $\text{LiAlH}_4$  or  $\text{BH}_3$ , the monocyclic diamine is condensed with a second mole of diacid chloride, and reduced with  $\text{BH}_3$  to produce the bicyclic cryptand. This sequence is illustrated schematically below.

$$\begin{bmatrix} 1 \end{bmatrix} \begin{pmatrix} C(0)C1 & H_2^N \\ C(0)C1 & H_2^N \end{pmatrix} \xrightarrow{-2HC1} \begin{pmatrix} C(0)N \\ C(0)N \\ H \end{pmatrix} \xrightarrow{LAH} \begin{pmatrix} H \\ N \\ H \end{pmatrix}$$

$$\begin{bmatrix} 2 \end{bmatrix} \begin{pmatrix} \begin{pmatrix} N \\ N \\ H \end{pmatrix} + \begin{pmatrix} C(0)Cl \\ C(0)Cl \end{pmatrix} \xrightarrow{-2HCl} \begin{pmatrix} \begin{pmatrix} N \\ N-C(0) \end{pmatrix} \xrightarrow{BH_3} \begin{pmatrix} N \\ N \end{pmatrix} (Cryptand)$$

Dye and coworkers developed a continuous flow method to perform these same cyclizations without the need for high dilution techniques.<sup>116</sup> Either of these methods gives quite acceptable results in the synthesis of the ligand; however, the appropriate diacid chlorides and diamines are not commercially available. The traditional methods of synthesizing these precursers are expensive and time consuming. Simplified procedures have been developed by

Gansow and coworkers, and are described below. Figure 6 summarizes an abbreviated nomenclature used throughout this thesis in place of the cumbersome, systematic, IUPAC nomenclature.

## 1. 1-diacid chloride

The 1-diacid chloride (diglycoyl chloride) may be synthesized directly from commercially available diglycolic acid as follows: 156.4 gm PCl<sub>5</sub> (0.748 mole) is slurried in 300 ml of CHCl, in a l liter, 3 neck flask equipped with a mechanical stirrer, nitrogen atmosphere, and an efficient condenser. Gases escaping from the reaction flask are bubbled through aqueous NaOH (6 M) to remove HCl. 50 gm (0.374 mole) of 1-diacid are added in small portions to produce a steady stream of HCl bubbling from the reaction mixture. The reaction mixture becomes a thick slurry during this addition. When all of the l-diacid has been added the mixture is stirred at room temperature for 4 hours. During that time the slurry dissolves leaving a clear, yellowish solution. Any unreacted acid or PCl<sub>5</sub> is removed by filtration and the solvent is removed with a rotary evaporator. The resulting product is then vacuum distilled. POCl<sub>3</sub> is removed at 28-30° (0.5 mm Hg) and the clear, water-white product distills at 71-73°. It must be stored under nitrogen at 0° to prevent decomposition. Its nmr spectrum is a sharp singlet at 4.6 ppm from TMS in CDCl<sub>3</sub>. Yield: 80%. This method was developed by



Figure 6. Abbreviated nomenclature for cryptand precursors

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Triplett,  $^{117}$  and is much faster than the oxalyl chloride method suggested by Lehn. $^{93}$ 

# 2. 2-diacid

The procedure described by Lehn<sup>93</sup> is used without modification. 150 ml of conc. HNO<sub>3</sub> is heated to 45° in a 500 ml, 3 neck flask. 10 ml (8.9 gm) triethylene glycol is added and in about 15 minutes the reaction mixture turns reddish brown as a vigorous, exothermic reaction evolves gaseous nitrous oxides. Small additions of triethylene glycol are made at such a rate as to keep the temperature of the reaction mixture at 45-50° in its oil bath. When a total of 40 gm (0.267 mole, 36 ml) of triethlene glycol has been added, the reaction mixture is heated to 80° and stirred for 1 hour, leaving a clear, yellow solution. As much water as possible is removed on a rotary evaporator. Further drying is accomplished by the addition and subsequent evaporation of toluene. When dry, the viscous yellow paste will crystallize upon cooling and may be purified by recrystallization from an acetone/benzene mixture. Yield: 80-88% of pure white crystals. In d<sub>6</sub>-acetone the product gives the following proton nmr spectrum:

3.66 ppm (s)	4 protons	о-сн <sub>2</sub> -сн <sub>2</sub> -о
4.07 ppm (s)	4 protons	о-сн <sub>2</sub> -соон
$\sim$ 10 ppm (s)	2 protons	-COOH
	N D 750	

Internal standard: TMS. M.P. 75°

## 3. 2-diacid chloride

40 gm (0.225 mole) 2-diacid, 150 ml ether, and 190 gm SOCl<sub>2</sub> are placed in a l liter flask equipped with a magnetic stirrer, reflux condenser and a trap for escaping SO<sub>2</sub> and HCl. This reaction mixture is refluxed 4 hours under nitrogen. After reflux the solvent is removed on a rotary evaporator. An additional 100 ml of ether are added and evaporated.<sup>118</sup> The remaining pale yellow liquid is dissolved in a 2:1 petroleum ether/ether mixture and cooled to  $2-50^{\circ}$  in a dry ice/isopropanol bath. White crystals of 2-diacid chloride precipitate and are filtered under dry nitrogen in a cold funnel. The product is obtained in 80% yield after drying at 0° under vacuum. It should be stored at 0° under nitrogen to prevent decomposition. In d<sub>6</sub>-acetone, chemical shifts versus TMS are:

3.77 ppm (s)	4 protons	о- <u>сн</u> 2-сн2-о
4.60 ppm (s)	4 protons	0-CH <sub>2</sub> -C(0)Cl

# M.P. 25°

## 4. 2-diamine

The synthesis of this molecule has been the most difficult, time consuming, and expensive problem in cryptand production. Several alternate synthetic routes have now been developed. All use inexpensive and readily available triethylene glycol as the starting material. Lehn developed the traditional Gabriel synthesis for the conversion of a primary alcohol to a primary amine.<sup>93</sup> This method is

effective, but takes some  $l\frac{1}{2}$  weeks to complete and requires the use of expensive potassium phthalimide. Kausar<sup>4</sup> used a modification of a method for converting polyalcohols to polyamines<sup>119</sup> and applied it to this problem. Initially, this method was used with some modification to produce the 2-diamine and is described as Method A below. The bulky 2-ditosylate intermediate was found to be unnecessarily clumsy towork with, and the final reduction with LiAlH, was also expensive and difficult. During the course of this research, an alternate route using the readily synthesized 2-dibromide or the commercially available 2-dichloride intermediate was developed. The final reduction was carried out with a Zn/HCl mixture, as described under Method B below.



 <u>2-ditosylate</u>: 150 gm (1 mole) of triethylene glycol and 950 ml of pyridine are placed in a 2 liter, 3 neck flask equipped with a mechanical stirrer and a low temperature thermometer. The solution is cooled to -10°

in an ice/acetone bath, and 2 moles (381.4 gm) of solid p-toluene sulfonyl chloride (tosyl chloride, TsOCl) are added in 5 or 6 portions. Additions are made at a rate such that the temperature of the reaction mixture does not exceed 0°. The mixture turns pink as the reaction proceeds. When the addition is complete, the reaction mixture is stirred for 1 hour at -10°. The stirrer is then removed, the flask protected from moisture with a calcium chloride drying tube and stored at 10° overnight. A white solid precipitates (py·HCl), leaving a pink solution.

After the reaction is complete, the reaction mixture is poured into a 4 liter flask containing a well agitated mixture of 300 gm ice in 300 ml conc. HCl. The initial white precipitate dissolves, and is replaced by a second white precipitate. When all the ice has melted, the product is filtered through a coarse frit, washed several times with distilled water, and allowed to dry. This crude product is of sufficient purity to be used directly in the next step of the synthesis. Yield: 80%. nmr:

Internal standard: TMS	Solvent: CDCl	<b>.</b>
2.6 ppm (s)	6 protons	-C <sub>6</sub> H <sub>4</sub> -CH <sub>3</sub>
3.6 ppm (s)	4 protons	о-сн <sub>2</sub> -сн <sub>2</sub> -о-
3.7 ppm (t)	4 protons	TSO-CH2-CH2-
4.2 ppm (t)	4 protons	TsO-CH2-
7.2 ppm (d)	4 protons	(aromatic)
7.7 ppm (d)	4 protons	(aromatic)

2-diazide: 350 gm (0.76 mole) of 2-ditosyl-2) ate are added to 3500 ml ethanol in a 5 liter flask equipped with a good magnetic stirrer and reflux condenser. The solid does not all dissolve until the solution has been heated. 150 gm (2.3 mole) of NaN, are dissolved in a minimum of water (approximately 300 ml) and added to the ethanol solution. The reaction mixture is refluxed overnight, producing a clear, pale yellow solution. The solvent is then removed by rotary evaporation and the thick slurry product and NaOTs is washed with chloroform. The organic wash is dried with MgSO,, and the solvent removed by rotary evapor-The crude product (90% yield) may range in color ation. from yellow to reddish-brown, depending on the degree of purity, and may be reduced directly, or purified by careful vacuum distillation (overall yield 83%) at 100-103° at 0.5 mm Hq. Caution: azides are potentially explosive; appropriate safety precautions should be observed. The pure product is a water-white liquid with a single nmr peak at 3.6 ppm versus TMS in CDCl<sub>2</sub>.

3) 2-diamine:  $^{120}$  800 ml of dry tetrahydrofuran (distilled from LiAlH<sub>4</sub>) is placed in a 2 liter, 3 neck flask equipped with a mechanical stirrer, efficient condenser, dropping funnel, and nitrogen atmosphere. 25 gm (0.66 mole) LiAlH<sub>4</sub> are carefully added to the reaction vessel. A solution of 66 gm (0.33 mole) 2-diazide in 200 ml dry THF is added dropwise to the LAH slurry at such a rate as to
maintain gentle reflux of the reaction mixture. When the addition is complete, the reaction mixture is refluxed overnight.

When the reaction is complete, heating is stopped and 200 ml of 1:1 THF:water is added dropwise and with good stirring to the reaction mixture. <u>Caution</u>: The water reacts violently with the unreacted LAH, and must be added very slowly in the initial stages of the addition. 50 ml of 6 <u>N</u> NaOH are then added. After cooling, the inorganic salts are removed by filtration and washed thoroughly with toluene. The washings are combined with the THF solution and solvents removed by rotary evaporation, leaving a crude, yellow product. Vacuum distillation gives the clear colorless amine at 95° (1 mm Hg). Yield: 75-80%, but may vary from 30 to 95% depending on how well the inorganic salts are washed. nmr in CDCl<sub>3</sub> versus TMS:

1.5 ppm (s)	4 protons	- <sup>NH</sup> 2
2.9 ppm (t)	4 protons	H <sub>2</sub> N-CH <sub>2</sub>
3.5 ppm (t)	4 protons	<sup>H</sup> 2 <sup>N-CH</sup> 2 <sup>-CH</sup> 2 <sup>-O</sup>
3.6 ppm (s)	4 protons	о-сн <sub>2</sub> -сн <sub>2</sub> -о



2-dibromide: (after Lehn)<sup>93</sup> 100 gm (0.37 1) mole) of PBr<sub>3</sub> are placed in a 250 ml flask equipped with a nitrogen atmosphere and magnetic stirrer and cooled to 0° in an ice bath. A solution of 66 gm (0.44 mole) triethylene glycol and 14 ml of pyridine is added dropwise to the PBr<sub>2</sub> with good stirring and cooling. White fumes are evolved, the solution turns red, and a white solid (py·HBr) precipitates. When the addition is complete, the ice bath is removed and the reaction mixture is stirred at room temperature overnight. The resulting slurry is poured into a 500 ml separatory funnel containing 250 ml of ice water. After mixing, the mixture is left to settle as the ice melts. A yellow aqueous layer floats to the top of a reddish yellow organic layer. The organic phase is removed, washed with 50 ml water, 75 ml HCl, another 50 ml water, and finally dried with  $MgSO_A$ . The crude yellow product is obtained in 75% yield and may be converted directly to 2-diazide or purified by vacuum distillation. The pure

2-dibromide is a clear, colorless liquid distilling at 91-93° (0.5 mm Hg) and gives the following nmr spectrum:

3.70 ppm (s)

3.40 - 4.0 ppm (complex multiplet) Solvent: CDCl<sub>3</sub>. Internal standard: TMS.

2) 2-diazide:<sup>122</sup> 35.4 gm (0.55 mole) of NaN<sub>3</sub> are dissolved in a solution of 600 ml ethanol and 150 ml water in a 1 liter flask equipped with a magnetic stirrer, reflux condenser, and heating mantle. Heating may be necessary to dissolve all the azide. 72.9 gm (0.264 mole) 2-dibromide [or 49.3 gm (0.264 mole) Baker reagent grade 2-dichloride] are added to the ethanol solution and the solution is refluxed overnight. When the reaction period is over, the solvents are removed on a rotary evaporator, and the product is washed from the inorganic salts with CHCl<sub>3</sub>. The chloroform solution is dried with MgSO<sub>4</sub>, and the solvent removed by rotary evaporation. The resulting crude, yellow product is obtained in 85% yield, and may be purified as described in Method A or used without purification.

3) <u>2-diamine</u>: 47.2 gm (0.236 mole) of 2-diazide is dissolved in 300 ml of ethanol in a l liter flask equipped with a magnetic stirrer, dropping funnel, and reflux condenser. 65 gm (l mole) of zinc powder is slurried into this solution. 250 ml of conc. HCl is added dropwise to this solution. The addition must be slow at

first to prevent excessive hydrogen evolution and allow gentle reflux of the solvent. After the addition is complete, the mixture is stirred for 2 hours. At the end of that time, any undissolved zinc residue is filtered off and the volume of the solution is reduced to 75 ml on a rotary evaporator. The solution is made strongly basic with 8 N NaOH, which produces a great deal of heat and precipitates Zn(OH)2. The inorganic salt is filtered off, washed with two 100 ml volumes of toluene, and the combined filtrates are again reduced to a volume of 75 ml. The yellow solution is extracted with CH<sub>2</sub>Cl<sub>2</sub> until no more color is removed into the organic phase. The methylene chloride solution is dried with MgSO, and the solvent is removed by rotary evaporation. The crude product is distilled as in Method A. Yield: 60%. The yield could probably be increased by Soxhlet extraction of the inorganic salts.

The above procedures are used to produce the 1-diacid chloride, 2-diacid chloride, and 2-diamine necessary to obtain 2:2:2 and 2:2:1 cryptand. The following high dilution cyclizations are essentially the method of Lehn.<sup>93</sup> Only the detailed synthesis of 2:2:1 cryptand is given here. The synthesis of 2:2:2 cryptand is identical, except in the first cyclization where the specified amount of 1-diacid chloride is replaced by an equimolar amount of 2-diacid chloride. These more symmetric reagents produce somewhat higher yields than the 2:1 and 2:2:1 cyclizations.

### 5. First cyclization.

All the toluene used as solvent in the first and second cyclization reactions is dried by distilling away the toluene/waterazeotrope. 1500 ml of toluene is placed in a 5 liter, 3 neck flask equipped with a mechanical stirrer, 2 dropping funnels, and a nitrogen atmosphere. The flask is cooled to 0° in an ice bath. One dropping funnel is charged with a solution of 54.1 gm (0.365 mole) of 2-diamine in 1 liter dry toluene. The second dropping funnel contains a solution of 31.2 gm (0.183 mole) 1-diacid chloride in 1 liter dry toluene. These two solutions are added dropwise at an equal rate over a period of 4 hours or more to the cold solvent. Vigorous stirring must be maintained throughout the addition. When the addition is complete, the mixture is stirred overnight and allowed to warm to room temperature. The hydrochloride salt of the diamine precipitates from solution. The reaction mixture is then filtered and evaporated to dryness, leaving a yellow crystalline solid. This is dissolved in a 1:1 chloroform/ benzene mixture and passed over an alumina (30 gm) column, which removes polymeric impurities. When the eluent is evaporated to dryness, a 50-70% yield of crude 2:1 is obtained. Recrystallization from THF/heptane yields snow white crystals melting at 149°.

#### 6. First reduction.

350 ml of dry tetrahydrofuran is placed in a l liter, 3 neck flask equipped with a mechanical stirrer, nitrogen atmosphere, reflux condenser, and heating mantle. 7.6 gm (0.20 mole) of LiAlH, are added carefully. 24.6 gm (0.10 mole) of solid 2:1 are added in small amounts to the LAH slurry. The reaction mixture is then refluxed overnight. After refluxing, excess LAH is destroyed by the careful addition of 100 ml of 1:1 THF/water, followed by 15 ml 6 N NaOH. After cooling, the inorganic salts are filtered away and washed several times with toluene. The combined filtrates are evaporated to dryness leaving a viscous yellow paste that crystallizes as it cools. If all the water is not removed, crystallization will not occur and it may be necessary to dry the crude product by coevaporating the water with toluene. The product is purified by recrystallization from benzene. Yield: 85%. M.P. = 90°.

# 7. Second cyclization.

1.5 liters of dry toluene are placed in a 5 liter, three neck flask equipped with a mechanical stirrer, two dropping funnels, and a nitrogen atmosphere. The flask is cooled to 0° in an ice bath. One dropping funnel is filled with a solution of 17.1 gm (0.0784 mole) of 2:1 and 15.9 gm (0.157 mole) triethylamine in 1 liter of dry toluene. The second funnel is charged with a solution of 16.9 gm (0.0784 mole) 2-diacid chloride in 1 liter dry toluene.

These two solutions are added dropwise at an equal rate over a period of six hours as the temperature of the reaction mixture is maintained at 0°. When addition is complete, the ice bath is removed and stirring is continued overnight at room temperature. The reaction mixture is filtered to remove the hydrochloride salt of the triethylamine, and The reddish solid is dissolved in evaporated to dryness. a 1:1 chloroform/benzene mixture and passed over a 30 gm alumina column. Removal of the solvent leaves a vellow solid, which is recrystallized by dissolving in a minimum amount of benzene and adding pertoleum ether until the solution turns turbid. Upon standing at 0°, white crystals of pure 2<sup>\*</sup>:2:1 precipitate and are filtered off. Yield: 40%. The nmr spectrum is a complex system from 2.6 ppm to 4.8 ppm versus TMS in CDCl<sub>3</sub>.

