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Preparation and Characterization of some Bifunctional Lanthanide Cryptates

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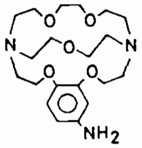
1:1 inclusive complexes of a bifunctional cryptand ($2B_{NH_2}$:2:1) with La^{+3}, Pr^{+3}, and Eu^{+3} metal ions were prepared using dry acetonitrile in the presence of triethyl ortho-formate. Upon encryptation, a fairly large decrease in ultraviolet extinction coefficient and large shifts to lower energy by 40–60 cm^{-1} in the absorptions due to C–O–C stretching vibrations were recorded. NMR spectra of cryptate complexes carrying paramagnetic lanthanide ions exhibited paramagnetic shifts in all the ligand proton resonances and were recorded over a 40 ppm range, confirming the location of a metal ion resident in the central cavity of molecule.

Introduction

The chemistry of synthetic macrocycles has been explored extensively in the last decade [1]. However, stable inclusive complex formation by sodium, potassium, and ammonium cations with these neutral macrocycles is an uncommon phenomena. Hence these recently synthesized macrocycles, especially cryptands, have provided great interest to researchers working in several divisions of chemistry [2].

Cryptands are macropolycycles, electrically neutral, and lipophilic molecules of various sizes. Each has the principal structure feature of a cavity in the centre of the molecule which may serve the purpose of holding a cation. A complete report on the synthesis and characterization of a series of bifunctional cryptands (*i.e.* cryptands which possess, in addition to the metal ion binding functionality, a reactive functional group which allows the entire cryptand (or metal cryptate) to be covalently attached to a host molecule and thereby act as spin label or tracers) has already been published elsewhere [3].



This report discusses the metal cryptate formation of a bifunctional aminobenzo-cryptand (structured above) with some of the lanthanide (lanthanum, praseodymium, and europium) metal cations. Vibrational, ultraviolet, and NMR spectroscopy was used to characterize the metal cryptates. The quantitative microanalyses were performed to complement the spectroscopic results and to confirm 1:1 stoichiometry of the complexes.

Experimental

General

All reactions were performed under strictly anhydrous conditions. Acetonitrile was distilled over P_2O_5 immediately prior to use. Filtration was performed using high vacuum techniques. Filtrates were kept under a nitrogen atmosphere even though the systems appear to be stable to air, although deliquescent.

Hydrated lanthanide nitrate salts were purchased from the Ventron Corporation, Belleville, New Jersey, U.S.A. and were used without further purification. The bifunctional amino-cryptand was synthesized in the laboratory and kept away from light and air.

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All proton NMR spectra were determined on a Bruker WH-180 spectrometer at probe temperature in d_3-acetonitrile using TMS as an internal standard. Ultraviolet spectra of acetonitrile solutions of cryptates were taken by using a Cary-17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer as nujol mulls (650–1600 cm^{-1} region). Elemental analyses were performed by Spang Laboratories of Eagle Harbor, Michigan, U.S.A.

Preparation of Ln-Cryptates $(NO_3)_3$ *(Ln = La, Pr, Eu)*

An equimolar amount of cryptand and hydrated metal nitrate were taken together in a 100 ml round bottom side arm flask. The flask was evacuated, filled with dry nitrogen gas and placed in a preheated (60–70 °C) oil bath. Next, 25 ml of dry acetonitrile and 3 ml of triethyl orthoformate were added to the flask and stirring was started. After 2 hours of reflux, the solution was filtered using high vacuum. To the filtrate, ethyl ether was added dropwise until cloudy. The solution was refrigerated under nitrogen atmosphere where the crystals of lanthanide cryptates grew. The solids were filtered, washed with cold ether and dried for 2–3 hours under high vacuum. The yields of the cryptate solids were in the range of 60–70%.

Results and Discussion

Formation of Metal Cryptates

It is important to note that the cryptands are tertiary amines, pk 10.5. The lanthanides tend to precipitate as hydroxide in the presence of any water. Only by using a non-aqueous medium can one successfully prepare the lanthanide cryptates. Even a slight amount of hydration water in the reaction medium hampered the whole reaction. They are easily prepared using anhydrous acetonitrile solvent. All cryptates are crystalline powders, and they possess the color characteristic of the coordinated ion. It was noticed that upon heating at high temperatures solid metal cryptates tend to decompose.

Spectroscopic Studies

Ultraviolet Spectra

Since the cryptand is a derivative of cathechol, hence it shows the absorptions characteristic of cathechol ethers. The ultraviolet spectra of cryptand and its lanthanide cryptates are quite different. The U.V. spectra for amino-benzo cryptand was recorded in acetonitrile. The absorption band had the maximum absorption recorded at 274 nm.

Upon encryptation, a fairly large decrease in extinction coefficients was observed. However the wavelength at maximum absorption was not changed more than 5 nm in any case.

Vibrational Studies

IR spectroscopy afforded clear evidence for the complexation of lanthanide nitrates by the cryptand ligand. The infrared spectra of all lanthanide complexes show marked changes compared to those of the pure free cryptand.

The free cryptand exhibits two different C–O–C absorption bands due to $H_2C–O–CH_2$ (1125 cm^{-1}) and H_2C–O–benzene CH (1254 cm^{-1}) ether linkages. Upon coordination of cryptand to metal ions, large shifts to lower energy by 40–60 cm^{-1} in the absorptions due to C–O–C stretching vibration were recorded. This lowering of energy results from the metal–ether oxygen ineraction upon cryptate formation and is similar to that reported for lanthanide benzo-crown ether complexes [4]. Furthermore this large shift was also helpful in detecting any free ligand present in the complexes prepared.

