Notes

New Insight to the Chemistry of Polyaza[*n*]paracyclophanes. A ^{15}N NMR Study

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Introduction

It has been our interest during the past few years the study of polyamine-type macrocyclic ligands, in particular polyaza[*n*]cyclophanes and related molecules.[1] These hosts form complex species with a variety of cationic and anionic guests, which have been studied by techniques such as potentiometric titrations, X-ray diffraction, and NMR spectroscopy. Among these tools, NMR can be especially useful in order to achieve accurate information about the structural features in solution of the supramolecular species.[2] Within this context it seems very interesting to analyze by NMR the nuclei that are directly involved in the binding to the guest species, namely nitrogen in the case of polyamines, which could provide useful information about the structure and properties of the complexes that are being studied.

The broad and interesting potential applications that ^{15}N NMR can find in different areas of chemistry have been described.[3] However, the low natural abundance of the ^{15}N isotope results in very long NMR experiments if direct detection is employed. The use of ^{15}N-enriched samples can overcome this problem, but this approach requires expensive materials and sometimes quite complex synthetic routes.[4] Nowadays, it is possible to perform ^{15}N NMR experiments at relatively low concentrations (10^{-2} M) in a few minutes. This is the result of the continuous advances in NMR technology and software which, for example, made available from the past few years the use of gradient enhanced indirect detection NMR methods, namely ^{1}H−^{15}N GHMQC (also called GHMBC when long-range couplings are involved).[5] The recent incorporation of those techniques to commercial instruments explains that only a limited number of data have been reported on its application to the study of small- and medium-sized polynitrogenated molecules.[6]

It is our aim here to report on our results which are intended to provide new insight both to the chemistry of polyaza[*n*]paracyclophanes and to the scope and advantages that ^{15}N NMR offers for the analysis of complex species in solution.

Results and Discussion

GHMBC experiments, which involved long-range ^{1}H−^{15}N couplings, were used to obtain the ^{15}N chemical shifts for the different molecules studied. In the case of molecules containing primary or secondary amino functions, this was also the experiment of choice since the protons directly attached to the nitrogen atom are, in general, in fast exchange with the medium. The δ values were calculated taken the resonance of nitromethane at 0 ppm as the reference.

Protonation and Anion Coordination. The study of the different protonated species that exist in water is needed to understand properly the properties of the ligands containing multiple amine functionalities. On this respect, NMR can provide structural information about the protonated species that is complementary to that afforded by thermodynamic data. In this way ^{1}H and ^{13}C NMR have been widely used to determine the average protonation sites of polyamines[7] but ^{15}N NMR has not been employed routinely due to the limitations described above which led to the use of highly concentrated samples.[8] The low number of nitrogen atoms in the ligands (when compared with ^{1}H and ^{13}C atoms) and the rather large shifts experienced by the ^{15}N resonances upon protonation, make the ^{15}N NMR an ideal tool for

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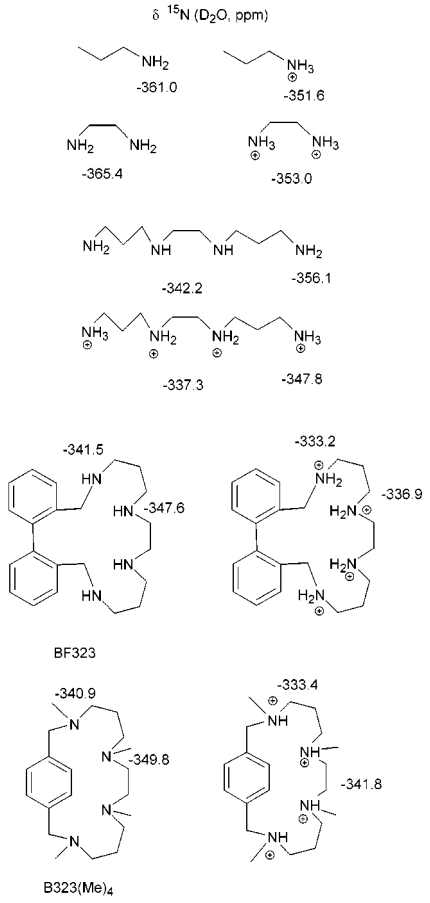
Chart 1. ^{15}N NMR Chemical Shift Variations upon Protonation of Selected Polyamines in D_2O