## 8. Second reduction.

9.6 gm (0.027 mole) of  $2^*:2:1$  are dissolved in 300 ml dry THF in a l liter, 3 neck flask equipped with a magnetic stirrer and cooled to 0° in an ice bath. 150 ml of 1 <u>M</u> BH<sub>3</sub> in THF are added dropwise with good stirring. When the addition is complete, the solution is stirred 30 minutes, then refluxed for one hour. During the course of the reaction, a fine white precipitate forms. After refluxing, the solution is again cooled to 0°, and 50 ml of water are added to decompose the excess BH<sub>3</sub>. The solvents are removed on a rotary evaporator, leaving a snow white mixture of boric acid and the diborane-2:2:1 adduct. This mixture is dissolved in 200 ml of 6  $\underline{N}$  HCl, refluxed one hour and evaporated to dryness leaving the snow white 2:2:1·2HCl adduct. The acid residues are removed by passing the adduct over a strongly basic anion exchange resin (Amberlite IRA-400 or Dowex 1-X8) in conductance water. The eluent is monitored with pH paper. It is neutral at first, strongly basic as the product is eluted, then again neutral. The water is removed by rotary evaporation and further drying is accomplished by coevaporation with toluene. The crude yellow product is purified by vacuum distillation. Pure 2:2:1 distills at 166-169° (0.1 mm Hg). Yield: 80%. nmr:

	2.65	ppm	(t)	12	protons	N-CH <sub>2</sub>
	3.65	ppm	(t)	12	protons	N-CH2-CH2
	3.65	ppm	(s)	8	protons	0-CH2-CH2-0
Solvent:	CDC	21 <sub>3</sub> .	Internal	st	tandard:	TMS.

B. SYNTHESIS OF LANTHANIDE CRYPTATES

The synthesis of several lanthanide cryptates has been reported elsewhere. 3, 4, 121 The method used here is a modification and simplification of earlier procedures. It has been used in the synthesis of complexes of the nitrate, perchlorate and chloride salts of all or most of the tripositive lanthanides with 2:2:1 and 2:2:2 cryptands. It has also been used for various 2:2:2, 2:2:1, and 2:1:1 complexes of In<sup>3+</sup>, Ga<sup>3+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> salts. Since the chloride salts behave somewhat differently than the perchlorates and nitrates, they will be considered separately. Hydrated nitrate and chloride salts were purchased from the Alpha-Ventron Corporation and used without further purification. Hydrated perchlorates were purchased from the G.Frederick Smith Chemical Company and used as received. Acetonitrile from various manufacturers was purified and dried by distillation from  $P_2O_5$ . The first 10% of the distillate was discarded and the next 75% collected and stored over molecular sieves for use in these syntheses. 1. Nitrates and Perchlorates

0.343 millimoles of hydrated lanthanide salt is dissolved in a solution of 40 ml dry acetonitrile and 10 ml trimethyl orthoformate (TMOF). The solution is refluxed 1 hour under dry nitrogen. A solution of 0.343 millimoles cryptand in 10 ml dry acetonitrile is then added and

refluxing is continued for an addition 2-3 hours. Some precipitate may form upon addition of the ligand to the nitrate salts, especially for the heavier lanthanides, but all or most of this dissolves as refluxing continues. The solution is then cooled and filtered through a fine porosity frit to remove any precipitate that may be present. In general, no measurable amount of solid is obtained. The solution is concentrated to a volume of approximately 20 ml. Diethyl ether is added until the solution becomes turbid and is then stored in the freezer. After crystallization, the product is collected on a medium porosity filter, washed with ether and hexane, then dried 24 hours at 100° under vacuum in an Abderhalden drying apparatus in the presence of  $P_2O_5$ .

## 2. Chlorides

0.343 millimoles of hydrated lanthanide chloride is dissolved in a solution of 40 ml acetonitrile and 10 ml TMOF. The solution is refluxed one hour under dry nitrogen. A solution of 0.343 millimoles of cryptand in 10 ml dry acetonitrile is added, and a precipitate immediately forms. Most of this precipitate redissolves with the lighter lanthanides, but as the atomic weight of the lanthanide increases, the amount of insoluable precipitate increases until, in the case of Lu, almost all of the salt is removed from solution by this initial precipitate. Refluxing longer than three hours does not affect the amount of precipitate

remaining, and eventually leads to discoloration of the solution. After cooling, the initial precipitate is filtered. The volume of the solution is reduced to approximately 20 ml. Diethyl ether is added until the solution becomes turbid and the solution is stored in the freezer. After crystallization, the product is collected on a medium porosity filter, washed with ether and hexane, then dried 24 hours at 100° under vacuum in an Abderhalden apparatus in the presence of  $P_2O_5$ .

#### C. PHYSICAL MEASUREMENTS

## 1. Elemental Analyses

All elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, Michigan, or Galbraith Laboratories, Knoxville, Tennessee.

## 2. Infrared Spectra

Infrared spectra in the region from 4000 cm<sup>-1</sup> to 250 cm<sup>-1</sup> were obtained by using a Perkin-Elmer 457 grating spectrophotometer. The instrument was calibrated by measuring the 1604.1, 1181.4 cm<sup>-1</sup> absorption of an internal polystyrene film. All spectra were taken in nujol mulls spread on KBr plates.

#### 3. Electronic Spectra

Electronic spectra in the 250 nm to 1000 nm wavelength region were obtained by using a Cary 17 recording spectrophotometer. Calibration of the instrument was checked by comparing absorption spectra of standard solutions of lanthanide salts with literature values. In all cases, experimental absorption maxima were within  $\pm$  1 nm of literature values, and molar absorptivities were within  $\pm$  2%.<sup>55</sup> Spectra of the lanthanide cryptates were obtained using 0.025 <u>M</u> aqueous solutions. The solutions were adjusted to pH 4 with nitric or hydrochloric acids for the nitrate and chloride salts, respectively. Spectra were recorded within minutes after the solutions were prepared.

# 4. Fluorescence Spectra

Fluorescence spectra of  $\text{Eu}^{3+}(\text{aq})$  and  $[\text{Eu}(2:2:1)]^{3+}$ were obtained by using a Perkin Elmer Model MPF-44A fluorescence spectrophotometer. The compounds were dissolved in 99.9% D<sub>2</sub>O (Stohler Chemical Company) to a concentration of 0.0160 <u>M</u>, and irradiated at 394 nm. The fluorescence spectra were recorded from 420 nm to 770 nm.

## 5. Cyclic Voltammograms

Cyclic voltammograms of a number of electroactive species were obtained on a PAR-174 electrochemical analyzer. Aqueous solutions were approximately 1 mM in  $M^{+n}$  and 0.5 <u>M</u> in tetraethylammonium perchlorate. A hanging mercury drop served as the working electrode, while platinum wire and saturated calomel electrodes were used as auxillary and reference electrodes, respectively. Sweep rates were varied from 50 to 500 mV/sec.

## 6. Nuclear Magnetic Resonance Spectra

Routine spectra of intermediates during the synthesis of the ligand were obtained on Varian T-60 or A-56/60 spectrophotometers. High field, 180 MHz proton spectra of lanthanide cryptate complexes were obtained on a Bruker WH-180 spectrophotometer using a Nicolet 1180 computer system for Fourier transform. The instrument was equipped for both variable temperature and automated decoupling experiments. Spectra were recorded both in  $D_2O$  solution (t-butanol reference) and in  $CD_3CN$  (TMS reference).

## 7. Fluoride Titrations

The coordination of fluoride ion to various lanthanide complexes of the 2:2:1 cryptand was followed by using a fluoride ion selective electrode<sup>124</sup> (Orion model 94-09) whose potential versus a saturated calomel electrode was measured with a Fluke Model 8000A Digital Multimeter. The electrode was calibrated before and after each series of titrations. The calibration varied little over the course of an ordinary working day, but changed by several millivolts over a period of several days. 10 ml samples of approximately 1 mM cryptate solution were titrated with  $2 \times 10^{-3}$  <u>M</u> and  $2 \times 10^{-2}$  <u>M</u> NaF. All solutions were 0.5 <u>M</u> in NaClO<sub>4</sub>. Stability constants for the formation of monofluoro and difluoro species at 20° were calculated directly from the measured fluoride concentrations as well as by the graphical method of Rossotti and Rossotti.<sup>125</sup>

D. SEPARATION OF CRYPTATES FROM UNCOMPLEXED METAL SALTS

80 mg of a lanthanide cryptate-lanthanide chloride mixture are dissolved in 2 ml water and 2 ml of Dowex A-1 ion exchange resin (50-100 mesh, lot #07088FC, HCl form) are added. The mixture is stirred 15 minutes during which time the solution becomes acidic. After filtering away the resin, which is washed three times with 4 ml water, the filtrate and combined washings are treated with a second 2 ml portion of resin. After a second filtration and washing, the solvent is removed under vacuum, preferably by freeze-drying, and the crystalline product is obtained. Uncomplexed lanthanide ions are strongly retained on the resin.

#### E. NITRATE ANALYSIS

Samples were analyzed for nitrate content by using an Orion liquid membrane nitrate ion selective electrode. The electrode was calibrated with standard  $\text{KNO}_3$  solutions by using a Fluke Model 8000A Digital Multimeter to measure its potential versus a saturated calomel electrode. All samples and standards were dissolved in 0.1 <u>M</u> Na<sub>2</sub>SO<sub>4</sub> to maintain constant ionic strength, and concentrations were obtained directly from the measured potential via a calibration curve prepared immediately prior to the analysis using standard  $\text{KNO}_3$  solution. 10 ml samples of approximately 1 mM cryptate were used for each analysis.

### F. CHLORIDE ANALYSIS

Samples were analyzed for chloride content by using an Orion chloride ion selective combination electrode. Conditions were as for the nitrate analysis described previously. Standard KCl solutions, also in 0.1  $\underline{M}$  Na<sub>2</sub>SO<sub>4</sub>, were used to prepare calibration curves before each series of analyses.

# CHAPTER III

# RESULTS AND DISCUSSION

#### A. LIGAND SYNTHESIS

When this research project was initiated, cryptands were commercially available from only one source at a cost of \$150.00 to \$200.00 per gram. This made it impractical to purchase large amounts for major research efforts, and so required the synthesis of the ligands from more readily available starting materials. As mentioned in the experimental section, the high dilution techniques of Lehn give good results when the appropriate diamines and diacid chlorides are available. The synthesis of the diamines was and is the most difficult problem in cryptand synthesis. The method developed by Fleischer, et. al., 119 and applied to this problem by Kausar<sup>4</sup> is less expensive and less time consuming than the traditional Gabriel synthesis used by Lehn. The method described in this thesis offers a third synthetic route that uses still less expensive and more easily handled reagents.

Fortunately, the cost of commercial cryptands has dropped to \$50.00 per gram or less, and they are available through several distributors. The monocyclic 2:2 and 2:1 precursors are also available at comparatively modest prices and can be used to produce any cryptand that has been of interest to date, without the need of synthesizing the troublesome diamines. It is quite probable that as the interest in macrocyclic ligands and their applications

continues to grow, their prices will continue to decline and it will become more economical to purchase the compounds than to invest in the starting materials and time needed to produce them in the laboratory. Currently, the cost of the materials needed to synthesize ligands is considerably less than that of commercial cryptands, but the time required to produce them almost entirely outweighs the difference in cost of materials. Thus, the ability to synthesize the various intermediates discussed herein has been much reduced in importance, except when it is necessary to produce specially modified cryptands (<u>e.g.</u>, deuterated compounds, benzo cryptands, etc.).

#### **B. SYNTHESIS OF LANTHANIDE CRYPTATES**

#### 1. 2:2:1 Complexes

The method described in section II.B can be used to synthesize pure, 1:1 complexes between 2:2:1 cryptand and the trivalent La, Ce, Pr, Nd, Sm, Eu, and Gd ions. Spectral results to be discussed later give strong evidence that the metal ion is actually inside the cavity of the ligand (<u>i.e.</u>, is "encryptated"). The representative analytical data for these compounds presented in Table 8 confirms the 1:1 stoichiometry of these complexes, and indicates that only non-stoichiometric materials, 2:2:1·bLnX<sub>3</sub> (b≈1.2 to 2.5; Ln = Sm to Lu, X = NO<sub>3</sub>; Ln = Tb to Lu, X = Cl ) are formed for the heavier lanthanides under these conditions. These results are reproducible when multiple syntheses are done.

The success of the method depends not only on the cation, but also on the anion in solution. Nitrate salts react stoichiometrically only from La through Nd, while the chloride salts may be used from La through Gd to produce 1:1 complexes.

An explanantion for the observed results may be proposed on the basis of the known properties of other cryptate and lanthanide complexes. First, the charge and size of the cations must be considered in predicting their behavior toward cryptands. The relationship between these

Compound		U %	Н %	8 N	\$ C1	۶ NO3	Ligand:metal ratio
[La(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	29.24 29.00	4.91 5.01	10.65 10.44		28.30 28.11	1:1
[La(2:2:1)]C1 <sub>3</sub>	calc found	33.27 33.44	5.58 5.55		18.41 18.01		1:1
[La(2:2:1)] (Cl0 <sub>4</sub> ) <sub>3</sub>	<b>calc</b> found	24.97 24.76	4.19 4.11		1   1   1   1	8 8 8 8 8 8	1:1
[Ce(2:2:1)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	28.18 28.96	4.90 4.91	10.63 10.54		28.25 28.06	1:1
[Pr(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	29.15 29.23	4.89 4.71	10.62		28.21 28.44	1:1
[Pr(2:2:1)]Cl <sub>3</sub>	<b>cal</b> c found	33.15 33.21	5.56 5.44		18.35 17.40	8 8 8 5 8 5	1:1
[Nd(2:2:1)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	29.00 29.07	4.87 4.92	10.57		28.07 28.27	1:1
[Nd(2:2:1)]Cl <sub>3</sub>	calc found	32.96 32.76	5.53 5.57		18.24 18.10		1:1

Table 8. Elemental analysis of 2:2:1 complexes

Compound		C %	Н 8	N 8	8 Cl	۶ NO	Ligand:metal ratio
[Sm(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	28.74 22.15	<b>4</b> .82 3.63	10.47 10.26		27.81 35.60	1:1.65
[Sm(2:2:1)]Cl <sub>3</sub>	calc found	32.62 32.60	5.47 5.55	4.75 4.72	18.05 18.10		1:1
[Eu(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	28.67 19.20	<b>4.81</b> 3.18	10.45 10.30	1 1 1 1 1 1	27.75 36.50	1:1.98
[Eu(2:2:1)]Cl <sub>3</sub>	calc found	32.53 32.20	5.46 5.50	4.74 4.83	18.00 18.41		1:1
[Gd(2:2:1)]Cl <sub>3</sub>	calc found	32.24 32.03	5.41 5.50	<b>4</b> .70 4.75	17.84 17.44		1:1
[Tb(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	28.37 24.20	<b>4</b> .76 3.99	<b>10.34</b> 10.56	  	27.46 32.04	1:1.34
[Dy (2:2:1) ] (NO <sub>3</sub> ) <sub>3</sub>	calc found	28.22 24.12	<b>4.74</b> 3.94	10.28 9.79		27.32 32.33	1:1.33
[Dy (2:2:1) ]C1 <sub>3</sub>	calc found	31.96 26.05	5.36 4.67		17.69 20.48		1:1.51

Table 8 (cont'd)

Compound		C %	Н 8	8 8	8 C1	8 NO3	Ligand:metal ratio
[Ho(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	28.12 22.49	<b>4.72</b> 3.72	10.25 10.27		27.22 32.86	1:1.49
[Er(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	28.03 25.52	4.70 4.18	10.21 10.35	  	27.13 29.85	1:1.19
[Yb(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	calc found	27.79 22.52	<b>4</b> .66 3.75	10.13 9.92		26.89 31.21	1:1.45
[Yb(2:2:1)]Cl <sub>3</sub>	<b>cal</b> c found	31.41 19.89	5.27 4.31		17.38 18.43		1:1.6
[Lu(2:2:1)]Cl <sub>3</sub>	<b>calc</b> found	31.31 19.44	5.26 4.18		17.33		1:1.66

Table 8 (cont'd)

two factors and cryptate stability, as discussed in section I.C, is simple: (1) the higher the charge the stronger the complex, and (2) the more nearly the radius of the cation matches the radius of the ligand cavity, the stronger the complex. If these factors apply to lanthanide cryptates, all of which are in the tripositive valence state, then the lighter lanthanides, whose radii most nearly match that of the 2:2:1 ligand cavity, might be expected to form the most stable complexes. (See Tables 5 and 6 for representative radii.) As the atomic number of the lanthanide increases, the radius of the ion decreases, and complex stability might be expected to decrease.

The anion effect described above has been observed with other lanthanide complexes as well. Nitrate is known to coordinate strongly to the lanthanides.<sup>29</sup> Even in the hydrated nitrate salts, it has been shown that all of the anions are coordinated to the metal.<sup>129</sup> In acetonitrile solution, the nitrate ion has been found to compete effectively with ethylenediamine for the coordination sphere of lanthanide ions.<sup>26</sup> Nitrate ions also interact strongly with lanthanide crown complexes,<sup>114</sup> which are perhaps the closest analogs to lanthanide cryptates that have been studied. By contrast, the chloride ion forms only weak, outer sphere coordination complexes with lanthanide ions.<sup>136</sup> The chloride salts behave very

similarly to the perchlorate salts when either the aquated ions<sup>136</sup> or the crown ether complexes<sup>114</sup> are studied. The perchlorate anion is generally considered as a non-complexing agent for Ln(III) ions in solution.<sup>29,114,136</sup> Clearly, if the nitrate ion coordinates more strongly to the Ln(III) ions than does the chloride ion, then it can compete more effectively with other ligands for the coordination sphere of these cations.

The observed synthetic results, then, might be a consequence of two factors. First, the smaller cations do not fit the 2:2:1 cavity as well, and so are expected to produce less stable complexes. Secondly, as the cryptand-Ln(III) complex becomes less stable, the nitrate ion is able to compete more effectively for the coordination sphere of the cation and prevent the stoichiometric formation of complexes that can form in the presence of the less coordinating chloride ion.

### 2. Separation of 2:2:1 cryptate-metal chloride mixture

Regardless of the reasons for the difficulties in producing stoichiometric complexes with the heavier lanthanides, some very recent separation experiments indicate that the excess metal salt may be efficiently removed from the lanthanide cryptate-lanthanide salt mixture by the use of Dowex A-1 (Dow Chemical Company) ion exchange resin. Preliminary experiments showed that an eightfold excess of Dowex A-1 stirred with an aqueous solution of NdCl<sub>2</sub>

removed 80-90% of the metal ions from solution. Similar treatment of pure [Nd(2:2:1)]Cl<sub>3</sub> resulted in the loss of only about 10% of the complex.

