Journal of Inclusion Phenomena and Macrocyclic Chemistry (2005) 52: 101–107
DOI 10.1007/s10847-004-5794-6

Investigation of Host–Guest Compounds of Cucurbit[*n* = 5–8]uril with Some Ortho Aminopyridines and Bispyridine

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(Received: 19 June 2003; in final form: 2 November 2004)

Key words: cavity binding, cucurbit[5]uril, cucurbit[6]uril, host–guest, portal binding, pyridine binding

Abstract

Host–guest complexes of cucurbit[*n* = 5–8]uril and some examples of ortho substituted pyridines or aminopyridines were examined by ^{1}H NMR spectroscopy. Portal binding of two ortho aminopyridine free bases, by cucurbit[5]uril, was observed in ^{1}H NMR spectra. Combined cavity and portal binding in cucurbit[6]uril were observed for both the free base 2-aminomethylpyridine, **ampy**, the HCl salt, **ampy·1HCl,** and the salt of 2,2′-bispyridine, **bpy·1HCl.** Two novel complexes were formed with cucurbit[6]uril. The free base **ampy** as a dual occupant, formed a 2:1 complex, and **bpy·1HCl** formed a stable asymmetric 1:1 complex. Only portal binding of 2,6-bisaminomethylpyridine and its salts was observed for cucurbit[6]uril. Fast exchange of the free base and pyridineammonium salts was observed for cucurbit[7-8]uril.

Introduction

Cucurbit[*n*]uril, Q[*n*], is a relatively new family of molecular hosts [1]. They are rigid macrocycles with a unique cavity [2], rimmed by carbonyl oxygens. Ingress and egress of guests is controlled by the size of the carbonyl portal. The portals of the Q[*n*] family range in size from 2.4 Å, Q[5] [1a–b], to the largest, 13.1 Å Q[10] [3]. A number of Q[*n*]–guest interactions have been studied, with Q[6] [4], the first of the Q[*n*] discovered, receiving greatest attention to date. Q[6] forms stable inclusion complexes with a number of amines and diamines through a combination of dipole–ion, hydrogen bonding and hydrophobic interactions [4c–e]. The higher homologues Q[7–10] generally form inclusion complexes with guests having a larger cross-section than that of a benzene ring [3, 4a, f, 5].

In this work, we wish to report the interaction and formation of host–guest complexes between Q[5–8] with a selection of ortho substituted aminopyridines, pyridineammonium ions and 2,2′- bispyridine, which unambiguously demonstrate cavity binding and/or portal binding. This extends the examples of already known portal binding involving metal ions, NH_4^+ or other organic ammonium ions [4b, 6–8]. Organic ammonium ion binding generally occurs in conjunction with cavity binding [4]. One example of portal binding without cavity binding has been demonstrated in the solid state of a crystal structure of Q[5] and 1,6 hexanediammonium chloride [1d]. Apart from our observations there is one other report of the binding of an organic amine in Q[6] as a free base [2].

The following pyridines or aminopyridines were examined as the free base or their hydrochloride salts: 2-aminomethylpyridine, **ampy, ampy·1HCl**; 2-aminoethylpyridine, **aepy, aepy·1HCl**; 2,2′-bispyridine, **bpy, bpy·1HCl**, and 2,6-bisaminomethylpyridine, **bampy, bampy·2HCl** (Figure 1). Each potential guest salt was prepared by the addition of 2 M HCl and crystallised from ethanol or acetone. Conventionally, meta or para substituted aminopyridines, which thread relatively easily through Q[6–8] [9], have been studied. In most cases these guests were studied in the conjugate acid form. Our objective was to study the effect of a localized positive charge near the pyridine N by using ortho pyridineammonium ions compared to the free base. We describe the effects on Q[5–8] by **ampy** and **aepy** and **bampy** as a base or their conjugate chloro acids**.** In addition, 2,2′-bispyridine, which can be protonated once or twice depending on pH, was studied for binding [10]. The separations between protonated amines and the pyridine N are short, and hence were expected to have different binding properties to those of para or meta pyridineammonium or pyridinium cations.