evaluating the structure of protonated species. To familiarize the reader with the magnitude of the protonation-induced ^{15}N shifts, the results obtained for different compounds which include some simple commercially available amines and the macrocycles **BF323** and **B323-(Me)$_4$** are summarized in Chart 1. There it can be seen that significant downfield shifts (ca. 7−12 ppm) of the ^{15}N NMR signals can be observed upon protonation. For the macrocycles shown, it is observed that the chemical shifts of the nitrogen nuclei in benzylic positions are downfield-shifted with respect to those in the central positions of the polyamine chain.

A study of the shift experienced by the ^{15}N resonances at different pD values[9] (pD = pH + 0.4) provides a direct and straightforward information regarding the protonation sites of the different species that can exist in aqueous solution. As an example, the results obtained in the study of the macrocycle **B323(Me)$_4$** are shown in Figure 1. Potentiometric titrations were used to calculate the species distribution diagram shown in that figure.[10] The ^{15}N NMR data indicate that, within the basic pH range, where the first two steps of the protonation of the ligand take place, shifts are experienced mainly by the resonance of the benzylic nitrogen atoms labeled as N1. Thus, for example, at pH ca. 9, where the monoprotonated species are predominant in solution, the δ shift for the

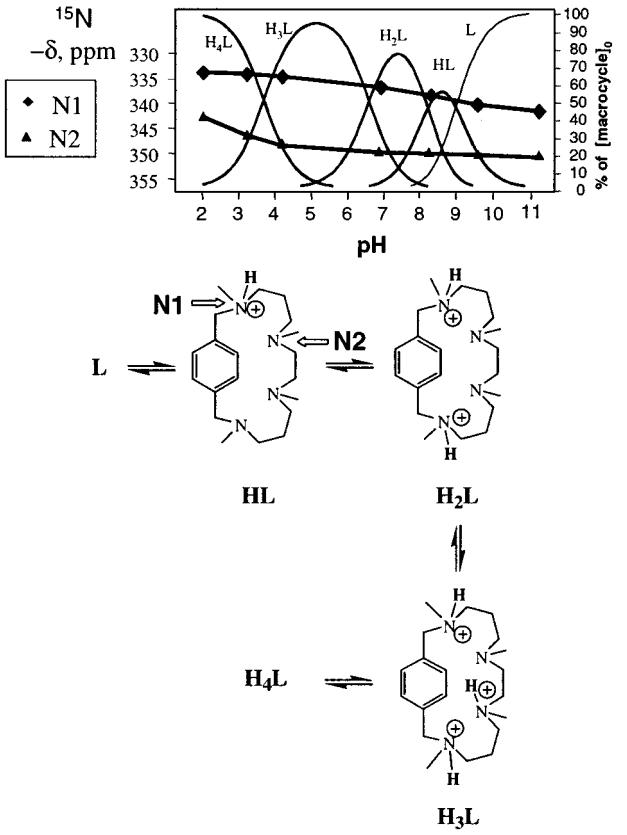


Figure 1. Study of the protonation of macrocycle **B323(Me)$_4$** in D_2O: Merged plots of ^{15}N NMR δ values (squared and triangular dots, left axis values) of the nitrogen atoms of **B323-(Me)$_4$** at different pH values and the species distribution diagram obtained for **B323(Me)$_4$** (curved lines, right axis values).

benzylic nitrogen atoms resonance is 35% of the maximum value attainable, while for the central nitrogen atoms it is only 10%. These data agree either with a situation where both species coexist in solution (being the species protonated at benzylic positions clearly the predominant ones) or considering the proton bridged between the two types of nitrogens, the proton being located much more closer to the benzylic nitrogen atoms. On the other hand, within the acidic pH range, where the third and fourth protonations occur, shifts affect mainly to the central nitrogen atoms labeled as N2 in the figure. These facts agree with the protonation scheme proposed that is also shown in Figure 1. Although conformational changes upon protonation could affect the ^{15}N nuclei shifts, the similar protonation-induced shift values obtained for the macrocycles with different aromatic rings and for acyclic polyamines indicates that they are not a main factor in this system. It is important to note the chemical relevance of those shifts due to the direct involvement of the nitrogen atoms in the protonation process, which results in sharper chemical shift variations than when ^{1}H and ^{13}C NMR are employed.[7]