This method, as described in section II.D, was used to remove some of the excess metal chloride from 2:2:1·xDyCl<sub>3</sub>, 2:2:1·xYbCl<sub>3</sub>, and 2:2:1·xLuCl<sub>3</sub>. The analytical data in Table 9 show that the method was successful in purifying the [Dy(2:2:1)]Cl<sub>3</sub> complex, which was isolated as the dihydrate. The method was less successful when applied to the Lu and Yb mixtures. Infrared data confirmed the presence of water in the compounds even after vacuum drying at 100°.

Continuing efforts are underway to improve the separation method in the hope that analytically pure complexes of each of the lanthanides may be obtained.

# 3. Comments on elemental analyses

It should be noted that the elemental analysis of these compounds is apparently complicated by the formation of metal carbonates during the combustion procedure. Spang Laboratories was able to give reproducible analyses that were consistent with spectroscopic data, electrochemical data, and potentiometric analyses. Galbraith Laboratories, especially for the heavier lanthanides, reported different results that were consistently low in carbon content. Analytical results quoted in Tables 8, 9, and 10 are from Spang Laboratories and in most cases are representative of

Compound		۶ C	8 H	% Cl
[Lu(2:2:1)]Cl <sub>3</sub>	calc before after	31.31 19.44 24.05	5.26 4.18 5.15	17.33
[Yb(2:2:1)]C1 <sub>3</sub>	calc before after	31.41 19.89 25.13	5.27 4.31 5.98	17.38 18.43
[Dy(2:2:1)]C1 <sub>3</sub> .2H <sub>2</sub> O	calc before after	30.15 26.05 29.66	5.69 4.67 5.68	16.68 20.48 16.81

Table 9. Elemental analysis of compounds before and after treatment with Dowex A-l ion exchange resin

duplicate analyses of multiple preparative attempts. Results from Galbraith Laboratories were used only as a qualitative guide and were only used for analyses not available from Spang Laboratories or when Spang Laboratories was not in operation.

Chloride and nitrate ion selective electrodes proved to be a reliable, fast and convenient means of checking the purity of a compound. Excellent linearity of response was observed for chloride or nitrate concentrations between  $10^{-6}$  M and  $10^{-1}$  M when the usual pA<sup>-</sup> versus potential plots were constructed (see sections II.E and F for experimental details). Millimolar anion concentrations could be reproducibly measured to within  $\pm 2$ %. Agreement between analyses done in this way, and the C, H, and N analyses done by the independent laboratories is good, as can be seen by analyzing the results in Tables 8 and 9. Complete calibration and analysis data for these analyses are included in the appendix.

# 4. 2:2:2 Cryptands

Analytical data typical of attempts to form 2:2:2 complexes are shown in Table 10. Here, stoichiometric complexes are obtained for the nitrate salts of La, Ce, and Pr and the chloride salts of La, Ce, Pr, Nd, and Sm. These results are quite analogous to those from the 2:2:1 complexes, but the larger 2:2:2 ligand forms stoichiometric complexes only with the largest lanthanides under the

Compound		U ~	н %	Z %	8 Cl	8 NO3	Ligand:metal ratio
[La(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	30.82 30.72	5.14 5.03			26.52 26.34	1:1
[Ce(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	30.77 30.20	5.16 5.00	9.96 9.53		26.47 26.55	1:1
[Pr(2:2:2(](NO <sub>3</sub> ) <sub>3</sub>	calc found	30.74 30.59	5.16 5.08			26.44 26.63	1:1
[Pr(2:2:2)]Cl <sub>3</sub>	calc found	34.66 34.69	5.82 5.88		17.05 17.30		1:1
[Nd(2:2:2)] (NO <sub>3</sub> ) 3	<b>calc</b> found	30.59 28.04	5.13 4.70	9.90 9.50	         	26.32 28.12	1:1.17
[Nd(2:2:2)]Cl <sub>3</sub>	calc found	34.47 34.52	5.79 6.02	4.47 4.52	16.96 16.44		1:1
[Sm(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	<b>calc</b> found	30.33 24.65	5.09 4.06	9.82 10.25		26.09 31.40	1:1.49
[Sm(2:2:2)]Cl <sub>3</sub>	calc found	34.14 34.03	5.73 5.75	4.42 4.46	16.80 16.91	1           	1:1

Table 10. Elemental analysis of 2:2:2 complexes

Compound		C &	Н 8	N 8	8 C1	۶ NO3	Ligand:metal ratio
[Eu(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	30.26 24.66	5.08 4.09	9.80		26.04 32.01	1:1.48
[Eu(2:2:2)]Cl <sub>3</sub>	calc found	3 <b>4</b> .06 27.10	5.72 4.73	<b>4.41</b> 3.56	16.75 22.06		1:1.63
[Gd(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	calc found	30.04 34.12	5.04 4.00	9.73		25.84 31.02	1:1.51
[Tb(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	calc found	29.97 22.08	5.03 3.69	9.70		25.78 33.77	1:1.75
[Ho(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	29.84 21.24	<b>4.99</b> 3.51	9.62	9 8 9 9 9 9	25.57 34.00	1:1.83
[Er(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	calc found	29.63 20.00	<b>4.97</b> 3.35	9.59		25.49 33.78	1:1.99
[Yb(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	29.39 19.95	<b>4.9</b> 3 3.67	9.52		25.29 33.58	1:1.97
[Lu(2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	calc found	29.32 19.87	<b>4.92</b> 3.3 <b>4</b>	9.50 10.30		25.22 33.89	1:1.97

Table 10 (cont'd)

synthetic conditions used. The results of C, H, N, Cl<sup>-</sup>, and NO<sub>3</sub> analysis again show an excess of free metal salt in the heavier lanthanide complexes, but an interesting pattern occurs with the nitrate salts that does not occur in the corresponding 2:2:1 compounds. The ligand-tometal ratios of the compounds fall into three distinct groups: 1:1 for La, Ce, Pr (Nd?); 1:1.5 for Sm, Eu, Gd; 1:1.8 for Tb, Ho and 1:2 for Er, Yb, and Lu. Further, these ratios are reproducible if the synthesis is repeated. There is no immediately apparent reason for these groupings, though they are not without precedent in the literature.<sup>5,6,10</sup> It will be interesting to see if it occurs when other salts are used.

Unfortunately, the separation techniques being developed for the 2:2:1 complexes cannot be readily adapted to separating the 2:2:2 complexes from excess metal salts. In aqueous solution the 2:2:2 complexes decompose too quickly to carry out the procedure. A nonaqueous solvent may give better results, but the compounds are only sparingly soluble in most solvents. The perchlorates will dissolve to some degree in acetone and methanol, but dimethyl sulfoxide and hexamethylphosphoramide destroy both the 2:2:1 and 2:2:2 complexes.

From infrared and nmr evidence, to be discussed later, it is quite certain that the lighter lanthanides (La, Ce, Pr, Nd, and Sm) are truly encryptated by the

2:2:2 ligand. Unfortunately, there is conflicting data as to the type of coordination that occurs between the heavier lanthanides (Eu to Lu) and 2:2:2 cryptand. A cyclic voltammogram attributed to the  $[Eu(2:2:2)]^{3+}$  species has been reported<sup>3</sup> and reproduced during the course of this research. Electrochemical studies<sup>126</sup> have shown the rate constant for the aquation of this complex is  $1 \times 10^{-3} \text{ s}^{-1}$ . indicating a half life of about 11 minutes. However. attempts to observe this species via the nmr experiments have failed. This problem will be discussed in greater detail after the infrared, nmr, and electrochemical results obtained in this investigation have been presented.

## 5. Other synthetic methods

A systematic study was done in the early stages of this research to determine the effect of using less than anhydrous conditions in the synthesis of these compounds. In the original communication reporting the synthesis of lanthanide cryptates,<sup>3</sup> anhydrous salts were prepared and used under rigorously anhydrous conditions. Aside from the usual mechanical difficulties involved with maintaining such conditions, the anhydrous lanthanide nitrates and chlorides are difficult to dissolve in anhydrous nonaqueous solvents. The readily available hydrated salts dissolved freely, but addition of the basic cryptands to a solution containing any appreciable amount of water resulted in the immediate precipitation of the lanthanide

hydroxides. This phenomenon gave rise to a qualitative, visual test to determine the dryness of the solvent and/or salts used in a preparative attempt. Commercial reagent grade acetonitrile contains about 0.3% water, and a solution of lanthanide salt in the untreated solvent will produce copious amounts of precipitate upon addition of a cryptand. Drying the solvent over molecular sieves will greatly reduce the amount of precipitate formed, while distillation from  $P_2O_5$  and careful handling under dry nitrogen will eliminate hydroxide formation completely. The nature of this precipitate is readily identified from its flocculent appearance, which is typical of the metal hydroxides, and its infrared spectrum showing the usual hydroxide band near 3300  $\rm cm^{-1}$  and no bands that can be attributed to the organic ligand. If the amount of metal ion and ligand is sufficiently large to react with all the water in the system, any remaining cryptand and cation can react to form a cryptate complex. The initial precipitate can be filtered off, and the complex precipitated with ethyl ether.

These experiments made it clear that anhydrous conditions were necessary to produce the desired complexes in good yield and without wasting large amounts of expensive reagents. The use of trimethyl orthoformate as an <u>in-situ</u> drying agent was found to be an ideal way to dehydrate solutions of hydrated lanthanide salts in acetonitrile as

described in section II.B

A few experiments were carried out using ethyl acetate as the solvent. The lighter lanthanides (La, Ce, Pr) were successfully encryptated in this medium, but this method was not pursued once the success of the acetonitrile was established.

#### C. PHYSICAL MEASUREMENTS

## 1. Infrared Spectra

Infrared spectra of the lanthanide cryptates, especially those made from nitrate salts, contain considerable information on the nature of the complexes. Indeed, the first evidence for coordination between a lanthanide salt and a cryptand found in this investigation was the shift in the frequency of the ether linkage stretching mode in the ligand. In this section, detailed analyses of lanthanide cryptate complex infrared spectra are presented.

a.) 2:2:1 complexes. Figures 7 and 8 show the infrared spectra of pure 2:2:1 and pure  $[\text{La}(2:2:1)](\text{NO}_3)_3$ . The pure cryptand (either 2:2:1 or 2:2:2) shows an absorbance at 1125 cm<sup>-1</sup> that is attributed to the stretching motion of the ether linkages. Upon encryptation, the frequency of this absorption is shifted to about 1075 cm<sup>-1</sup>. This is analogous to a similar shift that is diagnostic of the formation of crown complexes.<sup>51</sup> Since the infrared spectrum of all of the 1:1 complexes between 2:2:1 cryptand and  $\text{Ln}(\text{NO}_3)_3$  (Ln = Ln to Nd) are very similar, only the spectrum of the La complex is analyzed in detail. Identical analysis can be made for the other nitrate complexes and data for these compounds are included in Table 12.








As discussed in section I.B.3, the infrared spectrum of the nitrate ion will depend on whether it is coordinated  $(C_{2v} \text{ symmetry})$  or uncoordinated  $(D_{3h} \text{ symmetry})$ . Tables 11 and 12 list the complete assignment of the infrared bands of this ion in both forms. These assignments will be used throughout the following discussion.

The spectrum in Figure 8 establishes the presence of both coordinated and free nitrate ions in the solid. Absorbances at 735  $(\mathcal{D}_3)$ , 815  $(\mathcal{D}_6)$ , 1310  $(\mathcal{D}_1)$ , and 1490  $(\mathcal{D}_4)$  cm<sup>-1</sup> are characteristic of coordinated nitrate ions, while those at 830  $(\mathcal{D}_2)$  and 1355  $(\mathcal{D}_3)$  cm<sup>-1</sup> are characteristic of ionic nitrate ions.

The nitrate ion may coordinate as either a unidentate or bidentate ligand. Both types of coordination reduce the symmetry of the anion to  $C_{2v}$  and various methods of differentiating them have appeared in the literature.<sup>128</sup> The most successful is based on the appearance of two combination bands  $(\mathcal{V}_1 + \mathcal{V}_2 \text{ and } \mathcal{V}_1 + \mathcal{V}_6)$  near 1750 cm<sup>-1</sup>. These combination bands are generally split by 5-26 cm<sup>-1</sup>, in unidentate complexes, and by 29-54 cm<sup>-1</sup> in bidentate lanthanide nitrate complexes. On this basis, the two combination bands in the [La(2:2:1)](NO<sub>3</sub>)<sub>3</sub> complex (1745 and 1775 cm<sup>-1</sup>,  $\Delta \mathcal{V} = 30$ ) are apparently due to bidentate nitrate ion.

Because stoichiometric, 1:1 cryptate complexes have not been isolated, extreme care must be taken in

Туре	Infrared	N0 <sub>3</sub>	typical cm <sup>-1</sup>	Assignment
 A <sub>l</sub> '	inactive	$\boldsymbol{\nu}_{1}$	1050	N-O stretch
<sup>A</sup> 2"	active	ν <sub>2</sub>	831	NO <sub>2</sub> deformation
Е'	active	$\boldsymbol{\mathcal{V}}_{3}$	1390	NO <sub>2</sub> asym. stretch
Е'	active	V 4	720	planar rock

Table 11. Absorption frequencies for ionic  $NO_3^{-1}$  (D<sub>3h</sub> symmetry)<sup>52</sup>

Table 12. Absorption frequencies for coordinated  $NO_3^{-1}$  (C<sub>2v</sub> symmetry)<sup>52</sup>

Туре	Infrared	NO3	typical cm <sup>-1</sup>	Assignment
Al	active	$\nu_{_1}$	1290-1253	NO2 sym. stretch
A <sub>1</sub>	active	ປ 2	1034-970	N-O stretch
A <sub>1</sub>	active	$\boldsymbol{\nu}_{3}$	not obs.	NO <sub>2</sub> bend
B <sub>1</sub>	active	$\mathcal{V}_4$	1531-1481	asym. stretch
<sup>B</sup> 1	active	ע <sub>5</sub>	not obs.	planar rock
<sup>B</sup> 2	active	ν <sub>6</sub>	800-781	nonplanar rock

interpreting the infrared spectra of the materials that are obtained. The intensities of the bands in these spectra tend to be reduced from those of the lighter lanthanide cryptates. There is no apparent reason for this, but the shift in the absorbance of the ether linkage shows clearly that the metal ions are coordinating. As discussed in section III.B.1, nitrate ions appear only in a coordinated state in the Ln(NO3) salts. If this can be assumed true in a lanthanide cryptate/lanthanide nitrate mixture, then a band at 830  $\rm cm^{-1}$  appearing in the spectrum of the heavier lanthanide cryptates may be an indication that these complexes, like their lighter analogs, may contain both free and coordinated nitrate ions. The several bands attributable to coordinated nitrate are present, but of course there is no way of distinguishing between nitrate coordinated to lanthanide cryptate and nitrate coordinated to free lanthanide ion. The combinations bands, which are often difficult to see,  $^{128}$  are too weak to be useful in these spectra.

Infrared spectra of the 2:2:1 chlorides and perchlorates are somewhat less informative. Both show the shifted ether absorbance from the ligand. Chloride ion alone has no infrared spectrum, but Ln-Cl vibrations have been observed in some compounds in the far infrared region.<sup>130</sup> No attempt was made to observe these vibrations. The perchlorate band near 1100 cm<sup>-1</sup> overlaps with the ether

band of the ligand, making it difficult to interpret. A strong band at 620 cm<sup>-1</sup> is characteristic of uncoordinated perchlorate, and the absence of a strong band at 930 cm<sup>-1</sup> is good evidence for a lack of coordinated perchlorate.  $^{26,131}$ 

Table 13 lists the frequencies and assignments of the analytically useful infrared bands for some typical lanthanide nitrates, perchlorates and chlorates.

b.) 2:2:2 complexes. As might be expected from their similar structures, the infrared spectra of the 2:2:1 and 2:2:2 cryptands are essentially the same. The same is true of the  $[Ln(2:2:2)]X_3$  and  $[Ln(2:2:1)]X_3$ spectra, as an examination of the data in Table 14 will show. No 2:2:2 perchlorates were made.

## 2. Visible Spectra

Consistent with other studies of lanthanide complexes, encryptation has only a small effect on the electronic spectra of the lanthanide ions. Table 14 lists the wavelengths of a few representative absorbances and their molar absorptivities for several representative 2:2:1 and 2:2:2 lanthanide cryptates. Measured and literature values for corresponding bands in the aquated ions are included for comparison, and the so-called "hypersensitive transitions" are marked with an asterisk.