Infrared bands due to nitrate groups in all cryptate complexes indicate the presence of only coordinated nitrate ligands of symmetry type C_{2v} point group.

Proton-NMR Spectra

^{1}H-NMR spectra of free and complexed cryptands show noticeable differences. In the case of a diamagnetic lanthanum(III) cryptate complex, the cryptate formation causes downfield shift in all of the ligand 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 [5].

Free amino-cryptand in solution exhibits aromatic protons at 6.10, 6.26, and 6.62 ppm; whereas they are found at 6.23, 6.43, and 6.87 ppm respectively in its lanthanum cryptate complex in CD_3CN. The N–CH_2 methylene protons are recorded between 2.58–3.57 in the complex spectrum and the O–CH_2 methylene protons are found in the region 3.88–4.78 ppm. All of the methylene proton signals are recorded as multiplets.

The proton-induced shifts by paramagnetic lanthanoid cations make them useful as shift and relaxation reagents. in NMR. They are being used as a probe to monitor induced conformational changes in proteins, enzymes and other biomolecular structures [6]. Hence one of the radioactive lanthanoid isotope is presently being used in medicinal research.

Praseodymium metal ion causes the paramagnetic shifts in the proton nmr spectrum of its amino-cryptate complex. The peaks are located at 19.80, 19.37, 15.44, 14.80, 14.34, 13.88, 13.68, 13.31, 12.99, 12.81, 12.63, 11.89, 11.38, −15.08, −16.14, −21.23 and −22.52 ppm. The Eu^{+3} amino-cryptate is not very soluble in CD_3CN. However, the proton

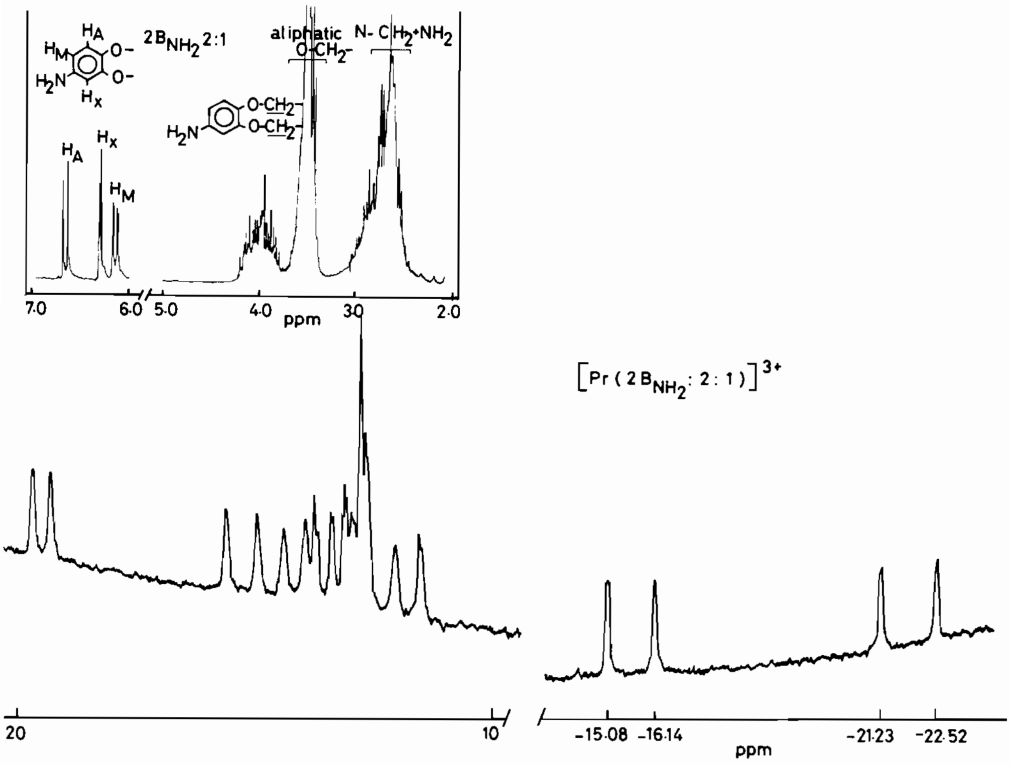

Fig. 1. ^{1}H-NMR spectra of deuterated acetonitrile solutions of free aminobenzo-cryptand and its cryptate complex with praseodymium(III) nitrate.

nmr spectrum of a dilute solution exhibits the induced shifts in the proton signals. The whole spectrum is recorded between 25.17—-16.87 ppm.

The paramagnetic shifts obtained by the paramagnetic cryptate complexes verify the metal ion residing in the cavity of the cryptand. The proton NMR spectra reported for some similar paramagnetic complexes also exhibits the induced paramagnetic shifts in methylene protons of the host molecules [7]. However if the metal ion is not resident in the cavity and just forms an adduct, no appreciable induced shifts in the ligand spectrum are observed [5]. Moreover the 1:1 ratio of metal:cryptand was confirmed by the elemental analysis. The following analytical determinations for the europium amino complex are representative; Calcd: C, 32.74; H, 4.50. Found: C, 32.99; H, 4.60.

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