It is well documented that protonated polyamines are one of the best-suited ligands for the interaction with anions in aqueous solution.[11] ^{15}N NMR can also provide a complementary insight to the study of anion complex species. As an example, when the interaction of **B323-(Me)$_4$** with ATP was studied by potentiometry, several complex species were found to exist in solution (see Figure 2). The protonation degrees of both substrate and

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(10) (a) Frias, J. C. Ph.D. thesis, University Jaume I (Spain), 2000. (b) The successive protonation constans (log K) of **B323(Me)$_4$** are 8.99, 8.22, 6.59, and 3.69.

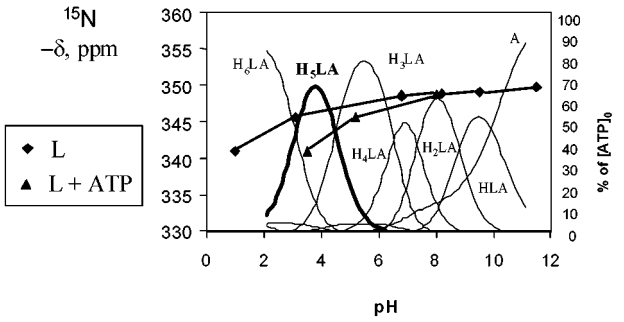
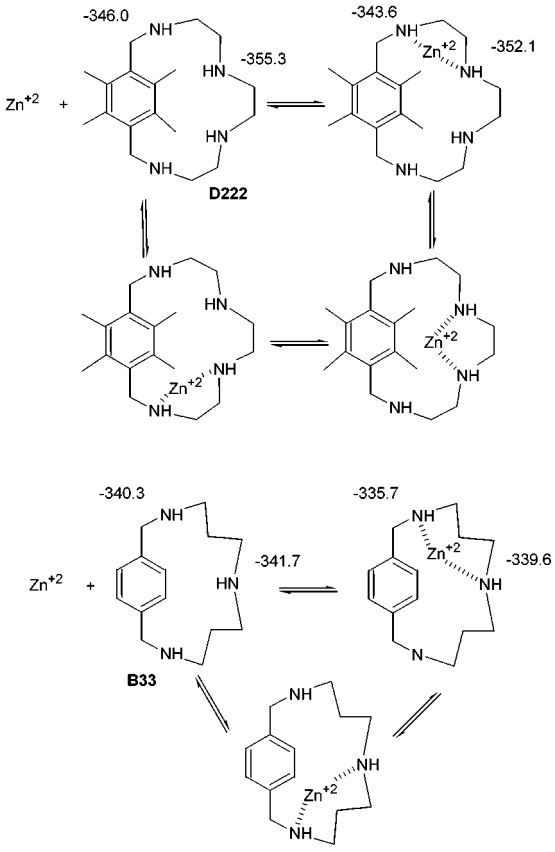


Figure 2. Study of the interaction of macrocycle **B323(Me)$_4$** (L) with ATP (A): Merged plots of ^{15}N NMR δ values of the benzylic nitrogen atom of **B323(Me)$_4$** at different pH values (squared and triangular dots, left axis values) and the species distribution diagram for the **B323(Me)$_4$**−ATP system (curved lines, right axis values).