## 3. Fluorescence Spectra

Lanthanide complexes, especially those of europium

đ
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lanthanide
of
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Assignment
13.
Table

Compound	-CH <sub>2</sub> -O-CH <sub>2</sub> ether stretch	υ <sub>3 NO3</sub> D <sub>3h</sub>	ν <sub>2 NO3</sub> D <sub>3h</sub>	<b>υ</b> <sub>1 N03</sub> <sup>C2υ</sup>	<b>υ</b> <sub>4</sub> ΝΟ <sub>3</sub> <sup>C2ν</sup>	ν <sub>6</sub> ΝΟ <sub>3</sub> <sup>C2V</sup>	υ <sub>3 NO3</sub> <sup>C2v</sup>	clo4 <sup>-</sup>	NO <sub>3</sub> comb band
2:2:1	1130	8	1	       	     	8 9 8	8		
2:2:2	1135	1	8 8 9	8 8 8 8		8 8 1	     		1 1 1
[La(2:2:1)] (NO <sub>3</sub> ) <sub>3</sub>	1080	1355	830	1310	1490	815	735		1745 1775
[La(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	1070	1360	830	1310	1490	815	745		1745 1770
[Ce(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	1070	1380	830	1310	1500 <sup>b</sup>	810	735		1740 1770
[Ce(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	1070	1380	830	1305	1500 <sup>b</sup>	815	735	1 1 1	
 [Pr(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	1065	1380	830	1310	1500 <sup>b</sup>	810	740	9 1 1 1	1745 1775
[Pr(2:2:2)](NO <sub>3</sub> ) <sub>3</sub>	1080	1380	830	1310	1500 <sup>b</sup>	820	735		

<sup>.</sup> a) all frequencies in cm<sup>-</sup>
b) shoulder

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Compound	-CH <sub>2</sub> -O-CH <sub>2</sub> ether stretch	$v_{3 n 0}$	<b>ν</b> <sub>2</sub> NO <sub>3</sub> D <sub>3h</sub>	$m{ u}_1^{ m NO_3}_{ m C_2v}$	<b>у</b> ио <sub>3</sub> с2v	ν <sub>6 NO3</sub> C2v	$\nu_{3 NO_{3}}$	c104 <sup>-</sup>	NO <sub>3</sub> comb band
[Nd(2:2:1)] (NO <sub>3</sub> ) <sub>3</sub>	1070	1365	830	1315	1505	815	740		1750 1780
[La (2:2:1) ]Cl <sub>3</sub>	1065			8	8 8 8 8				
[Pr(2:2:1)]Cl <sub>3</sub>	1070	( 6 8 8	8 6 8			1     	1 1 1 1	8 8 8	L 1 1
[Nd(2:2:2)]C1 <sub>3</sub>	1070		     	     		     		1     	
[La(2:2:1)](Cl0 <sub>4</sub> ) <sub>3</sub>	1075	1 1 1	8 8 8	1 1 1	1 1 1			620	
[Pr(2:2:1)](Cl0 <sub>4</sub> ) <sub>3</sub>	1080	5 9 9 1	     	1 6 1 1	1 1 1 1	1 1 1 1		620	     
	1								

a) all frequencies in cm<sup>-1</sup>. b) shoulder

Ln <sup>3+</sup>	Anion	Ln	(aq)	[Ln (2:	2:1)]	[Ln (2:	2:2)]	Ln''(aq)	literature
		۲a	<b>و</b> له	۲	J	~	Y	<b>۲</b>	Ł
Pr	NO	444	10.2	446	10.1	444	10.1	444.2	10.31
	, T	467	3.6	470	3.6	469	3.7	466.0	1
		480	2.8	478	2.1	477	2.4	481.4	8
		588*	2.0	(588 (598	(1.1 (1.4	(587 (594	(1.1 (1.3	588.0	
pn	c1 <sup>-</sup>			(573	(3.7	(572	(3.7		
		575*	7.2	(578	(4.7	(578	(4.7	575.5	6.93
				(584	4.4	(586	(4.3		
				(737	(4.2	(737	(4.4		
		739*	6.9	(743	(4.7	(743	(4.7	739.5	7.03
				(748	(3.9	(748	(4.0		
Sт	c1 <sup>-</sup>	401	3.2	402	4.0	401	3.1	401.5	3.31
Бu	c1 <sup>-</sup>	393	3.2	393	3.1	392	3.2	394.2	3.06

Selected visible absorptions in lanthanide ions and cryptates Table 14.

have found some application in chemical lasers,<sup>60</sup> and their emission properties have been thoroughly investigated. 132-135 The fluorescence spectrum of [Eu(2:2:1]Cl<sub>3</sub> was found to be essentially unchanged from that of the free metal ion in metal solution. (Table 15) However, the benzo cryptates, whose lanthanide complexes are currently under investigation, 4 may prove more interesting in this respect. It has been shown 132 that the Eu<sup>3+</sup> ion would be capable of exhibiting laser action if one of its absorption bands were strong enough to allow the ion to be excited at a rate sufficient to achieve the necessary degree of inversion. While  $Eu^{3+}$  cannot meet this requirement in conventional crystal hosts, chelation of the ion with a ligand possessing an intense absorption band (e.g., benzoylacetonate) provides a pathway by which inversion may be achieved. The absorption band of the ligand is used as a pump band from which the energy absorbed can be transferred intramolecularly to produce a population inversion. The aliphatic cryptands provide no appropriate pathway, but the benzo cryptands might. The interested reader is referred to the excellent treatments of this phenomenon found in the literature. 132-135

It should be noted here that the samples used to record the fluorescence spectra of these compounds must be exceptionally clean and pure. If even small amounts of impurities are suspended in solution, the intensities of

	$\lambda^{ extsf{a}}$	intensity <sup>b</sup>	$\lambda$ lit <sup>135</sup>	
EuCl <sub>3</sub>	594 616 698	100 46 40	594 619 698	
[Eu(2:2:1)]Cl <sub>3</sub>	594 616 686	98 46 38	 	

Table 15. Fluorescence bands of  $Eu^{3+}(aq)$  and  $[Eu(2:2:1)]^{3+}$  in  $D_2O$ 

a) wavelength in nm b) intensity in arbitrary units

the observed bands may be altered and new bands due to scattering may appear. Fluorescence experiments are, in general, sensitive to these effects, but the tendency of any uncoordinated lanthanide ion to form a colloidal suspension of its hydroxide is an additional complication with these compounds.

## 4. Cyclic Voltammetry

The remarkable electrochemical behavior of the europium 2:2:1 and 2:2:2 cryptates has already been reported,<sup>3</sup> and was repeated here only for the sake of completeness. Table 16 shows that the measured values of the mean potential between the anodic and cathodic peaks, which may be approximately identified with the formal potential,  $E_{f}$ , are in good agreement with the literature values. In addition, the potential for the  $[Yb(2:2:1)]^{3+}$ [Yb(2:2:1)]<sup>2+</sup> couple, which has not been reported but has been previously measured, <sup>126</sup> is included. Attempts to obtain cyclic voltammograms for the [Yb(2:2:2)]<sup>3+</sup>,  $[Sm(2:2:2)]^{3+}$ , and  $[Sm(2:2:1)]^{3+}$  species were unsuccessful. These six species, along with the analogous  $Ce^{3+}$  compounds, are the only lanthanide cryptates with potential electrochemical interest. This is unfortunate, since cyclic voltammetric measurements have proven to be an extremely powerful technique in the study of these compounds.<sup>3</sup> Complete electrochemical studies of these complexes are being carried out in the laboratory that initiated the

ion	<sup>E</sup> experimental	<sup>E</sup> lit	
Eu <sup>3+</sup> (aq)	- 645 mv	- 625 mv <sup>3,a</sup>	
[Eu(2:2:1)] <sup>3+</sup>	- 425 mv	- 435 mv <sup>3,a</sup>	
[Eu(2:2:2)] <sup>3+</sup>	- 225 mv	- 225 mv <sup>3,a</sup>	
Yb <sup>3+</sup> (aq)	-1450 mv	-1445 mv <sup>126,b</sup>	
[Yb(2:2:1)] <sup>3+</sup>	-1081 mv		
a) at 25°	۵		

Table 16. Reduction potentials of some  $\text{Ln}^{3+}/\text{Ln}^{2+}$  couples in 0.5 <u>M</u> NaClO<sub>4</sub> at 20°

b) at 25° in 1  $\underline{M}$  NaClO<sub>4</sub>

investigation<sup>126</sup> using, in part, compounds prepared in the course of this research.

The discussion of the stability of complexes between the 2:2:2 ligand and the post-Sm lanthanides in section III.B.4 should be recalled here. Attempts to obtain an nmr spectrum characteristic of  $Eu^{3+}$  fully encryptated by the 2:2:2 ligand have been unsuccessful, yet it is difficult to explain how the observed electrochemical data comes about if it is not due to the  $[Eu(2:2:2)]^{3+}$  species. An intensive effort is underway to resolve this apparent conflict. As will be seen, the electrochemical and nmr data for the  $[Eu(2:2:1)]^{3+}$  and  $[Yb(2:2:1)]^{3+}$  species are complementary.

## 5. Fluoride Titrations

The ability of  $[Eu(2:2:1)]^{3+}$  to complex small ions has been previously reported. Stability constants for the following equilibria were measured by a combination of electrochemical data and titration data obtained by using a fluoride ion selective electrode:<sup>3</sup>

$$[Eu(2:2:1)]^{3+} + F^{-} \stackrel{K_1}{\rightleftharpoons} [Eu(2:2:1)F]^{2+}$$
[1]

$$[Eu(2:2:1)F]^{2+} + F^{-} \stackrel{K_{2}}{\rightleftharpoons} [Eu(2:2:1)F_{2}]^{+}$$
 [2]

Cumulative stability constants were found to be 3 x  $10^4 M^{-1}$  (K<sub>1</sub>) and 3 x  $10^6 M^{-2}$  (K<sub>1</sub>K<sub>2</sub>) at an ionic strength of 0.5.

These data have been satisfactorily reproduced using only the fluoride titration data by the methods previously employed by Aziz and Lyle<sup>137</sup> to determine similar stability constants for the association of aquated  $Eu^{3+}$  and  $Gd^{3+}$  with fluoride. These methods were then applied to determine  $K_1$  and  $K_2$  for a number of the analytically pure [Ln(2:2:1)] $X_3$  systems reported in section III.B.1, as listed in Table 18.

Figure 9 shows a typical calibration curve for the fluoride electrode. A temperature of  $20^{\pm}1^{\circ}$  was maintained throughout all titrations, and a uniform ionic strength was provided by the addition of  $0.50 \ M \ NaClO_4$  to all solutions. The electrode was found to have excellent linearity of response when  $-\log[F]$  was plotted as a function of the potential measured versus a Saturated Calomel Electrode. As can be seen from Figure 9, the response of the electrode varied only slightly over the course of a six hour day.

Figure 10 shows a typical titration curve obtained by titrating 10 ml of 1.06 mM La(2:2:1)]<sup>3+</sup> in 0.50 <u>M</u>  $NaClO_4$ with 15 ml of 2 mM NaF followed by 15 ml of 20 mM NaF (the titrants were also 0.50 <u>M</u> in  $NaClO_4$ ). The complexes formed are too weak to produce clear breaks in the titration curve under these conditions, but the stability constants may be extracted by the graphical method of Rossotti and Rossotti.<sup>125</sup> A complete derivation may be



Figure 9. Calibration curve for fluoride selective ion electrode





found in the literature<sup>125</sup> which shows that a plot of  $\bar{n}/(1-\bar{n})$  [F] versus  $(2-\bar{n})$  [F]/ $(1-\bar{n})$ , will produce a straight line with intercept K<sub>1</sub> and slope K<sub>1</sub>K<sub>2</sub> as [F] $\rightarrow 0$ .  $\bar{n}$  is the "degree of formation of the system" or the "ligand number" and may be defined as the average number of ligands combining with each cryptate ion. Thus,  $\bar{n} = (C_F - [F])/C_C$  where  $C_F$  and  $C_C$  are the total analytical concentrations of fluoride and cryptate (or  $Ln^{3+}(aq)$ ), respectively.

Such a plot is shown in Figure 11 for the  $[La(2:2:1)]^{3+}$ system already described. The slope is 7.5 x 10<sup>6</sup> and the intercept is 1.0 x 10<sup>4</sup>. Hence,  $K_1 = 1.0 \times 10^4 \text{ M}^{-1}$  and  $K_1K_2 = 7.5 \times 10^6 \text{ M}^{-2}$ . Similar treatment of data for the  $[Eu(2:2:1)]^{3+}$  system yield cumulative stability constants of 3.8 x 10<sup>4</sup> M<sup>-1</sup> and 4.1 x 10<sup>6</sup> M<sup>-2</sup>.

These two compounds effectively bracket the list of analytically pure  $[Ln(2:2:1)]^{3+}$  complexes available (Ln, Ce, Pr, Nd, Sm, Eu, Gd, and Dy), and the stability constants obtained can be used to produce approximate fraction of species profiles for the  $[Ln(2:2:1)]^{3+}$  fluoride system. These in turn may be used to determine the fluoride concentration range over which only equilibrium [1] or equilibrium [2] is occuring to an appreciable extent. At low fluoride concentrations  $K_1$  can be calculated directly from the measured fluoride concentration. When the fluoride concentration has been increased to a point where essentially all of the cryptate in solution



Figure 11. Rossotti and Rossotti plot for titration of [La(2:2:2)]<sup>3+</sup> with fluoride ion

has associated with at least one fluoride ion  $(\underline{i.e.}, [Eu(2:2:1)]^{3+}/C_c < 0.01)$ , then  $K_2$  can be calculated directly. The validity of the calculations can be checked by simply examining the values of  $K_1$  or  $K_2$  obtained within the calculated concentration range to see if they remain constant. This method of obtaining  $K_1$  and  $K_2$  was also used and typical results are shown in Table 17. The values are indeed constant within experimental error. Potentials could only be read to within  $\pm 1$  mv, which produces a larger variation in  $K_2$  than in  $K_1$ .

One or both of these methods was applied to calculate  $K_1$  and  $K_2$  for each of the available analytically pure 2:2:1 complexes as well as for aquated  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Dy^{3+}$ ,  $Yb^{3+}$ , and  $Lu^{3+}$ . The results are summarized in Table 18 along with some available literature values.

There is no obvious trend in the values of the stability constants obtained. However, analytically pure compounds were available only for the first two-thirds of the lanthanide series. An intensive effort is underway to prepare analytically pure 2:2:1 complexes of the heavier members of the series to determine whether or not a "gadolinium break" occurs in the number of fluorides which will coordinate to the complexes or in the strength of the complexes formed.

It is interesting to note that the cryptate complex coordinates fluoride ion more strongly than does the

[F]	к <sub>1</sub> м <sup>-1</sup>	[F]	к <sub>2</sub> м <sup>-2</sup>
$1.06 \times 10^{-5}$ $1.87 \times 10^{-5}$ $2.98 \times 10^{-5}$ $4.14 \times 10^{-5}$ $5.75 \times 10^{-5}$ $7.26 \times 10^{-5}$ $9.18 \times 10^{-5}$ $1.11 \times 10^{-4}$ $1.40 \times 10^{-4}$	$0.9 \times 10^{4} \\ 1.1 \times 10^{4} \\ 1.1 \times 10^{4} \\ 1.2 \times 10^{4} \\ 1.2 \times 10^{4} \\ 1.3 \times 10^{4} \\ 1.3 \times 10^{4} \\ 1.4 $	$1.00 \times 10^{-3}$ $1.53 \times 10^{-3}$ $2.02 \times 10^{-3}$ $2.43 \times 10^{-3}$ $2.94 \times 10^{-3}$ $3.38 \times 10^{-3}$ $3.89 \times 10^{-3}$ $4.27 \times 10^{-3}$ $4.69 \times 10^{-3}$	$4.7 \times 10^{2}$ $4.4 \times 10^{2}$ $4.5 \times 10^{2}$ $7.3 \times 10^{2}$ $5.5 \times 10^{2}$ $5.5 \times 10^{2}$ $2.8 \times 10^{2}$ $3.2 \times 10^{2}$ $3.4 \times 10^{2}$
average	$\frac{1.1 \times 10^{-4}}{1.2 \times 10^{4}}$	average	$4.4 \times 10^2$

.

Table 17. Calculation of  $K_1$  and  $K_2$  for [La(2:2:1)]<sup>3+</sup>

Table 18. Stability constants for the coordination of one and two moles of fluoride ion to various  $[Ln(2:2:1)]^{3+}$  and  $Ln^{3+}(aq)$  species

ion	к <sub>1</sub> (м <sup>-1</sup> )	к <sub>2</sub> (м <sup>-2</sup> )	κ <sub>1</sub> κ <sub>2</sub> (м <sup>-3</sup> )	method <sup>a</sup>
(1 - (2 - 2 - 1) - 3+	$1.0 \times 10^4$	$7.2 \times 10^2$	$7.5 \times 10^6$	A
[La(2:2:1)]	$1.2 \times 10^4$	$4.4 \times 10^2$	5.3 x 10 <sup>6</sup>	В
3+	$4.4 \times 10^4$	5.1 x $10^2$	$2.3 \times 10^{7}$	A
[Ce(2:2:1)]	$4.3 \times 10^4$	4.7 x $10^2$	2.0 x $10^7$	В
2.1	$6.3 \times 10^4$	$1.9 \times 10^2$	$1.2 \times 10^{7}$	A
[Pr(2:2:1)] <sup>3+</sup>	5.6 $\times$ 10 <sup>4</sup>	$2.0 \times 10^2$	$1.1 \times 10^{7}$	В
2.	2.9 x $10^4$	$1.1 \times 10^{3}$	$3.1 \times 10^7$	A
[Nd(2:2:1)] <sup>3+</sup>	$3.2 \times 10^4$	7.4 x $10^2$	$2.4 \times 10^7$	В
2.	$1.6 \times 10^4$	$1.2 \times 10^2$	$1.9 \times 10^{6}$	А
[Sm(2:2:1)] <sup>3+</sup>	$1.6 \times 10^4$	2.1 x $10^2$	3.4 x $10^{6}$	В
- b	$3.8 \times 10^4$	$1.1 \times 10^2$	$4.1 \times 10^{6}$	А
[Eu(2:2:1)] <sup>3+-</sup>	$3.8 \times 10^4$	$1.4 \times 10^2$	$5.3 \times 10^6$	B
	$1.3 \times 10^4$	$2.6 \times 10^2$	$3.3 \times 10^{6}$	Δ
[Gd(2:2:1)] <sup>3+</sup>	$1.3 \times 10^4$	$2.2 \times 10^2$	$2.9 \times 10^{6}$	В
	3 0 v 10 <sup>4</sup>	$29 \times 10^{2}$	9 0 v 10 <sup>6</sup>	λ
[Dy(2:2:1)] <sup>3+</sup>	$3.2 \times 10^4$	2.7 X IU	9.0 X 10	R
	J. Z A IV			

a) method of calculation: A = graphical method; B = direct calculation b) literature values:  $K_1 = 3 \times 10^4$ ;  $K_1K_2 = 3 \times 10^6$  (ref. 3) c) literature values:  $K_1 = 2.5 \times 10^3$ ;  $K_1K_2 = 3.0 \times 10^6$ ) ref. d) literature values:  $K_1 = 2.5 \times 10^3$ ;  $K_1K_2 = 4.0 \times 10^6$ ) 137

10 <sup>3</sup> 10 <sup>3</sup>	$2.8 \times 10^2$	7.0 x 10 <sup>5</sup>	A
10 <sup>3</sup>			
2			В
103	$1.5 \times 10^3$	$3.3 \times 10^{6}$	А
10 <sup>3</sup>			В
10 <sup>3</sup>	$3.6 \times 10^2$	$1.0 \times 10^{6}$	A
10 <sup>3</sup>			В
10 <sup>3</sup>	$2.5 \times 10^2$	7.6 x 10 <sup>5</sup>	А
10 <sup>3</sup>			В
10 <sup>3</sup>	$0.7 \times 10^2$	$2.2 \times 10^5$	A
10 <sup>3</sup>			В
	$   \begin{array}{c}     10^{3} \\     10^{3} \\     10^{3} \\     10^{3} \\     10^{3} \\     10^{3} \\     10^{3} \\     10^{3} \\   \end{array} $	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

D)	IILEIALUIE	varues:	<u></u>	- J X	тı	J ; K	1^2 -	2	XI	U	(Ter	L. 3)
c)	literature	values:	K <sub>1</sub> =	= 2.5	x	10 <sup>3</sup> ;	<sup>K</sup> 1 <sup>K</sup> 2	=	3.0	x	106)	ref.
d)	literature	values:	к <sub>1</sub> =	= 2.5	x	10 <sup>3</sup> ;	<sup>K</sup> 1 <sup>K</sup> 2	=	4.0	x	10 <sup>6</sup> )	137

aquated metal ion. Several explanations may be offered to account for this observation.<sup>140</sup> The presence of a bulky organic ligand around a metal ion may cause a decrease in the local dielectric constant compared to that of the bulk solvent. This would tend to increase the strength of ion-ion interactions between the cation and an ion that have approached within some critical distance. Further, it would increase the strength of these ion-ion interactions more than the ion-dipole interactions between the solvent (water) and the metal ions. This would allow the anion to compete more effectively for the coordination sphere of the anion by increasing the net amount of energy gained in a desolvation-ion coordination reaction.

