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Complexes of Lanthanide Nitrates with the Cryptand 2B:2:1

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Abstract

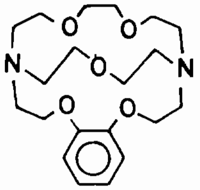
Lanthanide cryptate complexes of cryptand 2B:2:1 were prepared using the medium of acetonitrile containing triethyl-orthoformate. Upon encryptation, a fairly large decrease in the ultraviolet extinction coefficient of the benzo-cryptand is observed. Infrared spectra established the unsolvated nature of the complexes prepared in this study. The coordination of the cryptand's ether oxygens to encapsulated metal ions result in a large shift to lower energy up to 60 cm^{-1}, in the absorptions due to C–O–C stretching vibrations. Proton nmr spectra of the lanthanide(III) cryptate complexes show noticeable differences when compared to the free cryptand spectrum. Along with down field shifts in all the methylene and benzene-ring protons, the aromatic protons in the diamagnetic lanthanum(III) cryptate spectrum are now recorded as $A'_2B'_2$ symmetric multiplets. Paramagnetic induced shifts are observed in the nmr spectra of all the paramagnetic lanthanide cryptate complexes. The Pr(III) cryptate spectrum is recorded in the range –23.4–21.4 ppm whereas the whole spectrum for the Eu(III) complex is obtained between –15.0–18.5 ppm.

Introduction

The macrocyclic complexes, crowns and cryptates, of alkali and alkaline earth cations have been formed and characterized fully during the last two decades [1, 2]. There are also several reports of complexes prepared and isolated with various transition metal ions. However, there are very few reports of macrocyclic complexes with lanthanide metal ions as compared to those of the alkali and alkaline earth metal cations [3, 4].

The bicyclic cryptands are known to possess, in some of their conformations, a spheroidal cavity which may present oxygen and nitrogen binding sites to an encapsulated metal ion. Hence if the spherical tripositive lanthanide metal ions whose ionic radii vary in the range of 0.85–1.15 Å could be encapsulated inside the cryptand cavity, they might produce a series of systematically varied, substantially inert, yet thermodynamically stable cryptate complexes.

Studies of lanthanide cryptates were reported first from our laboratory [5]. We have also reported the formation of some bifunctional lanthanide cryptates and have published the methods of covalently attaching these cryptates to proteins [6]. The research work presented here describes in detail our results on the preparation and characterization of all lanthanide complexes with the benzo-cryptand 2B:2:1.



Experimental

All reactions were performed under strictly anhydrous conditions. Acetonitrile was distilled over P_2O_5 just prior to use. All solutions were stored under a nitrogen atmosphere even though the systems appear to be stable in air, although deliquescent.

Materials

Hydrated lanthanide nitrate salts were purchased from Ventron Corporation, Beverly, MA and Research Organic and Inorganic Corporation, Belleville, N.J. and were used without further purification. The benzo-cryptand 2B:2:1 was synthesized in our laboratory [7] and was kept away from light and air. Spectral grade acetonitrile was purchased from Burdick & Johnson, Inc. of Muskegon, Mich.

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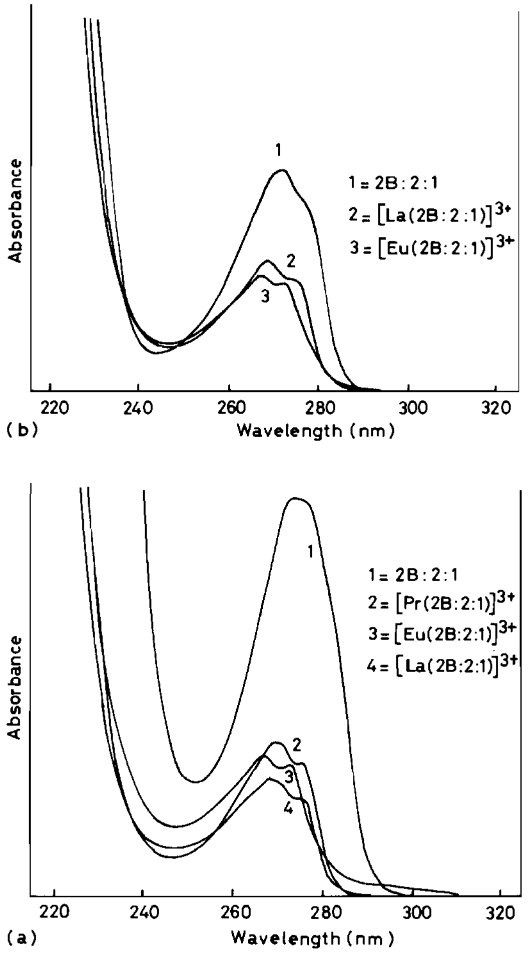