ligand in those complex species are difficult to assess in most instances, but these are important data in order to try to understand and rationalize the observed selectivity trends. In the particular case of the pentaprotonated species, the calculated equilibrium constants suggest two reasonable structures.[10a,12] One of them is formed by the interaction of the triprotonated ligand with diprotonated ATP ($H_3L + H_2A$) and the other one is formed by the interaction of the tetraprotonated ligand with monoprotonated ATP ($H_4L + HA$). ^{15}N NMR studies show that upon addition of an equivalent amount of ATP, an appreciable shift of the ^{15}N resonance assigned to the central nitrogen atoms of the ligand takes place in the pH range 4−8. These shifts should be ascribed to changes in the protonation degree of the ligand rather than to the hydrogen bonding or electrostatic interactions with the anion. This is supported, for example, by the behavior of the benzylic nitrogen atoms whose shifts in the complex species are almost identical to those of the free ligand all over the pH range. It is also to be noted that at pH = 8, where a diprotonated complex species is predominant in solution, the shifts of both nitrogen atom types of the macrocycle are identical to those obtained in the absence of ATP. Around pH = 4, where the pentaprotonated species (H_5LA) is predominant, the ^{15}N chemical shifts of the central nitrogen nuclei are coincident with those described for the fully protonated ligand. This clearly supports that, at that pH value, the H_5LA species derives from the interaction of the fully protonated ligand (H_4L) with monoprotonated ATP (HA). ^{1}H NMR spectra are in accordance with these conclusions and, for example, the chemical shifts of adenine protons at the studied pH agree with the presence of diprotonated ATP (H_2A). In this case, thermodynamic data would not allow for discarding the other possible equilibrium. ^{1}H NMR spectra also suggest an interaction between aromatic rings of receptor and ATP, as indicated by the observed shift (0.1 ppm) of the aromatic signal of the macrocycle upon complexation. This behavior is related to that described by us for related systems.[1b]

Scheme 1



Cation Complexation. ^{15}N NMR signals should also experience shifts upon metal cation complexation.[3b] Those can be used to obtain information both on the thermodynamics and on the structure of the species being formed. We have analyzed some aspects of metal coordination capabilities of polyaza[*n*]cyclophanes with the help of ^{15}N NMR (see Scheme 1). These macrocycles present an aromatic spacer that precludes the simultaneous involvement of all the donor nitrogen atoms in the binding to a single metal cation guest.[1] The results that had been obtained previously for the reactivity with alkylating reagents in acetonitrile and the stability constants of the Zn(II) complexes calculated potentiometrically in aqueous media, suggest the coordination patterns shown in Schemes 1 and 2.[1b] Compound **B323** (log K = 6.8), which presents a more flexible polyamine chain than **D222** and **B33**, can make use of three of its four nitrogen atoms to coordinate the metal cation. On the other hand, macrocycles **B33** and **D222** present lower stability constants (log K < 4 and log K = 4.6, respectively) that might well correspond to complexes in which only two of the nitrogen atoms of a macrocycle can interact with a single metal cation. ^{15}N NMR spectra of the complex species give interesting information regarding the structural hypotheses depicted in Schemes 1 and 2.

For the labile complexes **B33-Zn(II)** and **D222-Zn(II)**, when 1 equiv of zinc triflate was added to the macrocycle dissolved in CD_3CN, small downfield shifts of the two ^{15}N resonances present in the free macrocycle were observed and the ^{1}H spectra showed the same symmetry features as that one of the uncomplexed macrocycle. These data agree with the existence of labile complex species in rapid interconversion in the NMR time scale. In the case of

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(12) The calculated formation constants (log *K*) for the pentaprotaned complex (H_5LA) from $H_4L + HA$ and $H_3L + H_2A$ are, respectively, 6.31 and 6.10.