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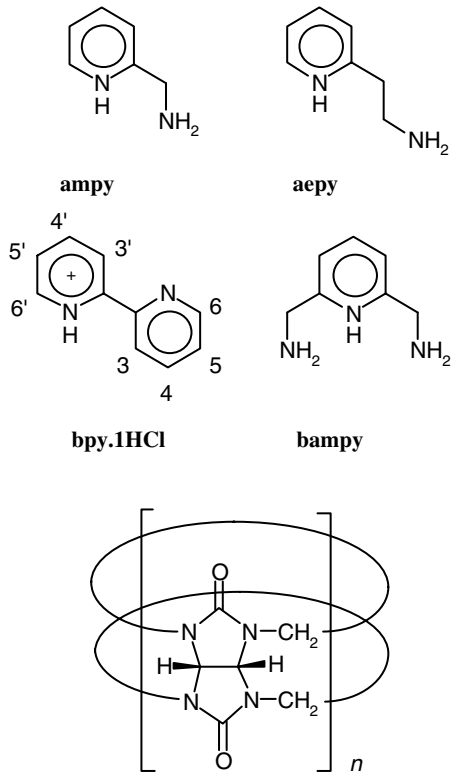

Figure 1. Pyridine and aminopyridine guests and the Q[*n*] hosts.

Experimental

2-Aminomethylpyridine, 2-aminoethylpyridine and 2,2′-bispyridine were obtained from Aldrich and used without further purification. 2,6-Bisaminomethylpyridine [11] and cucurbit[5–8]uril [1c], were prepared and purified in our laboratories. The corresponding HCl salts **ampy·1HCl**, **aepy·1HCl**, **bpy·1HCl**, **bampy·2HCl** and that of pyridine were prepared by dissolving the pyridines in 2 M HCl followed by crystallization with ethanol or acetone, collecting them by filtration and drying.

For the study of Q[*n*] host–guest complexation, 2.0–2.5 × 10^{-3} mmol samples of Q[*n*] in 0.5–0.7g D_2O with [aminepyridine]/[Q[*n*]] ranging between 1 and 100 were prepared. In some cases D_2O solutions of Na_2SO_4 0.1–0.2 M, were used to aid the solubility of Q[*n*], in particular, where amine alone was insufficient to solubilize them. A variation in the concentration of Na_2SO_4 had no measurable effect upon the binding of guests. Competitive binding experiments between alkali metal cations and the ortho substituted pyridines were prepared by combining the components in D_2O and heating until all was dissolved then cooled. The ^1H and ^{13}C NMR spectra and 2D NMR spectra were recorded at 20 °C on a VARIAN INOVA-400 spectrometer.

Results and discussion

Q[5–8] have cavities with approximate diameters of 4.4, 5.8, 7.3 and 8.8 Å, respectively. These cavities are accessible from the exterior through two carbonyl-fringed portals of 2.4, 3.9, 5.4 and 6.9 Å diameter, respectively [1]. Inclusion complex formation or cavity binding is generally attributed to hydrophobic forces and van der Waals contact forces. These forces lead to cavity binding of a hydrophobic alkyl or aryl moiety upon entering. Additional stabilization of the complex generally occurs due to the attraction between a cationic head attached to an alkyl or aryl moiety and the dipoles associated with the electron-rich carbonyl portals of Q[*n*]. The relative importance of each of the forces is dependent on the aqueous solubility, geometric shape, hydrogen bonding and the nature of the cation. In this work we explore primarily the role of a series of nitrogen cations and hydrogen bonding in portal binding with Q[5]. Also, by contrast, we examined the competitive cavity and portal binding of these salts with Q[6].