Fig. 1. Ultraviolet spectra of the benzo-cryptand and its lanthanide complexes present in similar concentration (a) in acetonitrile and (b) in water.

Spectroscopic and Analytical Studies

All proton NMR spectra were determined on a Bruker WH-180 spectrometer at prob temperature in d_3-acetonitrile using TMS as an internal standard. Infrared spectra were recorded using a Perkin-Elmer Model 457 spectrometer with KBr pellets and nujol (for 650–1600 cm^{-1} region) and hexafluorochlorobutadiene for (1600–3500 cm^{-1} region) mulls. Ultraviolet spectra of acetonitrile and aqueous solutions of cryptates were taken using a Cary-17 spectrophotometer. Melting and decomposition temperatures were determined in capillaries on a Thomas-Hoover apparatus in air and are uncorrected.

Elemental analyses were performed by Spang Laboratories of Eagle Harbor, MI or Galbraith Laboratories of Knoxville, TN.

Preparation of Ln-cryptates (NO_3)$_3$

The hydrated metal nitrates were dehydrated *in situ* prior to complexation. A solution of 0.2 mmol of hydrated metal nitrate, 2 ml of triethylorthoformate and 25 ml of dry acetonitrile was stirred and refluxed for 5 hours. A solution of 0.2 mmol of benzo-cryptand in 5 ml of dry acetonitrile was added to the dehydrated metal salt solution. The stirring and refluxing were continued for another 4 hours. After cooling, the solution was filtered, and to the filtrate was added ethyl ether dropwise to cloudiness. The mixture was refrigerated and solid cryptate salts precipitated. The solid was filtered and dried for 4–5 hours using high vacuum.

Results and Discussion

(i) Formation of Cryptate Complexes

The macrobicyclic cryptand is a tertiary amine, with $pK_1 \sim 10.5$, and $pK_2 \sim 7.5$. The lanthanide salts tend to precipitate as hydroxide in the presence of water. Hence one can prepare the lanthanide cryptates only by using the non-aqueous medium. Even the hydration water in the reaction medium hampered the lanthanide cryptate synthesis. The precipitate formation prompted us to use a dehydration process in order to strip the water molecules from the first coordination sphere. The precipitates do not form in appreciable amounts when the metal salts are dehydrated prior to addition of cryptand. Although cryptates appear to be relatively stable to air and moisture, they are however, best stored under nitrogen gas.

(ii) Spectroscopic Studies

(a) Ultraviolet spectra

The ultraviolet spectra of cryptand 2B:2:1 show a λ_{max} at 274 nm in acetonitrile and at 272 nm in water. Upon encryptation, a fairly large decrease in extinction coefficient and a second maxima about 5–8 nm to the longer wavelength side of the major band are observed.

The effects of encryptation of a metal ion on the ultraviolet spectrum of cryptand 2B:2:1 are shown in Fig. 1. The changes in the shape of spectra among the several complexes are slight and complex formation is suggested by a hypsochromic shift and a decrease in absorbance. However, since the new band is not very well separated from the main absorption band, no conclusions can be drawn as to its origin except to say that the metal ion perturbs slightly the degenerate $\pi-\pi^*$ transition of the benzene ring in the metal complexes resulting in a slight change in the degeneracy of the transition.