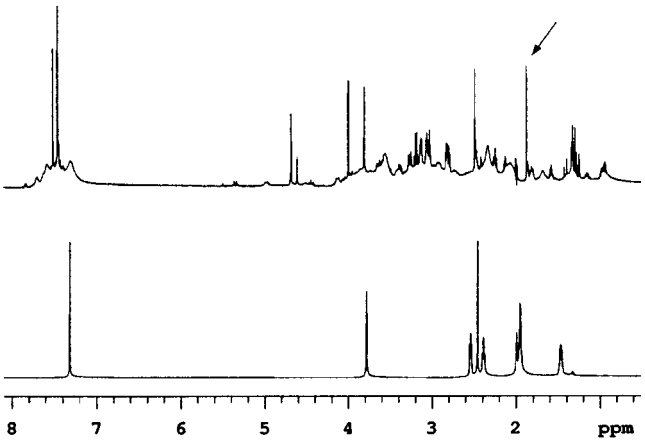
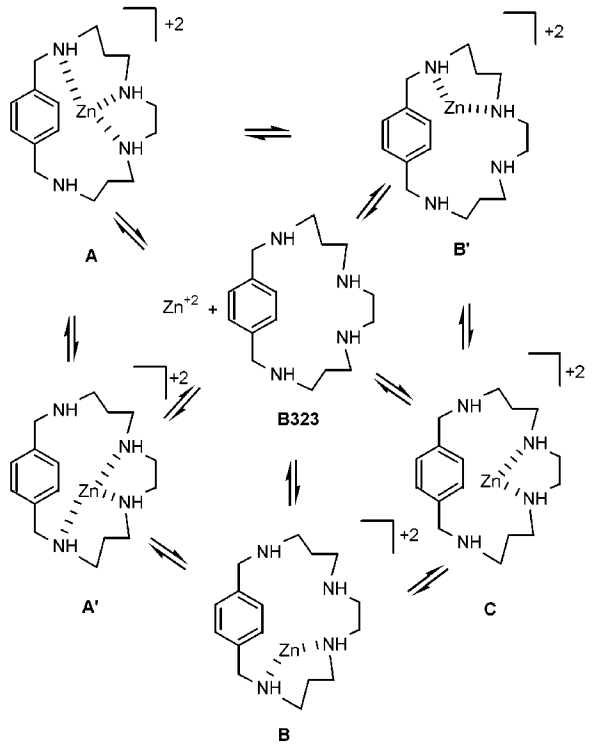


Figure 3. ^{1}H NMR spectra of **B323** (bottom) and **B323-Zn-(II)** (top) in CD_3CN.

Scheme 2



macrocycle **D222** the benzylic and central nitrogen nuclei experiment a shift of 2.4 and 3.2 ppm, respectively, suggesting that both nitrogen atoms contribute to the coordination of the metal cation in a similar way. For ligand **B33**, the observed shifts for benzylic and central nitrogen nuclei are, respectively, 4.6 and 2.1 ppm. which suggest that the benzylic nitrogen atoms are the ones that more intensely contribute to the complex formation. When the NMR experiments were carried at lower temperature (228 K, just above freezing point of acetonitrile) similar spectra where obtained both for **B33** and **D222** complexes confirming the high conformational mobility of these species.

In the case of the complex **B323-Zn(II)**, up to five different nitrogen resonances where observed in the amine region of the ^{1}H−^{15}N GHMBC spectrum (see Figure 4). This situation is accompanied by a very complex ^{1}H NMR spectrum (Figure 3). These data, together with those obtained from ^{1}H−^{13}C correlation,

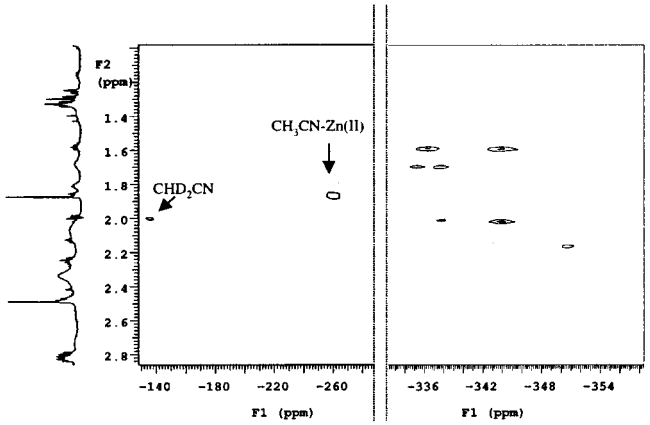


Figure 4. ^{1}H-^{15}N GHMBC correlation for **B323-Zn(II)** in CD_3CN (CHD_2CN was present in small quantities in the solvent used for these experiments).

indicate the presence of different complex species that coexist in solution in slow equilibrium on the NMR time scale. For example, correlation with aromatic carbon atoms in the ^{1}H−^{13}C HMBC spectrum reveals the presence of three different ^{1}H NMR benzylic signals.