Interaction of Q[5] with ortho substituted aminopyridines and pyridineammonium salts

A surprising binding interaction of Q[5] with an excess of the free bases **ampy** or **aepy** in D_2O solutions of alkali metal cations, was clearly evident from the corresponding ^1H NMR spectra (Figure 2). However, there was no evidence of an interaction between Q[5] and **ampy·1HCl**, **aepy·1HCl**, **bpy** or **bpy·1HCl**. The interaction was significant in that it occurred strongly in the presence of K^+ ions, weakly in the presence Na^+ ions but not at all with Cs^+ ions.

The physical dimensions of the aromatic ring/s of the three pyridines or pyridinium ions (>4.3 Å) excludes their entry into the cavity of Q[5] (dia. 4.4 Å), as the portal opening is only 2.4 Å in diameter. The intrusion of amine or ammonium arm into the cavity is excluded on the basis that there is no chemical shift effect on the methylene protons of **ampy** or the ethylene protons of **aepy**. Commonly an upfield shift is observed for protons within the cavity of Q[*n*] [4]. However, the appearance of two sets of well-defined doublets with a separation of 0.08 ppm, for one set of the non-equivalent methylene protons of Q[5] between 4.1 and 4.3 ppm, suggests a close association of **ampy**, or **aepy**, with the portals of Q[5]. This is also supported by a very small effect on the methine protons. The second set of upfield resonances indicate that a complex is formed with Q[5] that is in slow exchange on the NMR time scale. The ratio between the two sets of doublets (between 4.1 and 4.3 ppm) was variable and dependent upon the concentration of K^+ ions or **ampy/aepy**. In addition, if K^+ ions were replaced by Cs^+ ions this effect was not observed. Na^+ ions gave a small effect. A plausible explanation is a portal inclusion complex, whereby a slow exchange is observed for competitive binding between Q[5] and either K^+ ions or aminopyridine (**ampy** or **aepy**). The set of methylene and methine proton resonances of Q[5] as a K^+ ion complex are indicated by wedges. No interaction with Q[5] was found with bispyridine or its HCl salt. The interaction of **ampy** and **aepy** with Q[5] to

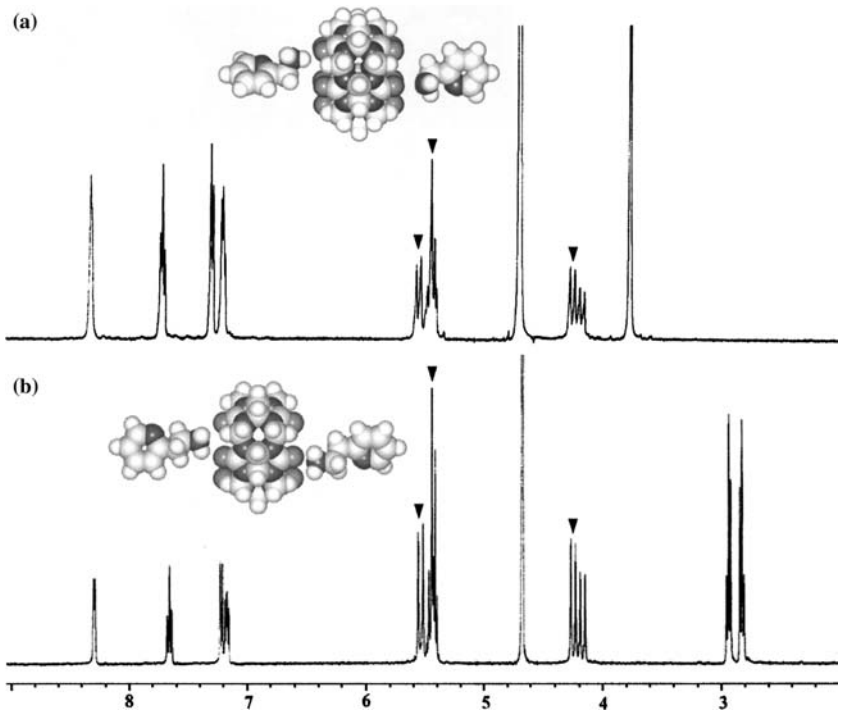

Figure 2. ^{1}H NMR spectra in D_2O/KCl and molecular models demonstrating likely interactions of: (a) Q[5] and **ampy**; (b) Q[5] and **aepy**. Wedges indicate proton resonances for the K^+@Q[5] complex.