(b) Infrared spectra

Infrared spectroscopy was used more extensively for characterization of the cryptate complexes. It provided several important types of information. First, the presence of water or any solvent molecule

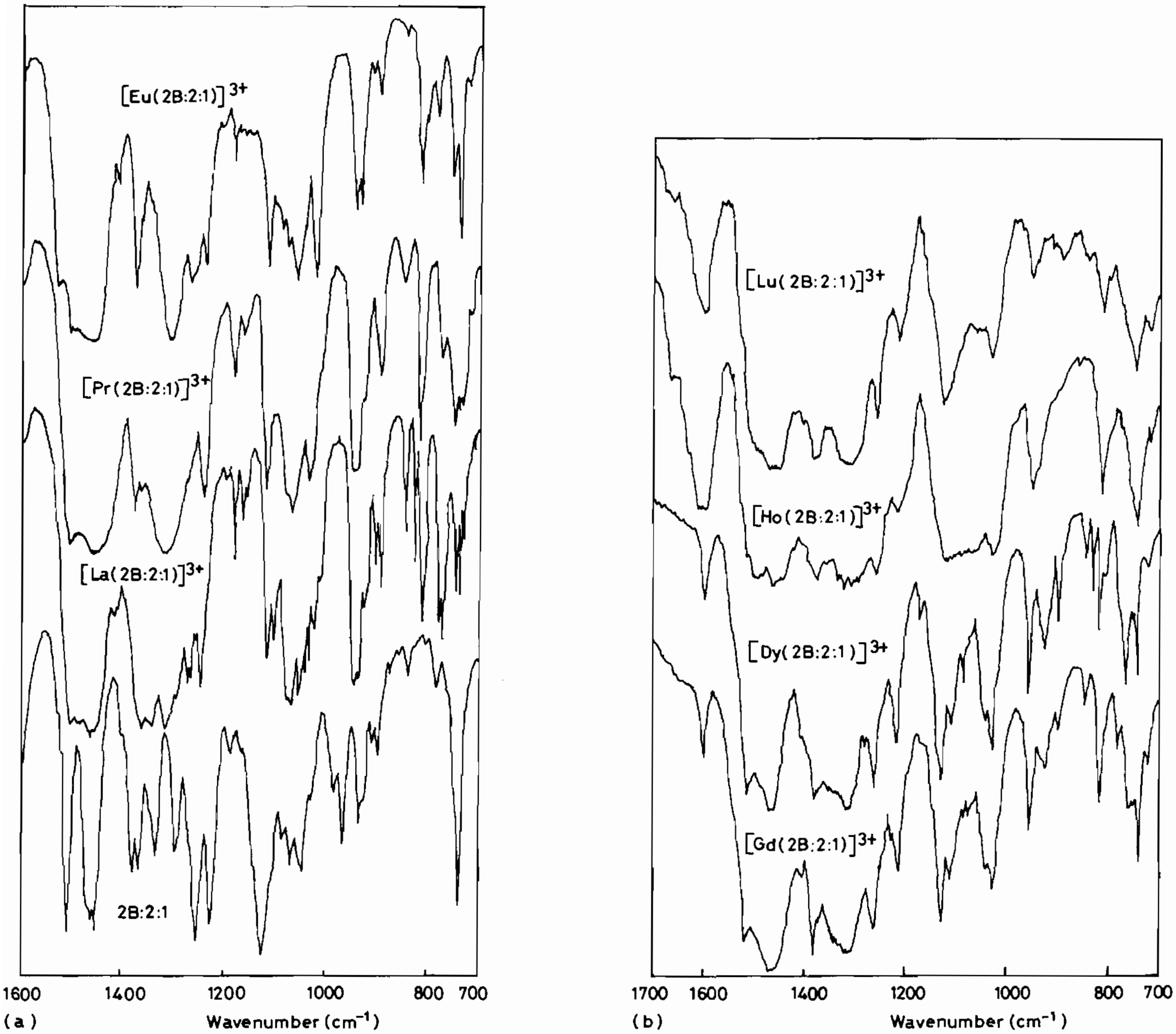

Fig. 2. Infrared spectra of $Ln(2B:2:1)^{3+}(NO_3)_3$ cryptates.