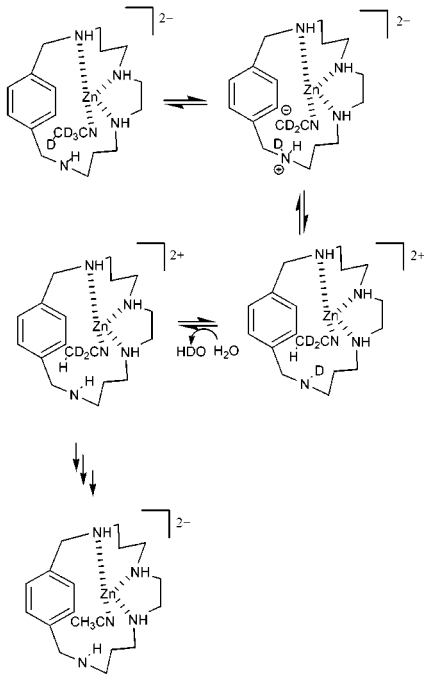
These facts point out that it is not accurate to ascribe the observed properties for these complex species (reactivity in N-functionalization for example) to the presence of a single predominant species such as those depicted in Scheme 2 as A and A′.[1b] In this system three different complex species could be considered. The first one (A and A′) would involve the coordination of three out of the four nitrogen atoms. On the contrary, the other two complexes would involve the coordination of only two nitrogen atoms: one benzylic and one central (B and B′) or the two central nitrogen atoms (C). An analysis of the ^{15}N chemical shifts revealed signals slightly shifted upfield that tentatively could be ascribed to noncoordinated benzylic and central nitrogen atoms of complex species. ($\delta = -350.6$ and -344.0 ppm, respectively; δ values for uncomplexed **B323** in CD_3CN are -347.3 and -341.3 ppm, respectively). The other three signals (-335.4, -336.4, and -338.0 ppm) are considerably shifted downfield and would correspond to nitrogen atoms coordinated to the Zn(II) cation. This situation, as well as the very complex NMR spectra observed, would be explained through the consideration of the existence of a slow equilibrium between the complex species A and B (see Scheme 2). The participation of complex species such as C instead of B should be discarded, since their presence in solution would not explain the resonances ascribed to noncoordinated central nitrogen atoms. The spectra were not simplified when recorded at higher temperatures (354 K, just below acetonitrile boiling point), indicating a high energetic barrier for the exchange between the isomeric complex species present.

An interesting aspect of the complex species **B323-Zn-(II)** in acetonitrile-d_3 emerged when the ^{1}H spectra was analyzed in more detail. It was noticed that a sharp singlet appeared at 1.87 ppm after several minutes of the complex formation (see in Figure 3 the signal pointed with an arrow). ^{1}H−^{13}C NMR correlation indicates that this signal corresponds to protons attached to a carbon atom whose resonance appears at 10 ppm. Morevover, the long range ^{1}H−^{13}C correlation indicated that those protons were coupled with a carbon atom signal at 165 ppm. Interestingly enough, this ^{1}H signal also correlates

with a ^{15}N resonance at −260 ppm in the HMBC experiment (see Figure 4). These data altogether indicate the strong coordination of solvent molecules to the metal cation. This agree with the mentioned $^{1}H-^{13}C$ correlation, the ^{13}C signals at 10 and 165 ppm correspond, respectively, to the nitrile and methyl carbon atoms of a coordinated acetonitrile molecule. The ^{15}N resonance at −260 ppm presents a chemical shift that is in accordance with those described for acetonitrile molecules where the nitrogen atom is donating its electron density, like in the case of protonated or N-alkylated acetonitrile molecules (for example, in the case of $[CH_3CN-H]^+$ the chemical shift value reported is −239.2 ppm).[3b] Obviously, the singlet at 1.87 ppm detected by ^{1}H NMR must correspond to solvent molecules which have experienced H−D exchange with the protons from water molecules present in the medium. Most likely once the solvent molecules are coordinated they became activated for the mentioned exchange which would take place in a few minutes. This would explain that after the complex formation some time is needed before the signal at 1.87 ppm is observed. To confirm this hypothesis, a few microliters of D_2O were added to the dissolution, which caused the disappearance of the signal of the coordinated acetonitrile as a result of H−D exchange. Assuming a first-order kinetics (being the limiting step the deprotonation of acetonitrile), a half-life time of 57 min was measured. Further evidence of acetonitrile complexation was obtained by ES mass spectroscopy where a peak at 208.6 (double charged with the isotopic pattern of Zn) could be assigned to the complex $Zn(B323)(CH_3CN)(H_2O)_2$. The fragmentation of this ion lead to a peak at M = 188.09 assigned to the loss of the coordinated acetonitrile molecule. However, it has to be noted that the concentration of the samples for MS is much lower than that of the dissolution analyzed by NMR, and therefore the complex species present may not be exactly the same. In the experiments carried out in the absence of macrocycle or Zn(II) the process described above was not observed. Negative results were also obtained for the complexes formed by the macrocycles **B33** and **D222**.