If, as has been suggested<sup>3</sup>, the anion reaches the metal ion by moving between the strands of the cryptate, the smaller fluoride ion may have an advantage over the larger water molecules in competing for these coordination sites. In the aquated ion such steric effects would be less important.

Each of these hypotheses are presented only as points for discussion, and no attempts have been made to experimentally confirm or reject them.

6. Nuclear Magnetic Resonance Studies

Historically, nuclear magnetic resonance has played a key role in the study of cryptate complexes. For example, proton magnetic resonance was used very early to follow the encryptation process in solution.<sup>93</sup> Later, alkali metal nmr was found to be a powerful technique to differentiate inclusion and exclusion complexes, follow exchange rates, and determine other physical properties of cryptates.<sup>100,104-107</sup> High field proton nmr analysis has been used to study the structure of crown complexes<sup>78</sup> and cryptands.<sup>91-96</sup> High resolution spectra of each of the alkali metal and alkaline earth cryptands have been obtained, and are recorded in the literature.<sup>156</sup>

While the lanthanides are poorly suited for direct observation in nmr experiments, the large chemical shifts they induce on proton spectra have been used to determine both quantitative and qualitative information on molecular geometries, as discussed in section I.A.2. As might be expected from these earlier results, nuclear magnetic resonance has been of great utility in the study of lanthanide cryptates.

a.) The diamagnetic 2:2:1 complexes.

1) Lanthanum: In order to fully interpret the nmr spectra of paramagnetic lanthanide complexes, it is

often useful to understand the spectra of the corresponding diamagnetic La and Lu complexes. The labeling scheme shown in Figure 12 and the spectrum of  $[La(2:2:1)](NO_3)_3$  in acetonitrile solution (Figure 13) will be frequently referred to in the following discussion.

While the crystal structures of the 2:2:1 cryptates reported to date (Na, K, and Co)<sup>110,139</sup> show that the ligand does not adopt a rigorously symmetrical conformation, there are two approximate planes of symmetry that may be drawn through the molecule. One is shown as a dashed line in Figure 12, and the other bisects the 2:2 ring of the bicycle, passing through the two bridgehead nitrogen atoms. For convenience in discussing the various sections of the 2:2:1 ligand, the -CH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub>- residues will be referred to as "2-strands" while the -CH<sub>2</sub>CH<sub>2</sub>-OCH<sub>2</sub>CH<sub>2</sub>- residue will be called the "1-strand". In Figure 12, one 2-strand has been removed for clarity, and eight non-equivalent types of protons have been labeled  $(H_A, H_M, H_X, H_Y, H_E, H_F, H_K,$ and  $H_{\tau}$ ). Consideration of the symmetry of the molecule will show that, to a good approximation, there are four protons of each type, thus accounting for all 32 protons on the ligand.

A glance at Figure 13 shows that the nmr spectrum of  $[La(2:2:1)](NO_3)_3$  in acetonitrile contains extensive spin-spin coupling. Considerable theoretical  $^{138,141-146}$  and



Figure 12. Labeling scheme for protons in the 2:2:1 cryptand



Figure 13. Spin-spin coupling in the nmr spectrum of  $[La(2:2:1)](NO_3)_3$  in acetonitrile solution

experimental<sup>147-152</sup> work has been done to understand the origin of spin-spin coupling and, especially for proton nmr spectra, to make use of spin-spin coupling patterns to determine molecular structure in solution.<sup>147-152</sup> Very useful reviews of the theory and application of geminal,<sup>144</sup> vicinal,<sup>144</sup> and long range proton-proton coupling<sup>154</sup> are available and may be consulted by those wishing a deeper insight into the subject. Only a few of the more important results that relate directly to the spectrum under consideration will be mentioned here.

In general, it is found that the sign and magnitude of the coupling constants between two nuclei depend not only on the number of intervening bonds, but on molecular structure and geometry as well.<sup>145</sup> Geminal coupling constants (i.e., those between two protons on the same carbon atom) are found to vary over a large range, typically from 1 to 15 Hz.<sup>145</sup> Vicinal coupling constants (i.e., those between protons on adjacent carbon atoms) vary over a smaller range (ca. 0 to 10 Hz), but both types of coupling may be strongly influenced by substituent effects.<sup>145</sup> Karplus <sup>138,153</sup> used valence bond calculations to predict that vicinal coupling of protons on adjacent sp<sup>3</sup> carbon atoms should depend on the dihedral angle between the protons as shown in Figure 14. The observed couplings are generally larger than those predicted from Karplus' equations, but the general trends in the





Figure 14. The Karplus function describing the magnitude of vicinal proton-proton J coupling as a function of dihedral angle  $\emptyset$  in the H-C-C-H bond system

magnitude of vicinal coupling constants are satisfactorily predicted by this treatment.

When the size of the coupling constant between two protons is comparable to the chemical shift difference between them, complex spectra often result with no obvious regularities in spacing or intensity.<sup>155</sup> Such spectra may be analyzed by using quantum mechanical methods to compute the energy levels and stationary-state wave functions of a system of coupled spins in a static magnetic field, and then using perturbation methods and selection rules to give the probabilities of transitions occuring between these levels when a resonant rf field is applied. The line positions will be functions of the energy level separations, and their relative intensities will correspond to the transition probabilities.<sup>145,146,155</sup>

Fortunately, such arduous techniques are not necessary each time a so-called "strong coupled" (<u>i.e.</u>,  $J \approx \Delta \lambda$ ) system is encountered. These calculations have been carried out for a number of spin systems of common occurrence in organic compounds, and the results compiled in tables,<sup>145</sup> similar to the familiar infrared and chemical shift correlation tables now in routine use.

The nomenclature suggested by Pople, Schneider, and Bernstein<sup>155</sup> has been almost universally adopted for systems of nuclear spins within molecules. Briefly, nonequivalent protons which have chemical shift differences

comparable to their mutual couplings are designated A, B, C,..., etc. A second group of protons or other nuclei separated from the first group by large chemical shifts, but which among themselves are separated by chemical shifts comparable to their spin-spin couplings are designated X, Y, Z, ... etc. If a third group of protons having intermediate chemical shifts are present, they would be denoted by K, L, M, ... etc. Finally, two protons which are equivalent by symmetry, but are magnetically nonequivalent, are distinguished by the use of primes. For example, in l,l-difluoroethylene,



 $H_1$  and  $H_2$  are symmetrically equivalent, but magnetically nonequivalent, and so are designated  $H_A$  and  $H_A$ . The entire molecule is, then an AA'XX' system. A complete discussion of this system of nomenclature may be found in the literature.<sup>155</sup>

In the  $[La(2:2:1)](NO_3)_3$  complex, the geminal methylene protons  $(H_A \text{ and } H_M) \ll$  to the coordinated nitrogens on the 2-strands of the ligand give rise to an AM pattern which is further split by vicinal coupling to an adjacent  $\beta$ -CH<sub>2</sub> group shown as protons  $H_X$  and  $H_Y$ . Observation of a simple AMXY pattern for all four of the -N-CH<sub>2</sub>CH<sub>2</sub>-O 2-strand fragments of the molecule implies either that both 2-strands have the same rigid conformation, or that only one such conformation is highly favored thermodynamically but rapid conformational motion still occurs. If the molecule were rigid, but each 2-strand had a different conformation, then the protons of each strand would have different chemical shifts and spin-spin couplings, and the complexity of the spectrum would be correspondingly increased.<sup>155</sup> If the molecule were undergoing rapid conformational motion among a number of conformations that were more or less equally favored thermodynamically, then the observed spectrum would be characteristic of a weighted average of each of these conformations, rather than that of a single, highly favored configuration.<sup>147-152</sup>

The vicinal coupling patterns of the AM protons are consistent with a ligand conformation in which the equitorial  $\ll -H_A$  protons are coupled to the axial  $\ll -H_M$  proton  $(J_{AM} = 13.5)$ , and further coupled equivalently to the two  $\beta$ -CH<sub>2</sub> protons  $(J_{AX} = J_{AY} = 3.55)$  as diagrammed in Figure 13. Similarly, the  $\ll -H_M$  proton is split by the  $\ll -H_A$   $(J_{AM} = 13.5)$ , but differently by the  $\beta$ -CH<sub>2</sub> protons  $(J_{MX} = 9.45; J_{MY} = 6.15)$  due to dihedral angle differences as expected from Karplus' equations.<sup>138</sup> The final triplet in the N-CH<sub>2</sub> region pictured in Figure 13 is due to the  $\ll -CH_2$  of the 1-strand coupling to the equivalent  $\beta$ -CH<sub>2</sub> protons of the 1-strand  $(J_{KL} = 5.25)$ . The O-CH<sub>2</sub> region is complicated by more extensive overlap than the N-CH<sub>2</sub> region, but the A and B branches of an AA'BB' pattern<sup>145</sup> due to protons H<sub>E</sub>, H<sub>F</sub>, H<sub>E</sub>, and H<sub>F</sub>,  $(J_{EF} = 36.5 \text{ Hz})$  may be seen on either side of a complex pattern which is made up of the triplet due to the  $\beta$ -CH<sub>2</sub> protons of the 1-strand  $(J_{KL} = 5.25 \text{ Hz})$  and the multiplet from the  $\beta$ -CH<sub>2</sub> protons of the 2-strands.

This analysis of the  $[La(2:2:1)](NO_3)_3$  spectrum was verified by decoupling experiments. For example, Figure 15 shows the result of decoupling the  $\beta$ -CH<sub>2</sub> protons of the molecule on the  $\alpha$ -CH<sub>2</sub> region of the spectrum. The signal from the  $\alpha$ -CH<sub>2</sub> protons of the 1-strand becomes a singlet, which is flanked by two doublets due to protons H<sub>A</sub> and H<sub>M</sub> and their mutual coupling. Similarly, the  $\alpha$ -CH<sub>2</sub> protons (H<sub>K</sub>) of the 1-strand may be decoupled, causing the triplet from the  $\beta$ -CH<sub>2</sub> protons (H<sub>L</sub>) in the O-CH<sub>2</sub> region to become a singlet.

Figure 16 compares the nmr spectra of the  $[La(2:2:1)]^{3+}$  nitrate, perchlorate and chloride salts in acetonitrile. Differences are obvious, but the same basic coupling pattern in maintained despite variations in coupling constants and chemical shifts. This is probably due to anion chelation, ion pairing, or other weak cryptate-anion interactions in acetonitrile solution. Figure 17 shows that the three compounds produce identical spectra in D<sub>2</sub>O where the anions are more tightly solvated.



Figure 15. Effect of decoupling protons  $H_X$ ,  $H_Y$ , and  $H_K$  on the nmr spectrum of protons  $H_A$ ,  $H_M$ , and  $H_L$  in [La(2:2:1)](NO<sub>3</sub>)<sub>3</sub> in acetonitrile solution



Figure 16. Nmr spectra of  $[Ln(2:2:1)]X_3$ in acetonitrile solution (TMS reference) a)  $X=NO_3^-$ , b)  $X=C1^-$ , c)  $X=C1O_4^-$


Figure 17. Nmr spectra of  $[La(2:2:1)]X_3$  in  $D_2O$ solution (t-BuOD reference) a)  $X=NO_3^-$ , b)  $X=C1^-$ , c)  $X=C1O_4^-$ 

The effect of anions in solution with the cryptate is clearly demonstrated in Figure 18, which compares the nmr spectrum of pure  $[La(2:2:1)](NO_3)_3$  in  $D_2O$ , with the spectrum obtained when a 2:1  $F^-:[La(2:2:1)]^{3+}$  excess of NaF is added to the solution. These results further establish the unusual ability of lanthanide cryptates to coordinate small anions. Note the changes in the chemical shifts that occur upon coordination of the fluoride ion and the appearance of several small new signals. These might be due to a second, as yet unidentified conformation of the molecule.

The temperature dependence of the spectra of the [La(2:2:1)]<sup>3+</sup> chloride and nitrate salts in acetonitrile was studied from -70 to +60°. No changes were observed in the spectrum of the nitrate compound. In the spectrum of the chloride the group of triplets near 2.8 ppm separated slightly as the temperature was raised until at 35°, three overlapping triplets were visible, centered at 2.71 (J = 10.3 Hz), 2.79 (J = 4.1 Hz), and 2.80 ppm (J = 5.3 Hz).These triplets tended to overlap more extensively as the temperature was lowered, until at -15° a small triplet separated from the downfield side of this pattern. This new triplet shifted about 0.3 ppm further downfield as the temperature was lowered to -70°. These small but significant changes indicate that the conformation of the ligand is changing and that contributions from a second



Figure 18. The effect of coordinate fluoride ion on the nmr spectrum of  $[La(2:2:1)](NO_3)_3$  (D<sub>2</sub>O solution, t-BuOD reference)

conformation may be significant at lower temperatures.

2) Lutetium: The difficulty in preparing samples of the heavier lanthanides free of uncoordinated metal salt has been discussed (section III.B.2). However, it was found that the addition of equimolar amounts of Ln(III) salts to solutions of pure (Ln(2:2:1)]X<sub>2</sub> or lanthanide cryptate/lanthanide salt mixtures in either  $D_2O$  or acetonitrile did not affect the nmr spectrum obtained. On the basis of these results, it was concluded that nmr spectra of the heavy lanthanide 2:2:1 cryptates that contained some excess metal salt, could be accepted, to a high degree of approximation, as the spectra that would be obtained in the absence of the free salt. This conclusion was found to be entirely justified when the purified [Dy(2:2:1)]<sup>3+</sup> species became available, and its spectrum was found to be identical to that obtained using the material before purification. These results are reasonable, since it is unlikely that a tripositive lanthanide ion would approach the tripositive complex very closely, and any anion effects would be very small compared to the large paramagnetic effect of the metal ion in the complex.

Efforts to obtain a high resolution spectrum of the [Lu(2:2:1)]<sup>3+</sup> species in acetonitrile solution were hampered by the very low solubility of the complex. The spectrum of the Lu complex shown in Figure 19 was



obtained by time-averaging a saturated solution of  $[Lu(2:2:1)](NO_3)_3$  in acetonitrile while supressing the solvent peak to maximize the signal-to-noise ration and resolution. Unfortunately, signals from trace impurities in the solvent and spurious peaks from noise in the electronics of the instrument tend to obscure the signals from the complex. The O-CH, region in the Lu complex is fairly well resolved and has been shifted slightly downfield from its position in the La complex as can be seen by comparing the two spectra in Figure 19. What appears to be the triplet from the  $\beta$ -CH<sub>2</sub> protons of the 1-strand has separated to the downfield side of the pattern. The N-CH<sub>2</sub> region is too obscured for accurate analysis. Comparison of the  $[Lu(2:2:1)]^{3+}$  and  $[La(2:2:1)]^{3+}$  spectra in acetonitrile is further complicated by unknown differences in the effect of the counter ion on each species.

The anion and solubility difficulties are removed in  $D_2O$  solution, but only at the expense of much of the fine structure that proved so useful in acetonitrile. Figure 20 compares the spectra of  $[Lu(2:2:1)](NO_3)_3$  and  $[La(2:2:1)](NO_3)_3$  in this solvent. In the Lu species, the three triplets from  $H_K$  and  $H_A$  (see Figure 13) have shifted very close together, and the splitting of the  $H_M$  multiplet is unresolved. The O-CH<sub>2</sub> region shows much less fine structure in both spectra, but in the  $[Lu(2:2:1)]^{3+}$  a clear triplet (probably due to  $H_L$ ) is seen on the





downfield side of this region. As was the case with  $[La(2:2:1)]^{3+}$ , the nmr spectrum of  $[Lu(2:2:1)]^{3+}$  in  $D_2^{0}$  is independent of the anion.

On the basis of these spectra, it appears that conformational differences between the  $[La(2:2:1)]^{3+}$  and  $[Lu(2:2:1)]^{3+}$  species are slight, since the spin-spin coupling patterns and chemical shifts observed in the nmr spectra of each are similar. However, the large isotropic shifts induced by the paramagnetic lanthanides are also a powerful probe for changes in the geometry of lanthanide complexes. These effects are considered in the following section.