could be detected. Second, the absorptions due to NO_3^- ion vibrations in the solid complexes were easily identified in the infrared spectra. Third, the coordination of cryptand to metal ions resulted in a large shift to lower energy up to 60 cm^{-1}, in the absorptions due to C–O–C stretching vibrations. This large shift was also helpful in detecting any free ligand present in the complexes prepared. Similar shifts have been reported for the lanthanide benzocrown complexes [3].

The infrared spectra of some lanthanide complexes are recorded in Fig. 2 and show marked changes compared to those of the pure cryptand 2B:2:1. The spectra obtained may be divided into three types. Those of the La–Eu spectra are quite similar, but different from the closely related spectra seen for Gd–Dy, which in turn are different from the spectra seen for Ho–Lu. The infrared spectra within a given class are independent of the lanthanide ion indicating that the metal–cryptand interactions are essentially identical within the experimental limitation of the infrared spectra.

No bands which could be attributed to water or the solvent, *i.e.* CH_3CN, are found in any of the spectra, establishing that the complexes are anhydrous and unsolvated.

The free cryptand exhibits two different (C–O) bands at 1123 cm^{-1} (aliphatic $H_2C–O–CH_2$) and at 1253 cm^{-1} (aliphatic–aromatic ether linkage; CH_2O–benzene–CH). These bands in all three classes of cryptates, are shifted to lower frequencies by 50–60 cm^{-1}. This lowering of energy results from the metal–ether oxygen interaction upon cryptate formation and is similar to that reported for all crown and cryptate complexes.

Infrared bands due to nitrate groups in the three classes of lanthanide(III) nitrate cryptate complexes indicate the presence of only coordinated nitrate

TABLE I. Vibrational Modes for C_{2v} Nitrates in Ln(2B:2:1) $(NO_3)_3$.

Ln	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_2(A_1)$	$\nu_3(B_1)$	$\nu_5(A_1)$
La	1470vs	1315vs	1055s	813m	771m
Pr	1469vs	1321vs	1039s	820m	772m
Nd	1460vs,br	1315vs	1039s	818m	755m,br
Sm	1465vs	1317vs	1038s	815m	756m,br
Eu	1469vs	1318vs	1023s	817m	751w
Gd	1465vs	1313vs	1028s	819m	758m,br
Tb	1469vs	1315vs,br	1028s	818m	755m
Dy	1468vs	1311vs	1028s	815m	765m
Ho	1463vs	1318vs	1028s,br	812m	745m
Er	1460vs	1322vs	1031s,br	813m	742m
Tm	1468vs	1315vs	1029s,br	811m	745m
Yb	1475vs,br	1318vs,br	1020	811m	760m
Lu	1470vs,br	1320vs,br	1028	812m	749m

v = very, s = strong, br = broad, m = medium; and w = weak.

ligands. The conclusion that all nitrates are coordinated to the metal ion is based upon the fact that even if one nitrate of the D_{3h} point group is present, along with coordinated nitrates, there should be an absorption band around 1350 cm^{-1} plus the band near 1300–1320 cm^{-1} due to the coordinated nitrates. This is also in agreement with the assignments of numerous authors who have prepared various oxygen- and nitrogen- donor complexes of lanthanide nitrates [8, 9]. The assignments of the nitrate bands recorded in Table I are based upon the symmetry type C_{2v} point group (coordinated NO_3^- group) according to the notations used by Foster and Hendricker. The same notations have been used for the interpretation of the nitrate infrared data of lanthanide crown complexes by King and Heckley and Duyckaerts and coworkers [3, 4].

