Spectroscopic Studies on Effect of Cationic Charge on Cryptate Formation

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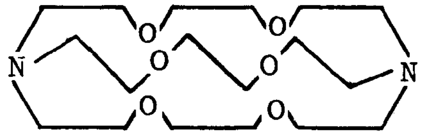
Summary : 1:1 inclusive complexes of cryptand (2:2:2) with Na^+, Ca^{+2}, and La^{+3} metal ions were prepared using dry acetonitrile in the presence of triethyl ortho-formate. Vibrational and nmr spectra were examined to see the effects of cationic charge on cryptate formation.

Introduction

Cryptands are macrobicyclic polyether molecules carrying a three dimensional cavity in the centre. These molecules have been synthesized only in the last decade by Lehn and coworkers [1]. The interest in these compounds have been generated since then because of their stable complex formation (cryptates) with alkali, alkaline earth, and ammonium ions[2]. The cations fit nicely in the cavity of the molecules. Information obtained from structural studies of these inclusive complexes makes it possible to investigate some of those factors which determine the type of coordination which occurs.

Moreover these novel macrocycles are electrically neutral molecules and typically contain central hydrophilic cavities and exterior flexible framework exhibiting hydrophobic behaviour. Hence their selective binding behaviour for alkali and alkaline earth cations is resulting in their use as models for carrier molecules in the study of active ion transport phenomena in biological systems[3].

The objective of the work reported in this article was to observe spectroscopically, how the difference in charge carried by similar sized metal ions will effect the process of cryptate fromation. Alongwith alkali and alkaline earth cations of similar ionic radius (~ 1.0A°), lanthanum was included because of its higher charge, similar size and due to the use of lanthanoid cations as an nmr probe in the structural elucidation of complex molecules. Results will also be compared with Th+4 cryptate complex which have also been reported to from 1:1 complex with cryptand (2:2:2)[4]



Experimental

(i) *General*

Cryptand (2:2:2) was synthesized in our laboratory. Metal salts were purchased from Alfa/ Ventron Corporation, U.S A. The other chemicals and reagents used were of analytical grade.

The nmr spectra were recorded on a Varian T–60 spectrometer at probe temperature with TMS being used as an internal standard. Infrared spectra were taken on Perkin Elmer 457 spectrometer. Elemental analysis was carried out by Galbraith Labs., Knoxille, Tennesse, U.S A.

(ii) *Preparation of Solid Cryptates*

An equimolar amount of cryptand and hydrated metal nitrates were taken together in a round bottom flask. 23ml of dry acetonitrile and 3ml of triethyl ortho-formate was added to the flask and placed in a preheated oil bath. After 2 hours, solution was cooled, filtered and ethyl ether was added to the filtrate until cloudy. Upon cooling the solution, crystals grew which were filtered and dried under vacuum. Solid cryptates were analysed for their elemental contents. The following analytical determination for lanthanum complex are representative. Calcd for $(La\ C_{18}H_{36}N_2O_6)(NO_3)3$, C, 30.79; H, 5.13. Found C 30.68; H 5.15.

Results and Discussion

(a) *Infrared spectra.*

Infrared spectroscopy provided several important types of information. The effect of cationic charge on cryptate formation was apparatently noticeable from a shift to lower energy upto 50 cm^{-1}

in absorptions due to C–O–C stretching vibrations. Upon complexation the charge carried by the cation enclosed in the cavity of the molecule is effecting the interaction between metallic centre and the six oxygens of three strands. This in turn is effecting the stretching of the C–O–C bonds in all three complexes.