form slow exchanging complexes, in contrast to the lack of complex formation with **bpy** or **bpy·1HCl**, could reflect an ability to hydrogen bond to the portal. Under our preparation conditions, **bpy** protonates only once [10]. **Bpy·1HCl** appears to have insufficient charge or capacity to hydrogen bond to form a competitive complex with slow exchange or is not a good fit for optimum interaction. However, we cannot discount portal binding completely, only that if it occurs exchange is faster than the NMR time scale.

The presence of K^+ ions has previously been demonstrated to show an increased formation of Q[5] during the synthesis of Q[*n*] [12]. Further, Q[5] has limited solubility in aqueous solutions containing K^+ ions resulting in crystallizing of a potassium salt complex of Q[5] [12]. Both of these results suggest that Q[5] has a high affinity for K^+.

The importance of the pyridine ring in Q[5] complex formation was investigated using benzylamine. Benzylamine has two structural similarities to **ampy**: a 1° amine centre α to an aromatic ring and an aromatic ring. Comparatively, these two amines demonstrate a similar interaction with Q[5], albeit the extent of complex formation with benzylamine is reduced. The competitive binding between Q[5] and either K^+ and the aminopyridines, **ampy** or **aepy,** appears to be a finely balanced dipole–ion interaction compared to hydrogen bonding and perhaps a contribution from van der Waals contact energies. The relative binding affinities have not been determined.

Clearly, dipole–ion interactions through a charged pyridinium or an ammonium ion are insufficient to explain the formation of the relatively stable competitive complexes.

Interaction of Q[6] with ortho substituted aminopyridines, pyridineammonium and pyridinium salts

The examination of D_2O solutions of Q[6], the ortho substituted pyridines, and the conjugate acids of **ampy**, **aepy**, **bpy** and **bampy** by ^{1}H NMR spectroscopy showed that slow exchanging inclusion complexes were formed. In the case of **ampy** and **bpy** we demonstrated that a combined portal and cavity inclusion complex was formed, and that with **bampy** only a portal complex was formed. By contrast, **aepy** and its conjugate acid showed fast exchange and cavity binding.

Ampy and Q[6]

Two sets of signals for the protons of the **ampy** guest were observed in the ^{1}H NMR spectra (Figure 3). The cavity-bound guest proton resonances (indicated by wedges) occurred upfield of the unbound **ampy**. This is a common observation for guests bound in the cavity of Q[*n*] [3, 4]. A downfield shift of 0.48 ppm for the methylene protons of **ampy** was also observed. This indicates that these protons are at the portal in the deshielding zone of the carbonyls [4].

When Q[6] and **ampy** were combined in a ratio of 1:2, respectively, an inclusion complex (or complexes) was formed with a Q[6] to **ampy** ratio of 1:0.75, respectively, suggesting a near 1:1 complex (Figure 3a). However, when the proportion of **ampy** was increased from 2 to 12, a 1:2 complex (Q[6]: **ampy**, respectively) was formed (Figure 3b). This is evident from the mole ratio of