## b.) The paramagnetic 2:2:1 complexes.

From symmetry considerations and the analysis of the nmr spectrum of  $[La(2:2:1)](NO_3)_3$  already discussed, it can be seen that the  $[La(2:2:1)](NO_3)_3$  complex contains 8 nonequivalent types of protons, and four protons of each type. Thus, if the complexes of the paramagnetic lanthanides also exhibit a rigid or highly favored conformation similar to that of the lanthanum complex, their nmr spectra should show 8 broad lines of equal intensity. Figure 21 shows that this is indeed the case, as exemplified by the spectra of  $[Pr(2:2:1)]^{3+}$  and  $[Er(2:2:1)]^{3+}$  in  $D_2O$ . Several features characteristic of the spectra of the paramagnetic 2:2:1 complexes may be illustrated by the two examples given. First, the induced paramagnetic shifts



Figure 21. Nmr spectra of a)  $[Pr(2:2:1)](IIO_3)_3$  and b)  $[Er(2:2:1)](NO_3)_3$  in  $D_2O$  solution (t-BuOD reference)

are large. The [Pr(2:2:1)]<sup>3+</sup> spectrum ranges over ~30 ppm, while that of  $[Er(2:2:1)]^{3+}$  is spread over nearly 200 ppm. Examination of Table 1 and/or Figure 3 shows that the sign of the shifts induced by Pr is the opposite of that produced by Er. Hence, the 8 line pattern of the Pr spectrum is the "mirror image" of the pattern of the Er spectrum. Note that the spectrum of  $[Pr(2:2:1)]^{3+}$  has a group of three signals on the left (downfield) side of the spectrum, a group of three signals toward the middle, and a pair of signals on the left. This pattern is exactly reversed in the [Er(2:2:1)]<sup>3+</sup> spectrum. An examination of the complete chemical shift data for each of the lanthanides (tabulated in the Appendix), shows that the Ce, Nd, Sm, Tb, Dy, and Ho 2:2:1 cryptates all display the pattern shown in the  $[Pr(2:2:1)]^{3+}$  spectrum, while the Eu and Yb 2:2:1 complexes produce the "mirror image" pattern seen in the  $[Er(2:2:1)]^{3+}$  spectrum.

On the basis of these observations, it might be hypothesized that the most upfield signal in the  $[Pr(2:2:1)]^{3+}$ spectrum is due to the same protons as the most downfield resonance in the  $[Er(2:2:1)]^{3+}$  spectrum. The second most upfield signal from  $[Pr(2:2:1)]^{3+}$  would then correspond to the second most downfield signal from  $[Er(2:2:1)]^{3+}$ , and so on. In this way, a correspondence can be carried through the other six signals in each spectrum, thus accounting for the numbering of the signals in Figure 21. Similarly, the correspondence between these two spectra can be continued to the spectra of each of the paramagnetic lanthanide cryptates that have been obtained.

The problem now remains of testing this hypothesis, preferably by assigning each of these signals to one of the eight types of protons labeled in Figure 12. Since little or no spin-spin coupling information is retained in the spectra of the paramagnetic complexes, the methods used to interpret the [La(2:2:1)]<sup>3+</sup> spectrum can not be applied here. A second standard technique for assigning the resonances of complex spectra is selective deuteration at each position on a molecule until all the assignments have been made. This may be done for the N-CH<sub>2</sub> protons of the 1-strand by using  $LiAlD_4$  in the 2,1\* reduction described in section II.A.5, thus assigning the signal due to  $H_{\mu}$ . The use of  $BD_3$  in the reduction of 2\*, 2, 1 (section II.A.7) will reduce the intensities of two signals ( $H_{A}$  and  $H_{M}$ ) at the same time, and so is somewhat less useful without further information. Deuteration of other positions of the ligand, while perhaps possible, is unrealistic from a practical point of view. Thus, the preparation of deuterated ligands would produce minimal information for the amount of effort involved.

Fortunately, as discussed in section I.B.2, the paramagnetic shifts and line widths in the nmr spectra of lanthanide complexes are related in a well defined way to

the geometry of the molecule. Line widths are inversity proportional to the sixth power of the radial distance from the paramagnetic center to the proton  $(y_1 \propto r^{-6})$ and for an axially symmetric complex, the dependence of the isotropic shift on the geometry of the molecule is described by Equation (1):

$$\delta_i = A_i(S_z) + D(3\cos^2\Theta - 1)r_i^{-3}$$

A more general form of this equation, for non-axially symmetric complexes may be written:<sup>43</sup>

$$\delta_{i} = A_{i}(S_{z}) + DG$$
 (1b)

where G is now a complicated function of  $r_i$ ,  $\theta$ , and  $\theta_i$  in spherical polar coordinates.

In order to use these two experimentally measurable parameters (line width and chemical shift) to assign the resonances in the spectra of the paramagnetic  $[Ln(2:2:1)]^{3+}$ complexes, information on the geometry of the molecule must be available. Unfortunately, none of the crystal structures for any of the lanthanide cryptates has been obtained. However, the recently published crystal structure of the [Na(2:2:1)]SCN cryptate<sup>139</sup> might be expected to serve as a model for the lanthanide cryptates since the radius of the Na<sup>+</sup> ion is similar to that of the Lu<sup>3+</sup> ion (Table 4), and the ligand might therefore adopt similar conformations in the two complexes.

An analysis of the crystal structure of [Na(2:2:1)]SCN was carried out with the assistance of Dr. D. Ward of the Michigan State University Crystallographic Services Department. Specifically, program HFINDR (available in the MSU X-ray library file) was used to locate the protons in the molecule from the published crystal structure. The coordinates of these protons were then analyzed by the use of program DISTAN, also in the X-ray library file, to determine the radial distances from the metal ion to the various protons. The results of these calculations are presented in Table 19, along with the ratios  $(r_{H_{1}}/r_{H_{2}})^{6}$ , where  $r_{H_{\underline{i}}}$  is the distance from the sodium ion to proton  $H_{\underline{i}}$ in the 2:2:1 cryptate. From Equation (5), it may be seen that, if the geometry of the paramagnetic lanthanide cryptate is similar to that of the Na<sup>+</sup> complex, then the ratio  $(r_{H_{A}}/r_{H_{i}})^{6}$  should be approximately equal to  $\mathcal{Y}_{\frac{1}{2}}^{H_{i}}/\mathcal{Y}_{\frac{1}{2}}^{H_{A}}$ , where  $\mathcal{Y}_{\frac{1}{2}}^{H}$  will be obtained from the narrowest line in the spectrum since  $H_{\lambda}$  is the proton farthest from the metal The success of this technique is demonstrated in center. Table 20, which includes data for each of the signals whose line widths could be obtained with reasonable accuracy (i.e., the line was unobscured by overlap with another signal, and no residual spin-spin coupling was visible). All of the protons except  $H_F$  and  $H_v$ , which have very similar radial distances from the metal center, have been assigned by this analysis, and the correlation between the

Table 19. Radial Na-H<sub>i</sub> distances in the [Na(2:2:1)]SCN cryptate

нX	3.42	4.41
н Н	3.58	3.35
НY	4.28	1.15
$^{\rm H}{ m A}$	4.38	1.00
H	3.72	2.66
н <sub>К</sub>	4.04	1.62
н F	4.30	1.12
$^{\rm H}_{ m L}$	4.10	1.49
proton <sup>a</sup>	r (Å)	$\left(\frac{r_{H_{A}}}{r_{H_{i}}}\right)^{6}$

a) see Figure 12

Table 20.  $\mathcal{V}_{\frac{1}{2}}^{H_{1}}/\mathcal{V}_{\frac{1}{2}}^{H_{A}}$  ratios for various [Ln(2:2:1)]<sup>3+</sup> species<sup>c</sup>

signal number <sup>a</sup>	Ч	7	m	4	Ŋ	Q	7	œ
assignment <sup>a</sup> ,b	нL	$^{ m H_F}_{ m Y}/$	н <sub>К</sub>	Н	НA	$^{\rm H}_{\rm F}$	н Н	Х <sub>Н</sub>
theory Ce Bu Bu Dy By Br Er	1 111111 4.1.5.5 6 1.5.5 9	1.12/ 1.15 1.12 1.12 1.12	1.62 1.62 1.6 1.6 1.8 1.8	2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5	00000000000000000000000000000000000000	$\begin{array}{c}1.15\\1.12\\1.12\\1.12\\1.12\\1.12\\1.12\\1.12\\$	3.35 3.3 2.1 4 2.1 4 2.1 4 2.3 3 3.3 3 3.3 5 1.4 1.5 5 1.5 5 1.5 5 1.5 5 1.5 5 1.5 5 5 5	4 4 4 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
a) see Figure 2	1							

see Figure 12 complete line width data are tabulated in Appendix A. G Q U

signals in the various spectra has been verified.

Chemical shift data may also be used to verify this correlation. Again recalling Equation (1b), a plot of  $\delta_i$ versus D for the i<sup>th</sup> proton of a series of lanthanide complexes with a given ligand should be a straight line passing through the origin, as long as contact interactions are negligible and the geometry of the molecule remains constant. Figures 22 through 29 show these plots for the eight types of protons in the paramagnetic [Ln(2:2:1)]<sup>3+</sup> spectra. Note that the chemical shifts are measured from the position of the corresponding signal in the diamagnetic La complex (which is essentially the same as measuring from the position of the signal in the Lu complex - see Figure 20). Good linearity is obtained, except for proton 5 (H<sub>A</sub>) and for proton 6 (H<sub>F</sub> or H<sub>Y</sub>) in the Ho and Tb complexes.

Taking all of these data (the correlation between the 8 line patterns obtained for each complex, line width measurements, and chemical shifts) into consideration several conclusions may be drawn about the structure and nmr spectra of the lanthanide 2:2:1 cryptates. The linearity of the plots in Figures 22 through 29 are good evidence that the geometry of the complex remains constant as the lanthanide ion is varied. This was also indicated by the simliarity of the  $[La(2:2:1)]^{3+}$  and  $[Lu(2:2:1)]^{3+}$  spectra discussed previously. The fact that these plots (except for Figure 26) pass through the origin (within the standard deviation



Figure 22. The paramagnetic shifts of  $H_L$  (proton "1") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 23. The paramagnetic shifts of  $H_F$  or  $H_Y$ (proton "2") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 24. The paramagnetic shifts of  $H_K$  (proton "3") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 25. The paramagnetic shifts of  $H_M$  (proton "4") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled ito Dy=-100)



Figure 26. The paramagnetic shifts of  $H_A$  (proton "5") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 27. The paramagnetic shifts of  $H_Y$  or  $H_F$ (proton "6") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 28. The paramagnetic shifts of  $H_{E}$  (proton "7") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)



Figure 29. The paramagnetic shifts of  $H_X$  (proton "8") in various [Ln(2:2:1)]<sup>3+</sup> species plotted against D (all shifts scaled to Dy=-100)

of the best fit line through the data points) demonstrates that contact shifts are negligible in these compounds. This is reasonable, since the Ln-O bonds are expected to have very little covalency, and the protons are separated from these coordination sites by two more bonds. Further, the protons which are closest to the paramagnetic center (#8, H<sub>X</sub>) produce a plot that passes closer to the origin than any other, while the protons that are farthest from the metal (H<sub>A</sub>, #5) give the least linear plot. If contact effects were important, they should be largest for the protons closest to the lanthanide ion and smallest for those farther away. Hence, the paramagnetic shifts exhibited in the nmr spectra of the paramagnetic [Ln(2:2:1)]<sup>3+</sup> species appear to be almost entirely pseudocontact in origin.

It is not clear why the graphical treatment of the chemical shifts of  $H_A$  should give such anomalous results. It is difficult to imagine how a structural change could affect these protons while leaving all the others unperturbed. It does not appear that contact shift contributions provide a plausible explanation, since even when contact shifts are important, a plot of  $\delta_i / \delta_z$  versus D/S<sub>z</sub> should still be linear,<sup>41</sup> and its intercept ( $A_i$ ) used to obtain the contact contributions to the paramagnetic shift. This is not the case for the data in Figure 26. The best explanation is probably that since  $H_A$  has the smallest

paramagnetic shift, any small errors from measuring the shifts, contact contribution, structural changes, <u>etc</u>., are significant relative to the observed paramagnetic shift, and so produce the greatest deviation from "ideal" behavior.

## c.) 2:2:2 complexes.

Attempts to obtain nmr spectra characteristic of  $[Ln(2:2:2)]^{3+}$  complexes have been successful only for Ln = La, Ce, Pr, Sm. These more highly symmetric molecules produce only a simple three line pattern, as shown by Figures 30 and 31. As with the 2:2:1 complexes, the chemical shifts of a given 2:2:2 cryptate in acetonitrile were slightly dependent on the anion in solution, but were identical in aqueous solution. Table 21 contains the chemical shifts measured for the lanthanide 2:2:2 cryptates obtained to date. Deuteration of the -N-CH<sub>2</sub> position of the ligand was used to assign the resonance due to these protons, as indicated in Table 21. Attempts to set up a correlation between the three signals of the various 2:2:2 spectra analogous to that obtained for the 8 lines of the 2:2:1 spectra were unsuccessful.

Nmr was used to follow the gradual dissociation of the  $[Sm(2:2:2)]^{3+}$  and  $[Nd(2:2:2)]^{3+}$  species in aqueous solution. Figure 32 shows the spectral changes that occur during the dissociation of  $[Sm(2:2:2)]^{3+}$  at 40°. As the cryptate dissociates, a new set of resonance signals



(t-BuOD reference)



Figure 31. Nmr spectrum of [Pr(2:2:2)](NO<sub>3</sub>)<sub>3</sub> in acetonitrile solution (TMS reference)

Ln	Chemical Shifts			Solvent	Reference
La	2.84	2.81	1.76 <sup>a</sup>	D20	t-BuOD
Ce	1.92	1.07 <sup>a</sup>	-0.87	D <sub>2</sub> 0	t-BuOD
Pr	- 0.34	-0.34 <sup>a</sup>	-4.81	D <sub>2</sub> 0	t-BuOD
Nd	5.65 <sup>a</sup>	3.58	1.62	D_0	t-BuOD
Sm	2.65	1.75 <sup>a</sup>	1.69	D <sub>2</sub> 0	t-BuOD
La	3.88	3.85	2.93 <sup>a</sup>	CD <sub>3</sub> CN	TMS
Ce	3.27	1.54 <sup>a</sup>	0.39	CD <sub>3</sub> CN	TMS
Pr	3.19	-0.07 <sup>a</sup>	-1.22	CD <sub>3</sub> CN	TMS
Nd	10.17 <sup>a</sup>	4.54	1.10	CD <sub>3</sub> CN	TMS
Sm	3.68 <sup>a</sup>	3.65	3.72	CD3CN	TMS

Table 21. Chemical shifts (in ppm) of various [Ln(2:2:2)](NO3) cryptates

a) N-CH<sub>2</sub> protons

begins to appear, and grows until all of the inclusion complex is dissociated. This new pattern, shown as (c) in Figure 32, can be obtained by mixing  $SmCl_3$  and pure 2:2:2 cryptand in water. Acidifying the solution results in the immediate disappearance of this pattern, which is replaced by that of the protonated cryptand shown as (d) in Figure 32. If the solution is acidified before all of the inclusion complex is dissociated, the intermediate pattern (c) does not appear, and the spectrum contains the characteristic patterns of protonated 2:2:2 (d) as well as those of  $[Ln(2:2:2)]^{3+}$  (a).

These experiments were carried out in a semiquantitative manner for Nd and Sm 2:2:2 cryptates, and the dissociation of the Sm cryptate was found to have a half life of about 45 minutes at 0°, compared to about 65 minutes for the Nd cryptate. Dissociation of the [La(2:2:2)]<sup>3+</sup> species required heating to 100° before an appreciable dissociation rate was observed.

These results have been interpreted to mean that a true inclusion complex is formed between the 2:2:2 cryptand and La, Ce, Pr, Nd, and Sm. It is this complex that produces the three resonances shown in Figures 30 and 31 and tabulated in Table 19. As this complex dissociates, a loose complex, perhaps with the ligand in the outer coordination sphere of the ion, is formed and gives rise to the spectrum labeled (c) in Figure 32. Acidification of the



Figure 32. The dissociation of  $[Sm(2:2:2)]^{3+}$ in D<sub>2</sub>O (t-BuOD reference)

solution breaks up this complex by fully protonating the ligand.

The apparent discrepency between electrochemical and nmr measurements on solutions believed to contain  $[Eu(2:2:2)]^{3+}$  has already been mentioned. Electrochemically, a complex can be observed which dissociates with a rate constant of about  $10^{-3} \text{ sec}^{-1}$  (t<sub>1</sub> ≈ 11 min.).<sup>126</sup> However, repeated measurements of the nmr spectrum of a compound producing the characteristic cyclic voltammogram used for the rate study yields only the pattern in Figure 32c. This same pattern is obtained when the nmr spectrum of any solution believed to contain [Ln(2:2:2)]<sup>3+</sup> with Ln = Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu is measured. In the case of the Eu and Tb compounds, what may be a pattern characteristic of the inclusion complex can be obtained at 0° if the spectrum is measured within seconds after the solution is made. However, these results are difficult to reproduce and in any case do not agree with the electrochemical measurements. Increasing the ionic strength or varying the temperature of the solution between 0 and 25° had no appreciable effect. Several of the researchers involved in the original report of lanthanide cryptates<sup>3</sup> are again collaborating in an attempt to understand these puzzling results. However, a perhaps related set of observations that were made on the Ln(III) chloride complexes of 18-crown-6 should be mentioned. 18-crown-6 and 2:2:2

ligand have similar cavity sizes (1.3 - 1.6 Å versus 1.4 Å, respectively) and so form a logical pair for comparing crown and cryptand behavior. Thermodynamic measurements have shown that the stability of the 18-crown-6 complexes decreases smoothly from La through Gd, and then drops abruptly to zero for Tb through Lu. 114 It has also been reported that dibenzo-18-crown-6 reacts very little or not at all with any post-Nd(III) ions. Examples of similar breaks in complex stability near the middle of the series are abundant,<sup>6</sup> but the crown complexes are most closely related to the cryptates studied here. It is difficult to state quantitatively how far the analogy between crown complexes and cryptate complexes may be carried since the dissociation of crown complexes is generally under kinetic control, while the dissociation of cryptates is generally under thermodynamic control, but in this case the similarities are striking.

## CHAPTER IV

# CONCLUSIONS

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### A. LIGAND SYNTHESIS

Several alternative synthetic routes to produce the diamine precursors of the 2:2:1 and 2:2:2 cryptand have been discussed. However, due to the increasing availability and decreasing cost of the commercially produced cryptands, it is now more desirable to purchase the materials than to synthesize them. Laboratory syntheses need be carried out only when specially modified cryptands (e.g., deuterated compounds) are desired.

#### **B. LANTHANIDE CRYPTATE SYNTHESIS**

### 1. 2:2:1 Lanthanide Cryptates

The synthesis of analytically pure 1:1 complexes of the 2:2:1 cryptand with  $LnCl_3$  (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) and  $Ln(NO_3)_3$  (Ln = La, Ce, Pr, and Nd) may be accomplished in anhydrous acetonitrile solution by the method described in section II.B. This same method produces a mixture of  $[Ln(2:2:1)](NO_3)_3$  and  $Ln(NO_3)_3$  for Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu, and a mixture of  $[Ln(2:2:1)]Cl_3$  and  $LnCl_3$  for Ln = Tb, Dy, Ho, Er, Yb, and Lu. The excess metal salt has been successfully removed from the DyCl<sub>3</sub> mixture by the use of Dowex A-1 ion exchand resin as described in section II.D. Partial separations have been accomplished for the heavier lanthanide mixtures, and efforts are continuing to perfect this procedure.