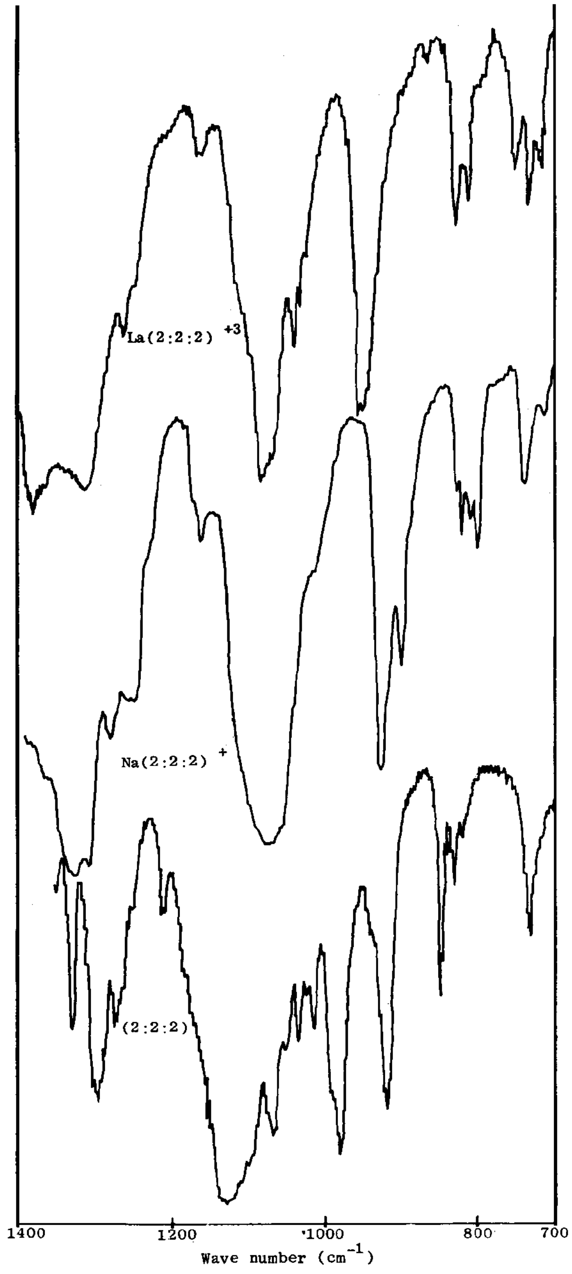


Fig 1. Infra red spectra taken as nujol mulls of free cryptand and its Na^{+} and La^{+}3 cryptate complexes.

The free cryptand exhibits C–O–C band at 1135 cm^{-1}. Upon cryptate formation these absorptions are found at lower frequencies as broad and unresolved bands. The frequency of this band in cryptates is recorded at 1130 cm^{-1} (Na^{+}) 1125 cm^{-1} (Ca^{+2}), and at 1087 cm^{-1} (La^{+3}). Similar shifts have been reported for various alkali, alkaline earth, and lanthanide crown complexes [5,6]. Infrared spectra of Na^{+} and La^{+3} cryptate are displayed in Figure 1, alongwith free cryptand. It is apparent that in the case of La^{+3} complex the shift has been at maximum.

(b) NMR Spectra

The cryptate formation in solution may be properly observed by nmr[7]. Cryptate formation causes down field shifts in all methylene proton resonances. The evidence of a tight complex made by encapsulation of lanthanum ion by cryptand is evident from the large down field shifts especially of N–CH$_2$ methylene protons resonance. It should be mentioned at this point that in the cryptate complex, both end nitrogens are in endo endo form and hence experience the maximum interaction between their lone pair and metal cation. Hence the extent of downfield shift in N–CH$_2$ methylene resonance alone, is indicative of the effects exhibited due to the ionic charge carried by the metal ion.

The 60 MHz proton nmr spectra of free cryptand and their cryptate complexes in CD$_3$CN solution are presented in figure 2. The spectrum for free cryptand contains two triplets of equal intensity for the N–CH$_2$ and O–CH$_2$ protons at 155 and 213HZ, respectively from TMS. However, the methylene protons signal due to O–CH$_2$ – CH$_2$ – O is recorded as signlet at 216HZ.

Upon encryptation, multiplicity of the signals is not altered and the large shifts in all proton resonances are recorded only for lanthanum (III) metal complex. Very little change is observed for sodium (I) cryptate, whereas calcium (II) inclusive cryptate complex experience a noticeable down field shifts in all signals. The N–CH$_2$ methylene protons signal in lanthanum complex is shifted by 22 HZ and O–CH$_2$ by 21 HZ. This large shift clearly indicate that the +3 charge carried by the lanthanum ion is interacting strongly with non-bonding electrons

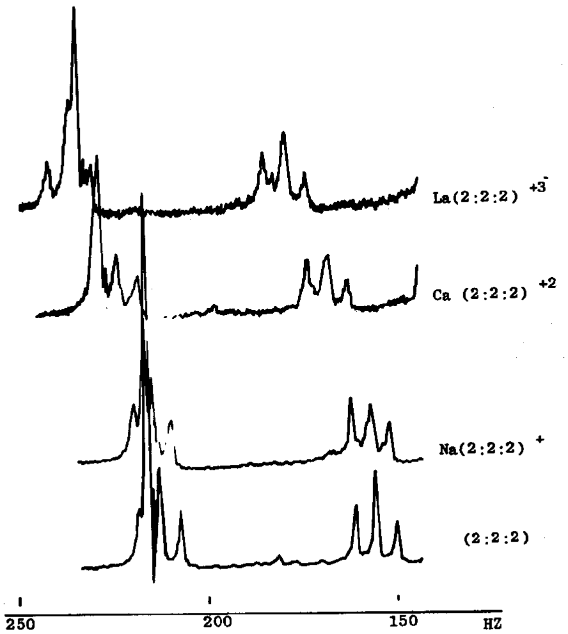


Fig 2. 60 MHZ ^{1}H NMR spectra of deuterated acetonitrile solution of free cryptand (2:2:2) and Its Na^{+}, Ca^{+2}, La^{+3} cryptate complexes.

present on the heteroatoms The $N–CH_2$ experience the downfield shift most, because of its lone pair involvement with metal ion being a prerequisite for encryptation. The down field shift reported for Th^{+4} cryptate has been about 25HZ[4].

Since the ionic radii of all three cations, cavity radius of the cryptand, number of heteroatoms for coordination, and the method of preparation is similar in all cases, the effects exhibited by infrared and nmr spectra can be easily assigned to the differences in charge carried by different ions.

This study is representative in its nature since most routinely used spectroscopic techniques provide the direct information on the nature and strength of interaction between host and guest species. Further work on these lines by varying certain parameters is in progress.

References.

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