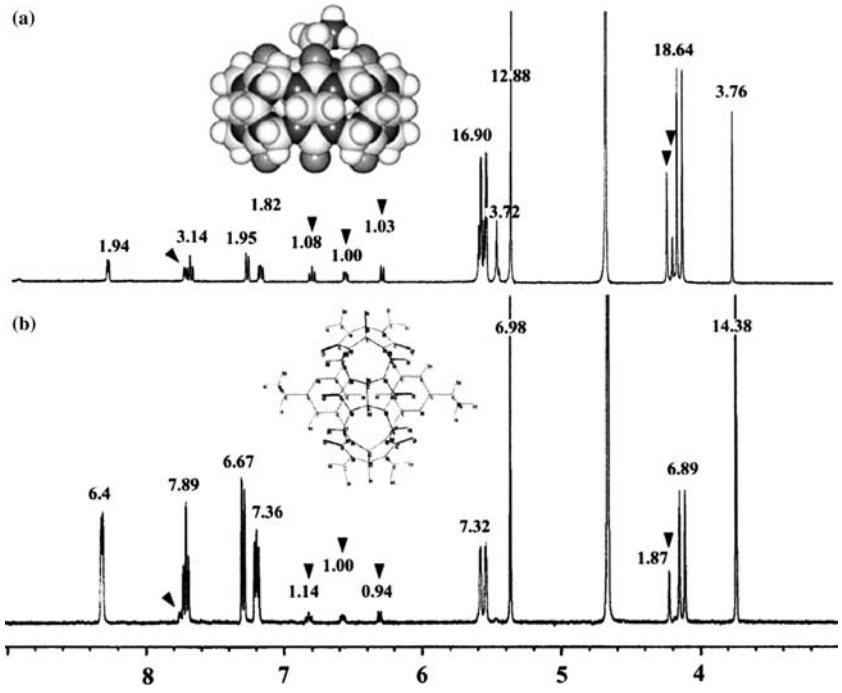

Figure 3. ^{1}H NMR spectra in D_2O/Na_2SO_4 and molecular models demonstrating likely interactions of Q[6] and **ampy** for two different ratios: (a) Q[6]: **ampy** at 1:2; (b) Q[6]:**ampy** at 1:12. Wedges indicate bound proton resonances for **ampy**. The integrals are indicated above each set of resonances.

bound guest to Q[6] (~1:1.7), based on the average of the integrals of the clearly defined resonances for the two components (3 of the 4 pyridine resonances at 6.31, 6.59, 6.82, and the Q[6] resonances at 4.14, 5.37, 5.57 ppm). Approximately 70% of the Q[6] was in this form. Not only does $(ampy)_2$@Q[6] demonstrate both cavity and portal binding, but also a dual occupancy of Q[6]. Dual occupancy was very dependent upon the amount of the excess **ampy.** This is the first demonstration of a stable dual occupancy of Q[6]. While dual occupancy necessarily does occur in the catalyzed synthesis of triazole in Q[6] [4d, 13], and dual occupancy has been demonstrated in Q[8][4a], two pyridines in the cavity of Q[6] was unexpected. In contrast, the ammonium salt **ampy·1HCl,** failed to form a dual occupant complex, and instead was always 1:1. This result, most likely, reflects the influence of the dipole–ion interaction with the ammonium ion forcing the pyridine ring, on average, deep into the cavity. Protonation of the pyridine ring to give **ampy·2HCl** in 10 M DCl in the presence of Q[6] showed no cavity or portal binding.

Strong binding of **bpy·1HCl** *and Q[6]*

As with the previous example, both cavity binding and portal binding was demonstrated for **bpy·1HCl** and Q[6] in D_2O. In the absence of protonation, however, neither cavity nor portal binding was observed. To ensure **bpy** was not protonated, we added NaOD to neutralize samples since Q[6] normally contains at least one molecule of acid of crystallization [1c].

The ^{1}H NMR spectra exhibit two sets of signals for the bound (indicated by wedges) and unbound protons of **bpy·1HCl**, and two sets of methylene proton doublets for Q[6] (Figure 4). Above a ratio of 1:1 of Q[6] to **bpy·1HCl,** the pairs of Q[6] methylene proton doublets remain equal in intensity regardless of an increase in the proportion of **bpy·1HCl**. In addition, there was no evidence of dissociated bpy·1HCl@Q[6] after the solution was diluted to 10^{-4} mol/l. This indicates that a strong interaction exists between Q[6] and **bpy·1HCl**, and that the association constant is $>10^5$ M^{-1}.