### 2. 2:2:2 Cryptates

The synthesis of analytically pure 1:1 complexes of the 2:2:2 cryptand with  $LnCl_3$  (Ln = La, Ce, and Pr) and  $Ln(NO_3)_3$  (Ln = La, Ce, Pr, Nd, and Sm) may be accomplished in anhydrous acetonitrile solution by the methods described in section II.B. As with the 2:2:1 complexes, the heavier lanthanide chlorides and nitrates produce a mixture of [Ln(2:2:2)]X<sub>3</sub> and LnX<sub>3</sub> when this synthetic procedure is employed. These results might be understandable in terms
of the dependence of cryptate stability on the size of the metal ion involved, which has been clearly demonstrated in the case of the alkaline earth and alkali metal cryptates, and also in terms of the differing ability of nitrate and chloride ions to coordinate to lanthanide ions (see section III.B.1). The separation procedures being developed for the 2:2:1 complexes are not easily applied to the 2:2:2 complexes, since these latter compounds dissociate much more rapidly in aqueous solution.

#### C. PHYSICAL MEASUREMENTS

## 1. Infrared Spectra

The coordination of lanthanide ions to the 2:2:1 and 2:2:2 ligands is readily observed via a shift in the stretching frequency of the ether linkage of the ligand from 1130 cm<sup>-1</sup> to near 1070 cm<sup>-1</sup>. The infrared spectra of the analytically pure  $Ln(NO_3)_3$  cryptates (2:2:1 and 2:2:2) show the presence of both ionic and coordinated nitrate ions in the solid state. Further, the coordinated nitrates act as bidentate ligands. There is no evidence for coordination of the perchlorate ion to the complexes.

## 2. Electronic Spectra

As expected from previous studies of lanthanide complexes, encryptation was found to have little or no effect on the visible spectrum of the lanthanide mions, with the exception of the several so-called "hypersensitive" transitions.

## 3. Fluorescence Spectra

Encryptation of Eu<sup>3+</sup> ion by 2:2:1 cryptand had no significant effect on the fluorescence spectrum of the ion. <u>4. Cyclic Voltammetry</u>

The reduction potentials of the  $[Eu(2:2:1)]^{3+}/$  $[Eu(2:2:1)]^{2+}$ ,  $[Eu(2:2:2)]^{3+}/[Eu(2:2:2)]^{2+}$ , and  $[Yb(2:2:1)]^{3+}/[Yb(2:2:1)]^{2+}$  couples, which had been previously reported or measured, were reproduced in the

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course of this research. The approximate  $E_f$  values for these systems were found to be -425 mv, -225 mv, and -1081 mv, respectively. However, efforts to detect the  $[Eu(2:2:2)]^{3+}$  species by nmr were unsuccessful. The apparent conflict between these results is currently being investigated.

#### 5. Fluoride Titrations

The stability constants for 1:1 and 1:2 lanthanide cryptate:fluoride ion complexes (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy) were determined by titrimetry using a fluoride ion selective electrode. These stability constants are summarized in Table 18. There is no trend in the values of these constants, within the accuracy of the technique employed.

## 6. Nuclear Magnetic Resonance Spectra

a.) 2:2:1. The nuclear magnetic resonance spectrum of each of the  $[Ln(2:2:1)]^{3+}$  species (except Ln = Pm, Gd, and Tm) have been recorded and interpreted. The geometries of the 2:2:1 complexes remain nearly constant across the series. Line widths, isotropic shifts, and the known crystal structures of [Na(2:2:1)]SCN and [K(2:2:1)]SCNmay be used to interpret and assign the resonances of the spectra of the paramagnetic complexes. The analysis of of the chemical shifts and spin-spin coupling patterns of the diamagnetic complexes can be used to interpret their spectra in terms of possible molecular geometries. The molecule must be rigid, or have one conformation that is thermodynamically highly favorable, to account for the observed spin-spin coupling patterns.

b.) <u>2:2:2</u>. Nmr spectra were obtained for only a limited number of the  $[Ln(2:2:2)]^{3+}$  species (Ln = La, Ce, Pr, Nd, and Sm). Compared to the corresponding 2:2:1 complexes, paramagnetic shifts are small. Spectra for the heavier members of the series, which are expected to produce much larger isotropic shifts, could not be obtained. The assignment of the N-CH<sub>2</sub> resonances of these compounds was accomplished by the synthesis of the deuterated ligand. Approximate rate studies for the aquation of Sm(2:2:2)]<sup>3+</sup> and  $[Nd(2:2:2)]^{3+}$  were also carried out. Approximate half lives for the two aquation reactions were found to be 45 and 65 minutes, respectively.

# CHAPTER V

SUGGESTIONS FOR FURTHER WORK

Two projects, which are currently in the process of being carried out, should be given the highest priority. First, an effective procedure for removing excess lanthanide salts from lanthanide cryptate/lanthanide salt mixtures must be developed. The ion exchange methods being developed at the present time show promise, but may require modifications to be determined by trial and error in the field of lanthanide separations.

Second, the apparent conflict between the electrochemical and nmr data on the  $[Eu(2:2:2)]^{3+}$  species must be resolved. This could be most effectively done with a joint effort between the electrochemical group and synthetic group, working with the same compound under identical experimental conditions.

The discontinuities in thermodynamic data across the lanthanide series (<u>i.e.</u>, "gadolinium break") present one of the most interesting problems in lanthanide chemistry. Once analytically pure samples of each of the  $[Ln(2:2:1)]X_3$  complexes have been isolated, a systemmatic study of the thermodynamic properties of these compounds should be undertaken. One such study should involve the fluoride ion association stability constants as determined in this thesis. By completing these measurements for the remaining members of the series, and repeating the measurements at several temperatures,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  for the system can be determined.

for X-ray studies should also be continued and intensified.

APPENDIX A

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DATA

	9:30 A.M.	4:00 P.M.	
[NaF] <u>M</u>	E mv <sup>a</sup>	E mv <sup>a</sup>	
$1.00 \times 10^{-7}$	-183	-182	
$1.00 \times 10^{-6}$	-131	-133	
$1.98 \times 10^{-5}$	- 65	- 65	
$3.92 \times 10^{-5}$	- 55	- 56	
5.83 x $10^{-5}$	- 47	- 46	
$7.69 \times 10^{-5}$	- 39	- 40	
$9.52 \times 10^{-5}$	- 36	- 35	
$1.82 \times 10^{-4}$	- 20	- 22	
$3.33 \times 10^{-4}$	- 7	- 9	
$4.62 \times 10^{-4}$	0	- 3	
5.71 x $10^{-4}$	2	1	
$6.66 \times 10^{-4}$	6	4	
$1.29 \times 10^{-3}$	20	18	
$1.88 \times 10^{-3}$	27	27	
$2.42 \times 10^{-3}$	33	34	
$2.94 \times 10^{-3}$	37	38	
$3.89 \times 10^{-3}$	43	46	
$4.74 \times 10^{-3}$	48	49	
$5.50 \times 10^{-3}$	52	53	
$7.00 \times 10^{-3}$	61	59	
$1.00 \times 10^{-2}$	63	64	

Table Al. Calibration data for fluoride specific ion electrode 29 June 1978

a) versus Saturated Calomel Electrode

[NaF] <u>M</u>	E mv <sup>a</sup>
$1.00 \times 10^{-7}$	175
$1.00 \times 10^{-6}$	130
$1.98 \times 10^{-5}$	57
$3.92 \times 10^{-5}$	50
5.83 x $10^{-5}$	43
$7.69 \times 10^{-5}$	39
$9.52 \times 10^{-5}$	35
$1.82 \times 10^{-4}$	24
$3.33 \times 10^{-4}$	12
$4.62 \times 10^{-4}$	6
$5.71 \times 10^{-4}$	1
$6.66 \times 10^{-4}$	- 2
$1.29 \times 10^{-3}$	- 18
$1.88 \times 10^{-3}$	- 28
$2.42 \times 10^{-3}$	- 33
$2.94 \times 10^{-3}$	- 38
$3.89 \times 10^{-3}$	- 45
$4.74 \times 10^{-3}$	- 47
$5.50 \times 10^{-3}$	- 49
$7.00 \times 10^{-3}$	- 61
$1.00 \times 10^{-2}$	- 62

Table A2. Calibration data for fluoride specific ion electrode 20 July 1978

a) versus Saturated Calomel Electrode

$ml$ (2 $ml^{-3}$ $mr^{-1}$ )	ml	E
		(107)
0.5	0.0	-82
1.0	0.0	-70
1 5	0 0	-60
2.0	0.0	-53
2.0	0.0	-55
2.5	0.0	-40
3.0	0.0	-41
3.5	0.0	-36
4.0	0.0	-32
4.5	0.0	-27
5.0	0.0	-24
5.0	1.0	15
5.0	1.5	24
5 0	2 0	30
5.0	2.0	34
5.0	2.5	20
5.0	3.0	38
5.0	3.5	41
5.0	4.0	44
5.0	4.5	46
5.0	5.0	48

Table A3. Titration of  $1.06 \times 10^{-2}$  mmoles [La(2:2:1)](NO<sub>3</sub>)<sub>3</sub> in 10 ml of 0.5 <u>M</u> NaClO<sub>4</sub> with standard sodium fluoride solutions 29 June 1978

Table	A4.	Titra	tion	of	1.2	29 x	10	-2 mmo]	es	
[Ce(2:	2:1)]	(NO <sub>3</sub> ).	3 in	10	ml	0.5	<u>M</u> 1	NaClO <sub>4</sub>	with	standard
sodium	fluc	oride a	solut	io	ns	29 3	June	e 1978		

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	ml (2 x 10 <sup>-2</sup> <u>M</u> F <sup>-</sup> )	E (mv)
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	-119 -102 -,91 - 83 - 75 - 72 - 65 - 58 - 52 - 45 11 21 28 33 36 40 43 45
5.0	5.0	4 /

Table	A5.	Titrat	ion (	of	9.1	0 x	10	<sup>3</sup> mmo]	les	
[Pr(2:	2:1)	] (NO <sub>3</sub> )	in 3	10	ml	0.5	<u>m</u> n	aC104	with	standard
sodium	n flud	oride s	solut	ion	ns 2	9 J1	ıne	1978		

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	$(2 \times 10^{-2} \underline{M} F)$	E (mv)
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5	0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	$ \begin{array}{r} -113\\ -102\\ -91\\ -81\\ -72\\ -63\\ -54\\ -45\\ -40\\ -30\\ 19\\ 27\\ 32\\ 36\\ 40\\ 42\\ 45\\ 47\\ 42\end{array} $
3.0	5.0	

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ml (2 x $10^{-3} M F^{-}$ )	ml (2 x 10 <sup>-2</sup> <u>M</u> F <sup>-</sup> )	E (mv)
$\begin{array}{c} 0.5\\ 1.0\\ 1.5\\ 2.0\\ 2.5\\ 3.0\\ 3.5\\ 4.0\\ 4.5\\ 5.0\\ 5.0\\ 5.0\\ 5.0\\ 5.0\\ 5.0\\ 5.0\\ 5$	$\begin{array}{c} 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0$	$ \begin{array}{r} -108 \\ -95 \\ -85 \\ -77 \\ -70 \\ -64 \\ -58 \\ -53 \\ -47 \\ -45 \\ 10 \\ 20 \\ 27 \\ 32 \\ 36 \\ 40 \\ 43 \\ 44 \\ 47 \\ \end{array} $

Table A6. Titration of  $1.29 \times 10^{-2}$  mmoles [Nd(2:2:1)]Cl<sub>3</sub> in 10 ml 0.5 <u>M</u> NaClO<sub>4</sub> with standard sodium fluoride solutions 29 June 1978

Table .	A7.	Titrat	ion	of	1.3	L5 x	10	-2	mmol	.es	
[Sm(2:	2:1)]	(NO <sub>3</sub> ) <sub>3</sub>	in	10	ml	0.5	M	NaC	10 <b>4</b>	with	standard
sodium	fluc	ride s	olut	io	ns	29	Jun	e 1	978		

$(2 \times 10^{-3} \underline{M} F^{-})$	ml (2 x 10 <sup>-2</sup> <u>M</u> F <sup>-</sup> )	E (mv)
0.5	0.0	-95
1.0	0.0	-80
1.5	0.0	-71
2.0	0.0	-62
2.5	0.0	-54
3.0	0.0	-46
3.5	0.0	-40
4.0	0.0	-34
4.5	0.0	-31
5.0	0.0	-28
5.0	1.0	16
5.0	1.5	25
5.0	2.0	30
5.0	2.5	35
5.0	3.0	38
5.0	3.5	42
5.0	4.0	44
5.0	4.5	48
5.0	5.0	50

Table A8.	Titration	of l	$1.12 \times 10^{-2}$ mmoles
[Eu(2:2:1)	]Cl <sub>3</sub> in 10	ml O	0.5 <u>M</u> NaClO <sub>4</sub> with standard
sodium flu	oride solu	tions	s 29 June 1978

ml (2 x $10^{-3} M F$ )	ml (2 x $10^{-2} M F^{-}$ )	E (mv)
0.5	0.0	-110
1.0	0.0	- 96
1.5	0.0	- 84
2.0	0.0	- 77
2.5	0.0	- 69
3.0	0.0	- 63
3.5	0.0	- 56
4.0	0.0	- 49
4.5	0.0	- 42
5.0	0.0	- 38
5.0	1.0	17
5.0	1.5	26
5.0	2.0	32
5.0	2.5	36
5.0	3.0	39
5.0	3.5	42
5.0	4.0	44
5.0	4.5	49
5.0	5.0	50

Table A	<b>А9.</b> Ті	tration of	1.54 x 1	10 <sup>-2</sup> mmoles	5
[Gd(2:2	2:1)]Cl	3 in 10 ml	0.5 <u>M</u> Na	aClO <sub>4</sub> with	standard
sodium	fluori	de solutio	ons 29 Ju	une 1978	

$(2 \times 10^{-3} \underline{M} F^{-})$	$    ml  (2 \times 10^{-2} \underline{M} F^{-}) $	E (mv)
0.5	0.0	-98
1.0	0.0	-83
1.5	0.0	-72
2.0	0.0	-63
2.5	0.0	-60
3.0	0.0	-54
3.5	0.0	-48
4.0	0.0	-44
4.5	0.0	-37
5.0	0.0	-32
5.0	1.0	11
5.0	1.5	20
5.0	2.0	27
5.0	2.5	32
5.0	3.0	36
5.0	3.5	40
5.0	4.0	42
5.0	4.5	47
5.0	5.0	47

Table Al0. Titration of 2.34 x  $10^{-2}$  mmoles [Dy(2:2:1)]Cl<sub>3</sub> in 10 ml 0.5 <u>M</u> NaClO<sub>4</sub> with standard sodium fluoride solutions 20 July 1978

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	E (mv)	
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5	119 105 95 89 84 79 75 71 68	

Table All. Tit	ration of 6.7	3 x 10 <sup>-2</sup> mmoles
EuCl <sub>3</sub> in 10 ml	0.5 <u>M</u> NaClO <sub>4</sub> v	with standard
sodium fluoride	e solutions 20	) July 1978

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	E (mv)	
0.5 1.0 1.5 2.0 2.5 3.0 3.5	92 77 69 63 58 55 51	
4.0 4.5 5.0	48 45 43	

Table Al2. Titration of  $6.74 \times 10^{-2}$  mmoles GdCl<sub>3</sub> in 10 ml 0.5 <u>M</u> NaClO<sub>4</sub> with standard sodium fluoride solutions 20 July 1978

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	E (mv)	
0.5 1.0 1.5	90 76 68	
2.0 2.5 3.0	62 58	
3.5 4.0	51 49	
4.5 5.0	46 44	

Table Al3. Titration of  $6.31 \times 10^{-2}$  mmoles DyCl<sub>3</sub> in 10 ml 0.5 M NaClO<sub>4</sub> with standard sodium fluoride solutions 20 July 1978

$(2 \times 10^{-3} \underline{M} F^{-})$	E (mv)	
0.5	93	
1.0	78	
1.5	70	
2.0	64	
2.5	59	
3.0	56	
3.5	52	
4.0	49	
4.5	46	
5.0	44	

Table	A14.	Titr	ation	of	6.63	x	10 <sup>-2</sup>	mmoles	J
YbC13	6H20	in 10	ml O	.5 <u>M</u>	NaC	104	with	n stand	ard
sodium	n fluc	oride	solut	ions	20	Ju	ly 19	78	

$(2 \times 10^{-3} \text{ M F})$	E (mv)	
0.5	96	H
1.0	82	
1.5	73	
2.0	67	
2.5	62	
3.0	59	
3.5	55	
4.0	52	
4.5	49	
5.0	47	

Table	A15.	Titra	ation	of	6.60	x 10	-2 mm	oles
LuCl <sub>3</sub> .	6H20	in 10	ml O.	.5 <u>M</u>	NaCl	.0 <sub>4</sub> wi	th s	tandard
sodium	n fluo	ride :	soluti	ions	20	July	1978	

ml (2 x 10 <sup>-3</sup> <u>M</u> F <sup>-</sup> )	E (mv)	
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0	97 82 74 67 63 59 55 52 50 47	

(NaNO <sub>3</sub> )	E(mv) <sup>a</sup>	
$5.00 \times 10^{-4}$	141.4	
$1.00 \times 10^{-3}$	112.8	
$5.00 \times 10^{-3}$	69.2	
$1.00 \times 10^{-2}$	52.0	
5.00 x $10^{-2}$	12.0	
$1.00 \times 10^{-1}$	- 2.7	