A proposed mechanism for the acceleration of the H−D exchange in acetonitrile is outlined in Scheme 3. The coordination of acetonitrile to the Zn(II) cation activates the hydrogen (deuterium) atoms of the methyl group and, with the assistance of the noncoordinated nitrogen atom, H−D exchange occurs. The participation of this nitrogen atom could be direct of through the mediation of water molecules. Assuming this mechanism, the system **B323-Zn(II)** can be considered as a minimalist artificial enzyme that would consist on a metal with vacant coordination positions and a nucleophilic group (the free amino function) placed in the right place to act as a general acid−base catalyst. The Zn(II) complex would stabilize the intermediate ketimide in a situation that is related, for example, to the Kimura's model of class II aldolases in which a modified cyclen−Zn(II) complex stabilizes enolates.[13] Our model is in accordance with the results described for the same macrocycle in H_2O where the **B323-Zn(II)** complex was found to act as a Carbonic Anhydrase model.[14a] There it was also shown the importance on the noncoordinated nitrogen atom in the vicinity of the metal cation. Macrocycle **B323** has also been described as especially useful in the activation of ligand substitution reactions on some platinum complexes.[14b]

Scheme 3



Experimieental Section

Propylamine, ethylendiamine, *N*,*N*′-bis(aminopropyl)ethylendiamine, and zinc triflate were purchased from Aldrich. Macrocycles **BF323**, **B323**, **D222**, and **B33** were obtained as described in the literature.[1a] ATP was purchased from Sigma. **B323(Me)$_4$** was prepared in quantitative yields from **B323** and **D222** using the Eschweiler−Clarke procedure.[10]

Potentiometric Studies. The potentiometric titrations were carried out in 0.15 mol dm^{-3} $NaClO_4$ solutions at 298.1 ± 0.1 K, by using the equipment (potentiometer, buret, stirrer, microcomputer, etc.) that has been fully described.[15] The acquisition of the emf data was performed with the computer program PASAT.[16] The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen concentration probe by titration of accurately known amounts of HCl with CO_2-free NaOH solution and determining the equivalent point by the Gran's method[17] which gives the standard potential of the electrode, $E°'$, and the ionic product of water. The computer program SUPERQUAD[18] was employed to calculate the protonation and stability constants. The DISPO[19] program was used to obtain the distribution diagrams. At least three titration curves were performed for each one of the studied systems. Concentrations of the nitrogenated ligands varied in the range $1 \times 10^{-3}-10^{-2}$ mol dm^{-3}. The titration curves for each system were treated as a single set or separately without

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(19) DISPO is a program to determine the stability constants, mass balance equations and distribution of species in multiequilibria systems created by Prof. A. Vacca from the University of Florence, Italy, unpublished work.

significant variations in the values of the equilibrium constants. Furthermore, the sets of data were merged together to obtain the final values of the stability constants.

NMR. The NMR experiments involving ^{15}N were recorded on a Varian INOVA 500 spectrometer equipped with a 5 mm tunable, broadband, inverse-detection probe. The spectrometer operates at 500 MHz for ^{1}H, and 50.7 MHz for ^{15}N. The spectra were determined at 30 °C. Neat nitromethane was used as reference (0 ppm) to calculate ^{15}N chemical shifts. $^{1}H-^{15}N$ HMBC-type correlation experiments were recorded using the GHMQC Varian pulse sequence setting up the experiment for long-range couplings. The studies were carried out in solutions containing 5−15 mg of the nitrogenated ligands dissolved in 0.6 mL of the corresponding deuterated solvent. In general accumulations of 2−8 transients with spectral widths of 4000−12000 Hz and number of increments = 128−512 were used.

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