The resonances in the ^{1}H NMR spectrum show that the two pyridine rings of **bpy·1HCl** are in different magnetic environments. The spectrum shows 8 proton resonances, with one ring showing proton resonances shifted upfield by 0.8–1.5 ppm and the other ring protons shifted downfield by 0.15–0.37 ppm (Figure 4). Clearly this shows that one ring is contained within the cavity and that the other is contained within the portal. The very large upfield shifts of the protons on the pyridine ring indicate deep cavity binding. Additionally, the magnitude of both the upfield and downfield shifts may also indicate a localization of the charge on the ring outside the cavity. A comparison of the integrals of the protons of the bound **bpy·1HCl** with the protons of Q[6] revealed the complex to be 1:1. This 1:1 state was unaffected even with a large increase in the proportion of **bpy·1HCl**. The consequence of a 1:1 complex is an asymmetric structure with part of the guest protruding from only one portal, hence the 8 proton resonances for **bpy·1HCl**. Additional supporting evidence for an asymmetric structure are the two sets of equally intense doublets for the methylene protons of Q[6], and one singlet for the methine protons. This indicates that the guest affects each of the portals differently, with

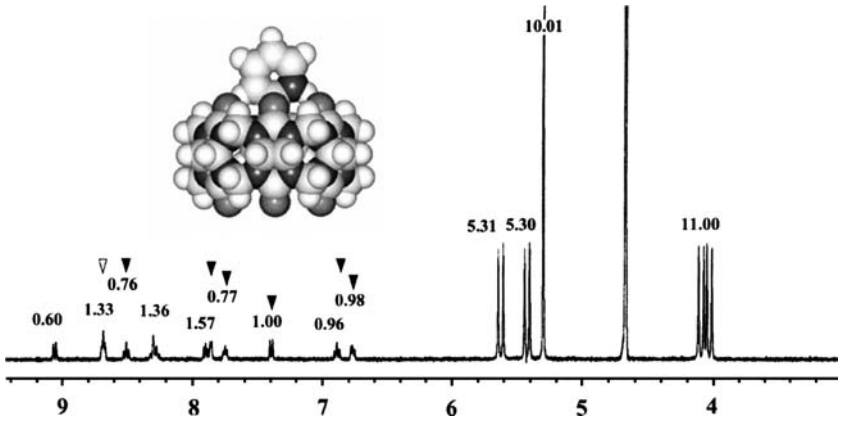

Figure 4. ^{1}H NMR spectra in D_2O and molecular models demonstrating a probable interaction of Q[6] and **bpy·1HCl** for a ratio of Q[6]:**bpy·1HCl** at 1:1.3. Wedges indicate bound proton resonances for **bpy·1HCl**. The integrals are indicated above each set of resonances.

bpy·1HCl protruding from only one portal. Our assignments and interpretation of the structure were further confirmed by the 2D-COSY spectrum (Figure 5). The resonances at 6.84, 6.88, 7.46, and 7.84 ppm are the cavity bound pyridine protons 5, 4, 3 and 6, respectively and the resonances at 7.91, 8.53, 8.70 and 9.02 ppm are the portal bound pyridine protons 4′, 5′, 3′ and 6′ respectively. The resonance 3′ is obscured by the protons of the unbound pyridine resonance of 6 and 6′.