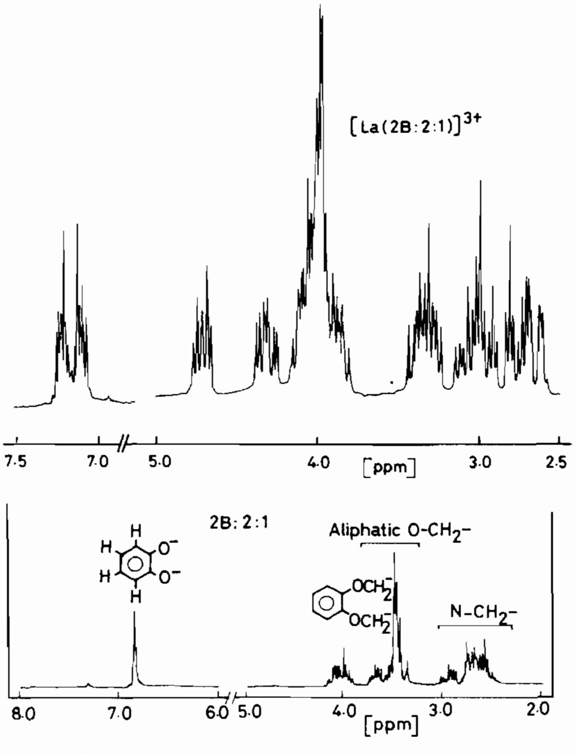

Fig. 3. ^{1}H-NMR spectra of cryptand 2B:2:1 and its lanthanum complex in CD_3CN.

(c) Proton-nmr Spectra

^{1}H-nmr spectra of the free and complexed benzocryptand show noticeable differences. Proton nmr spectra of the free cryptand and its lanthanum(III) cryptate complex are presented in Fig. 3. Cryptate formation causes downfield shifts in all proton resonances. The proton nmr spectra of other diamagnetic cation cryptates (alkali and alkaline earth) also exhibit similar downfield shifts of the various methylene proton resonances [10].

The proton nmr spectrum of the diamagnetic La $(2B:2:1)^{3+}$ provides strong evidence that the metal ion indeed resides in the central cavity of the molecule. The four aromatic protons in the free cryptand are recorded as an A_2B_2 doublet. Upon encryptation, the metal ion coordinates with the oxygens attached to the benzene ring and holds it tight with the net result that the aromatic protons are now recorded as AA'BB' symmetric multiplets, centered at 7.15 ppm. This downfield shift in aromatic proton resonance from 6.90 (in the free cryptand) to 7.15 (in the complex) and change of symmetry is caused by cryptate formation. The remaining methylene protons are divided into two distinct groups. Both of these groups are shifted downfield relative to their resonances in free cryptand. The N–CH_2 protons are found in the range 3.81–4.86 ppm. All of these methylene protons are split into complex multiplets.

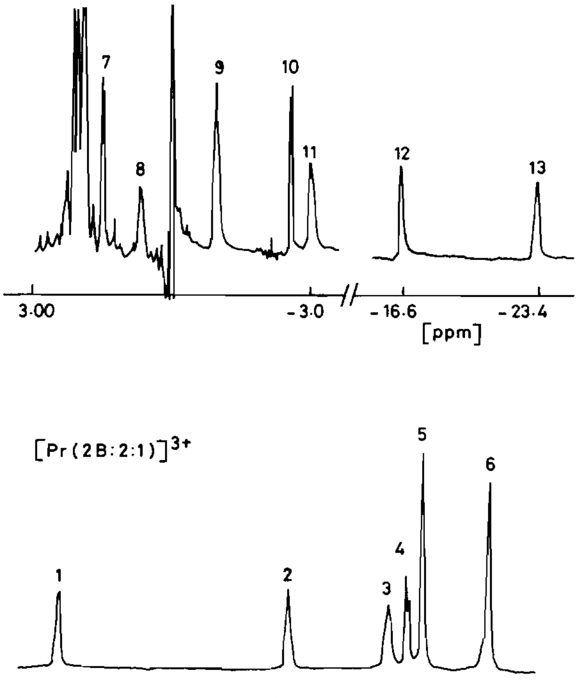

Fig. 4. ^{1}H-NMR spectrum of a deuterated acetonitrile solution of [Pr(2B:2:1)]$^{3+}$.