Table Al6. Calibration data for nitrate specific ion electrode

a) versus Saturated Calomel Electrode

cryptate	mg <sup>a</sup>	E(mv) <sup>b</sup>	
$[La(2:2:1)](NO_3)_3$	25.9	50.5	
$[Ce(2:2:1)](NO_3)_3$	25.0	51.5	
$[Pr(2:2:1)](NO_3)_3$	26.1	50.0	
$[Nd(2:2:1)](NO_3)_3$	26.9	49.3	
[Sm(2:2:1)](NO <sub>3</sub> ) <sub>3</sub>	25.7	44.4	
[Eu(2:2:1)] (NO <sub>3</sub> ) <sub>3</sub>	25.1	44.3	
$[\text{Tb}(2:2:1)](\text{NO}_3)_3$	30.0	43.1	
$[Dy(2:2:1)](NO_3)_3$	31.6	41.4	
$[Ho(2:2:1)](NO_3)_3$	32.0	40.6	
$[\text{Er}(2:2:1)](\text{NO}_3)_3$	31.4	43.7	
$[Yb(2:2:1)](NO_3)_3$	28.6	45.0	
		<b>60</b> 0	
$[La(2:2:2)](NO_3)_3$	18.8	60.9	
$[Ce(2:2:2)](NO_3)_3$	22.7	55.6	
$[Pr(2:2:2)](NO_3)_3$	7.6	84.9	
$[Nd(2:2:2)](NO_3)_3$	18.1	60.1	
$[Sm(2:2:2)](NO_3)_3$	33.8	40.4	
$[Eu(2:2:2)](NO_3)_3$	14.7	62.2	
$[Gd(2:2:2)](NO_3)_3$	26.1	47.7	
$[\text{Tb}(2:2:2)](\text{NO}_3)_3$	24.9	60.4	
[Ho (2:2:2)] (NO <sub>3</sub> ) <sub>3</sub>	24.4	47.0	
$[\text{Er}(2:2:2)](\text{NO}_3)_3$	31.6	40.2	
$[Yb(2:2:2)](NO_3)_3$	20.3	52.3	
$[Lu(2:2:2)](NO_3)_3$	30.4	41.2	

Table Al7. Analysis of nitrate content of various lanthanide cryptates via a nitrate ion selective electrode

a) all samples dissolved in 10.0 ml of 0.1  $\underline{M}$  Na<sub>2</sub>SO<sub>4</sub> at 20°

b) versus Saturated Calomel Electrode

(NaCl)	E(mv) <sup>a</sup>	
$5.00 \times 10^{-4}$	86.7	
$1.00 \times 10^{-3}$	71.3	
$5.00 \times 10^{-3}$	32.6	
$1.00 \times 10^{-2}$	15.8	
5.00 x $10^{-2}$	-21.9	
$1.00 \times 10^{-1}$	-38.0	

Table Al8. Calibration data for chloride specific ion electrode

a) versus Saturated Calomel Electrode

cryptate	mg <sup>a</sup>	E (mv) <sup>b</sup>	)
[La(2:2:1)]Cl <sub>3</sub>	19.8	16.1	
[Pr(2:2:1)]Cl <sub>3</sub>	26.1	10.4	
[Nd(2:2:1)]Cl <sub>3</sub>	13.4	25.2	
[Sm(2:2:1)]Cl <sub>3</sub>	26.6	9.0	
[Eu(2:2:1)]Cl <sub>3</sub>	30.1	5.7	
[Gd(2:2:1)]Cl <sub>3</sub>	13.1	26.6	
[Dy(2:2:1)]Cl <sub>3</sub>	25.2	7.3	
[Yb(2:2:1)]Cl <sub>3</sub>	10.0	31.7	
[Pr(2:2:2)]Cl <sub>3</sub>	8.2	37.9	
[Nd(2:2:2)]Cl <sub>3</sub>	16.5	22.5	
[Sm(2:2:2)]Cl <sub>3</sub>	20.8	16.4	
[Eu(2:2:2)]Cl <sub>3</sub>	17.6	14.5	

Table Al9. Analysis of chloride content of various lanthanide cryptates via a chloride ion selective electrode

a) all samples dissolved in 10.0 ml 0.1  $\underline{M} \operatorname{Na}_2 \operatorname{SO}_4$  at 20°

b) versus Saturated Calomel Electrode

shifts of the paramagnetic [Ln(2:2:1)] <sup>3+</sup> species in $D_2O^a$	F <sup>/</sup> H <sub>K</sub> H <sub>M</sub> H <sub>A</sub> H <sub>Y</sub> <sup>/</sup> H <sub>E</sub> H <sub>X</sub> Y 3 4 5 6 7 8	.17 $1.34$ $2.54$ $3.02$ $4.05$ $4.05$ $4.05$ $6.97$ .88 $-2.60$ $1.80$ $5.38$ $10.50$ $12.37$ $14.25$ .36 $2.95$ $3.13$ $4.69$ $7.19$ $12.58$ $14.45$ .95 $1.10$ $2.42$ $2.48$ $2.92$ $3.06$ $4.69$ .67 $-53.50$ $-53.50$ $-2.82$ $26.58$ $78.62$ $205.15$ .08 $-78.17$ $-57.57$ $-34.52$ $79.55$ $79.55$ $234.81$ .82 $-29.74$ $-26.20$ $-3.68$ $17.45$ $48.52$ $149.98$ .98 $34.60$ $16.07$ $7.54$ $-44.75$ $-44.75$ $-71.39$ .90 $28.22$ $17.04$ $-16.80$ $-36.21$ $-58.67$
; of the parar	H <sub>K</sub> 3	
emical shifts	H <sub>F</sub> / HY 2	$\begin{array}{rrrr} - & 2.17 \\ - & 11.88 \\ - & 1.36 \\ 0.95 \\ -177.67 \\ -217.08 \\ -217.08 \\ -212.82 \\ 86.98 \\ 66.90 \end{array}$
vle A20. Ch	1 HL	- 2.17 - 14.85 - 2.20 0.74 - 199.72 - 264.79 - 114.05 107.40 83.89
Tat	ГЛ	Ce Nd Ce Dy Ce Er Vb

a) t-BuOD reference, shifts in ppm

Table specie	A21. I s in D <sub>2</sub>	uine widths o <sup>a</sup>	(HZ)	of the n	mr signals	of the	paramagnetic	[Ln (2:2:]	()] <sup>3+</sup>
5	н Н	H <sub>F</sub> / H <sub>Y</sub> 2		H <sub>K</sub> 3	H M H	H 5	H <sub>Y</sub> / H <sub>F</sub> 6	H <sub>E</sub> 7	HX 8
Ce	م م	q		23.8	29.8	10.6	а а	q q	44.5
Pr Nd	27.2	21.7		29.0 b	43.0 b	18.1 21.0	21.9	60.5 69.4	84.1
Eu	26.4	21.4		28.3	44.1	18.2	25.6	58.1	73.7
Tb	371	272		q	q	240	396	814	1040
A	577	392		101	876	341	q	q	1410
Ho	420	387	4	142	740	298	374	807	1199
Er	420	302	4	176	680	267	q	q	1071
Ϋ	83.4	60.1		92.4	q	q	64.6	161	203

a) t-BuOD referenceb) overlapping signals

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3 complexes	
n (2:2:1) ] (NO <sub>3</sub> )	s in ppm)
magnetic [L	, all shift
of some para	1S reference
ical shifts c	solution (TM
le A22. Chem	acetonitrile
Tab	in

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Ce	9.23	7.66	6.61	6.49	2.62	2.27	- 3.62	- 6.14
Pr	16.34	12.21	12.21	11.85	0.85	- 0.11	- 13.14	- 17.75
pn	14.55	12.68	9.24	7.41	5.85	3.45	- 4.28	- 6.97
Sm	4.69	3.06	2.92	2.48	2.42	1.10	0.95	0.74
Бu	8.92	6.35	4.00	<b>I.35</b>	- 2.09	- 3.93	- 9.25	- 9.89
đT	61.26	22.71	- 5.23	-41.40	-50.12	-80.68	-114.92	-183.50
Но	36.48	19.02	7.88	-19.28	-22.07	-50.08	- 63.81	-123.90
Er	88.39	70.70	33.39	16.29	-18.13	-25.00	- 37.90	- 53.13
Ţ	33.68	27.64	21.81	9.86	đ	- 7.57	- 13.50	- 36.50
$_{\rm Pr}^{\rm b}$	17.39	15.05	11.92	3.45	2.92	- 2.57	- 15.94	- 18.29
qpn	15.64	11.49	8.16	5.06	4.94	4.50	- 2.49	- 2.49

obscured by solvent peak chloride salts a) b)

APPENDIX B

## SEPARATIONS

#### APPENDIX B - SEPARATIONS

#### 1. Preparation of Complexes

1.54 mmoles of  $LnCl_3 \cdot 6H_2O$  (Ln = Tb, Dy, Ho, Er, Tm, Yb, or Lu) were dissolved in a solution of 100 ml dry acetonitrile and 20 ml trimethylorthoformate. After refluxing one hour under a CaCl, drying tube, 1.54 mmoles of 2:2:1 cryptand in 15 ml dry acetonitrile were added. A precipitate formed immediately, and did not dissolve after 3-4 hours of refluxing. This precipitate was filtered off, washed with ether, and used in the following separations experiments. The material does not analyze for  $[La(2:2:1)]Cl_3$  or a simple mixture of cryptate and free metal chloride. (Typical results: [Yb(2:2:1)]Cl<sub>2</sub> 31.41%C; 5.27%H; 17.38%Cl. found: 19.89%C; calc: 4.31%H; 18.43%Cl.) Approximately 550 mg, or 60% of the total amount of ligand and metal chloride were recovered. Attempts to increase the yield by concentrating the mother liquor and adding ether produced from 10 to 50 mg additional product.

## 2. Separation on a column of Chelex-100

50 ml of Chelex-100 ion exchange resin (100-200 mesh, 0.7 meq/ml, lot number 17223) were stirred with 400 ml 1 N HCl for 30 min. The acid was filtered away, and the treatment repeated with a second 400 ml portion of 1 N acid. This was filtered away, and the resin washed with

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distilled water until the filtrate was neutral. A column of 50 ml of resin in a 50 ml buret was prepared, and a 100 mg sample of crude  $[Ln(2:2:1)]Cl_3$  (Ln = Er, Yb, Lu) was dissolved in 2 ml  $10^{-3}$  N HCl and introduced on the column. The sample was eluted with 500 ml of  $10^{-3}$  N HCl. Under these conditions, pure YbCl, should not be eluted from the column.<sup>157</sup> The sample volume was reduced to 125 ml by rotary evaporation, then freeze dried. Finally, the product was dried 12 hours at 100° under vacuum (< 1mm Hg). Analysis of the chloride content of the product by potentiometric titration with standard AgNO<sub>3</sub> gave the following results: [Er(2:2:1)]Cl<sub>3</sub> - calc: 17.55%Cl. found: 20.0%Cl.; [Yb(2:2:1)]Cl<sub>3</sub> - calc: 17.38%Cl. found: 20.7%Cl.; [Lu(2:2:1)]Cl<sub>2</sub> - calc: 17.32%Cl. found: 19.4%Cl. The high chloride content of the product indicated that a large amount of metal chloride is being eluted through the resin (unlikely), or excess HCl is trapped in the product, or that the complex is thermally unstable, and the ligand is sublimed away from the metal salt during the drying process. Also, the amounts of product recovered from the column were quite low (33% of the Er material , 45% Yb, 38% Lu). Thus, this method is not useful in the purification of [Ln(2:2:1)]Cl<sub>3</sub> cryptates.

An attempt to improve the results of this method was made by using only a 15 ml resin column in a 50 ml buret

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and collecting 175 ml of eluent, which was again  $10^{-3}$  M HCl. However, results were much the same as for the larger column, as about 40% of the original weight of material was recovered, and the chloride content was again near 20-21%.

A final separation attempt was made with a very short (1 ml) Chelex-100 column using 200 mg [Yb(2:2:1)]Cl<sub>3</sub> and water as the eluent. Three experiments were done, varying the eluent volume collected from 25 to 75 and finally 150 ml. Freeze drying and drying the product 12 hours at 25° under vacuum yielded 15 mg (16.6%Cl), 18 mg (16.3%Cl) and 17 mg (18.0% Cl) of product, respectively. It is clear from these and earlier experiments<sup>158</sup> that this resin has a strong affinity for lanthanide cryptates and does not provide a practical method for their purification.

## 3. Separation on a column of Dowex A-1

Dowex A-1 and Chelex-100 are trade names of the Dow Chemical Company and Bio-Rad Laboratories, respectively, for a chelating ion exchange resin with imidodiacetate functional groups on a polystyrene support. In this work, the Dowex A-1 resin available (lot #07088FC) was 50-100 mesh size (0.4 meq/ml), and was found to have a much lesser affinity for lanthanide cryptates (see section III.B.2) than the 100-200 mesh (0.7 meq/ml) Chelex-100 resin. In fact, most of the lanthanide cryptate stirred in a beaker with an eightfold excess of Dowex A-1 could be recovered by merely filtering away the resin, while the Chelex-100 resin removed essentially all of the complex from solution.

A column of 12 ml of Dowex A-1 resin in the HCl form was prepared, and 100 mg of crude [Ln(2:2:1)]Cl<sub>3</sub> (Ln = Tb, Dy, Ho, Er, Yb, or Lu) was eluted with water. The first 10 ml of eluent were discarded, and the next 100 ml were collected, freeze dried, then dried at 100° under vacuum. A larger amount of material was recovered than in the Chelex-100 experiments, averaging near 70% for the Tb, Dy, Ho triad, and near 50% for the Er, Yb, Lu triad. However, the chloride content of the material recovered was uniformly low for the Er, Yb, Lu triad (calc (ave.): 17.5%Cl. found (ave.): 14.5%Cl.). This treatment of the Tb, Dy, Ho triad was more successful, and an analysis of the Dy compound by Spang Microanalytical Laboratory gave the following results: %C for [Dy(2:2:1)]Cl<sub>3</sub> -31.96%. found: 31.52%.; %H - calc: 5.36%. calc: found: 5.37%.; %N - calc: 4.66%. found: 4.63%. These results, along with those presented in section III.B.2 indicated that the members of the Tb-Dy-Ho triad may be prepared as pure anhydrous  $[Ln(2:2:1)]Cl_3$  or as the pure dihydrate by passing the crude complex over a column of Dowex A-1, or by the batch method described in (4) below.

# 4. Separation by stirring a solution of [Ln(2:2:1)]Cl<sub>3</sub> with Dowex A-1

This is essentially the method described in section II.D. However, in these experiments all samples were freeze dried and, except where otherwise noted, dried under vacuum at 25° instead of 100°. 200 mg of the initial precipitate was used and treated 3 times with 4 ml of Dowex A-1 in the HCl form. Initially, the sample was stirred with 4 ml resin and 4 ml water. After 10 min. the resin was filtered away, and washed 3 times with 8 ml water. The second and third 4 ml portions of resin were similarly stirred, filtered, and washed. In this way, a volume of 80-100 ml of solution was obtained to be freeze dried. The successful isolation of [Dy(2:2:1)]Cl<sub>3</sub>·2H<sub>2</sub>O was described in section III.B.2. [Ho(2:2:1)]Cl<sub>3</sub>:2H<sub>2</sub>O has now been isolated as well. Analytical results from Galbraith Laboratories were: %C - calc: 30.04. found: 29.72.; %H - calc: 5.67. found: 5.85.; %Cl - calc: 16.63. found: 16.84.

Encouraging results were also obtained when this method was applied to [Yb(2:2:1)]Cl<sub>3</sub>. Analytical results from Galbraith Laboratories were: %C for [Yb(2:2:1)]Cl<sub>3</sub> calc: 29.66. found: 27.57.; %H - calc: 5.60. found: 6.21.; %Cl - calc: 16.41. found: 16.76. The chloride analysis is very good, but the carbon content is reported low, and the hydrogen content high. However, as noted in
section III.B.3, Galbraith Laboratories often gave poor results in the C,H analysis of lanthanide cryptates usually reporting low %C and high %H. A "worst case" calculation, taking the reported values as accurate, indicates that the material obtained is about 85% pure  $[Yb(2:2:1)]Cl_3 \cdot 2H_2O$ . Consideration of the chloride analysis, and allowing for the probable error in the carbon analysis indicates the material may well be 90+% pure. This is a significant improvement over the initial precipitate, which may have contained only 50-60 mole %  $[Yb(2:2:1)]Cl_3$ .

Attempts to increase the purity of the material by a second treatment with 2, 4 ml portions of resin were not successful. An additional 30% of the material was lost, and the chloride content increased to 18.5%. Furthermore, drying the partially purified material at 100° for 12 hours increases the chloride content to 18.1%. Thus, it appears that prolonged exposure of [Yb(2:2:1)]Cl<sub>3</sub> to heat or Dowex A-1 results in the degradation of the complex.

## 5. Concluding remarks

Under carefully controlled conditions, Dowex A-l ion exchange resin may be used to obtain pure samples of the heavier lanthanide 2:2:1 cryptates. The amount of resin used and the length of time the cryptate is in contact with the resin should be minimized. A large mesh resin

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(50-100 or larger) should be used to minimize the concentration of functional groups per ml of resin. These criteria are best and most easily met by stirring an aqueous solution of the crude cryptate complex with small batches of Dowex A-l resin 50-100 mesh in the HCl form. The heaviest lanthanide cryptates (Ln = Er, Yb, Lu) appear to be thermally unstable at 100°.

It should also be noted that in each of the separation experiments that did not yield a pure lanthanide cryptate, some care must be taken in attempting to determine why the experiment "failed". The initial precipitate used in these experiments was of an unknown, and probably highly complex, composition. Some idea of the complexity of these materials can be obtained from a recently reported attempt to isolate  $[La(2:2:2)](NO_3)_3$  from methanol.<sup>159</sup> A crystal structure of the material obtained showed that it contained 4 moles of La,2 moles of cryptand, 12 moles of  $NO_3^-$  as well as some solvent molecules!

Stability constants for the association of one and two moles of fluoride ion were determined as in section III.C.5 for the  $[Ho(2:2:1)]Cl_3$  and  $[Yb(2:2:1)]Cl_3$  complexes. The results were: for  $[Ho(2:2:1)]^{3+}$ :  $K_1 =$ 4.6 x 10<sup>4</sup> M<sup>-1</sup>;  $K_2 = 1.9 \times 10^2 M^{-2}$ ; for  $[Yb(2:2:1)]^{3+}$ :  $K_1 = 2.9 \times 10^4 M^{-1}$ ;  $K_2 = 2.7 \times 10^2 M^{-2}$ . These values are very similar to those determined for the other lanthanide cryptates. It is interesting that the lanthanide cryptates not only coordinate two fluoride ions, but also tend to crystallize from aqueous solution as the dihydrate, further indicating the availability of space in the coordination sphere of the ion for two small molecules in addition to the 2:2:1 ligand. LIST OF REFERENCES

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