TABLE II. Analytical Data on Some Ln(Cryptand)(NO_3)$_3$.

Ln	Colour	%C		%H	
		Calc.	Found	Calc.	Found
La	white	34.40	34.19	4.53	4.48
Ce	white	33.98	33.72	4.52	4.55
Pr	pale green	33.95	33.41	4.51	4.32
Nd	pale pink	33.24	32.95	4.57	4.57
Eu	white	32.74	32.99	4.50	4.60

The proton nmr spectra of some paramagnetic lanthanide cryptates were also recorded. They show induced paramagnetic shifts in the proton nmr spectrum of the ligand. The proton paramagnetic induced shifts are essentially dipolar in origin [11].

The ^{1}H-nmr spectrum of Pr (2B:2:1)$^{3+}$ is displayed in Fig. 4. The pure cryptand exhibits signals only between 2.58–4.86 and at 6.90 ppm, whereas the Pr(III) cryptate exhibited signals due to different protons between −23.4–21.4 ppm. There were a total of thirteen signals recorded, ten of them were single intensity and three of double intensity. One would expect sixteen signals due to thirty-two protons of the molecule, because the molecule has a plane of symmetry.

An attempt was made to assign some of the signal observed in the spectrum. The more expanded and resolved spectrum revealed that the signals 5, 6 and 9, of double intensity, are singlet, singlet and a triplet, respectively. Moreover, signals 7 and 10, of equal intensity, are very similar to each other and are distorted quartets. The signals 7 and 10 are relatively sharp and located at 1.48 and −2.68 ppm. It is our opinion that these two signals belong to the two sets of aromatic protons. It is known that the coupling pattern of aromatic protons is relatively less effected by the paramagnetism present in the molecule [12]. The presence of two singlets and one triplet in the double intensity signals excludes the possibility of assignment to methylene protons of benzo-strand or the aliphatic-2-strand. For these strands, all three double intensity signals should be triplets. Probably signals 5 and 6, located at 13.41 and 11.93 ppm, belong to four protons of O–CH_2 and four protons of N–CH_2 of 1-strand. The third double intensity signal (triplet), found at −1.0 ppm, may be assigned to four protons of an N–CH_2 of a benzo-2-strand or an aliphatic-2-strand.

A similar proton nmr spectrum of Eu(2B:2:1)$^{3+}$ is obtained. The whole spectrum is recorded between −15.0–18.5 ppm. Although the spectrum is very complex in the region of CHD_2CN, which was the solvent, sixteen signals of equal intensity were recorded. The signals are found at 18.45, 17.14, 13.40, 10.12, 7.3 6.93, 5.36, 4.62, −5.92, −6.38, −9.19, −9.56, −9.64, −12.79, −14.17, and −15.19 ppm. They are all of equal intensity which accounts for all thirty-two protons of the molecule.

The paramagnetic shifts obtained by the above discussed paramagnetic cryptate complexes verify that the metal ion is resident in the cavity of the cryptand. If the metal ion is not resident in the cavity and just from an adduct, no appreciable induced shifts in the ligand spectrum are observed [3].

(iii) Analytical Measurements

The quantitative microanalyses were performed to complement the results obtained by the above mentioned methods. The C, H analytical data of lighter lanthanide cryptates are presented in Table II. Analytical data of heavier lanthanide cryptates did not match well with the numbers calculated for 1:1 anhydrous metal complexes. Formation of some metal-ligand adduct was thought to be the major impurity present with the cryptate complexes.

An attempt was made to remove the impurities by passing the cryptate aqueous solutions through a mixed bed ion exchange column. Lanthanide cryptate complexes of cryptands 2:2:1 and 2:2:2 were successfully purified in this way [13], whereas all attempts were unsuccessful for cryptand 2B:2:1 lanthanide complexes.

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