The deep cavity binding indicated by the large upfield shifts shows that the pyridine protons are at the centre of the cavity of Q[6]. The observation that bispyridine is protonated on only one ring also supports the proposed depth into the cavity. ^{1}H NMR spectra of bispyridine and Q[6] in 0.1 M DCl/D_2O show the same result as described earlier, but at 10 M there was no discernable binding. At 10 M, bispyridine is protonated twice [10]. Dual occupancy of Q[6] by **bpy·1HCl** was not observed. This may indicate a higher degree of flexibility of **ampy** to manoeuvre within the cavity to allow ring stacking, or alternatively, the pyridine rings are not as deep within the Q[6] cavity. The downfield shift for the methylene protons of **ampy** or **ampy·1HCl** indicate limited cavity penetration of the pyridine ring.

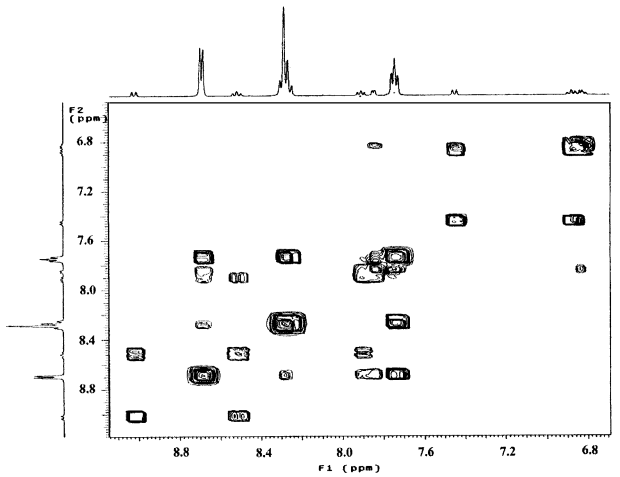

Figure 5. 2D-COSY spectrum of the pyridine proton resonances of unbound and bound **bpy·1HCl** in Q[6]. The Q[6]: **bpy·1HCl** ratio is 1:12.

The two pyridines **aepy·1HCl** and **bampy·2HCl** appear to exhibit anomalous behaviour in their interaction with Q[6] in D_2O. The ^{1}H NMR spectra of the solutions containing **bampy·2HCl** indicated only portal binding while those containing **aepy·1HCl** showed cavity binding. The interaction of **bampy·2HCl** with Q[6] was evident from the appearance of a second set of Q[6] proton resonances. These resonances increased in intensity with increasing concentration of **bampy·2HCl**. However, surprisingly, there appeared to be no penetration by the pyridine ring into the portal. This contrasts with the demonstrated cavity interaction of **ampy·1HCl** already discussed, and with pyridine HCl and Q[6] (Figure 6). Pyridine HCl at a ratio of 1:1 with Q[6] shows broadening of the pyridinium ring protons, indicating average to fast exchange. As the proportion of the pyridine HCl is increased up to 10 times, the rate of exchange decreases, and clearly defined proton resonances appear upfield at 6.60, 7.07 and 7.72 ppm for the pyridinium ring protons. A new set of downfield proton resonances also appear for one of the Q[6] methylene doublets at 4.23 ppm, and the methine at 5.40 ppm. The remaining methylene doublet was unchanged. Obviously, the association of **bampy·2HCl** with the portal of Q[6] is driven largely by the ion–dipole interaction of the dication of **bampy·2HCl** and the carbonyl O.

The binding behaviour of **aepy·1HCl** in Q[6] appeared anomalous considering the relatively minor structural difference between **aepy·1HCl** and **ampy·1HCl,** but these two examples reflect subtle differences affecting the balance of competing binding modes. This scenario results in a fast exchange detected only as cavity binding by ^{1}H NMR spectroscopy. A single set of averaged proton signals was observed for **aepy·1HCl**. These signals were shifted upfield by 0.26–0.4 ppm for the pyridine protons, and downfield by 0.14 ppm for the protons of the ethane arm (Q[6] to **aepy·1HCl** ratio of 1:0.25). In addition the resonances are broadened, and as the proportion of guest is increased to >1 the resonances shift to the chemical

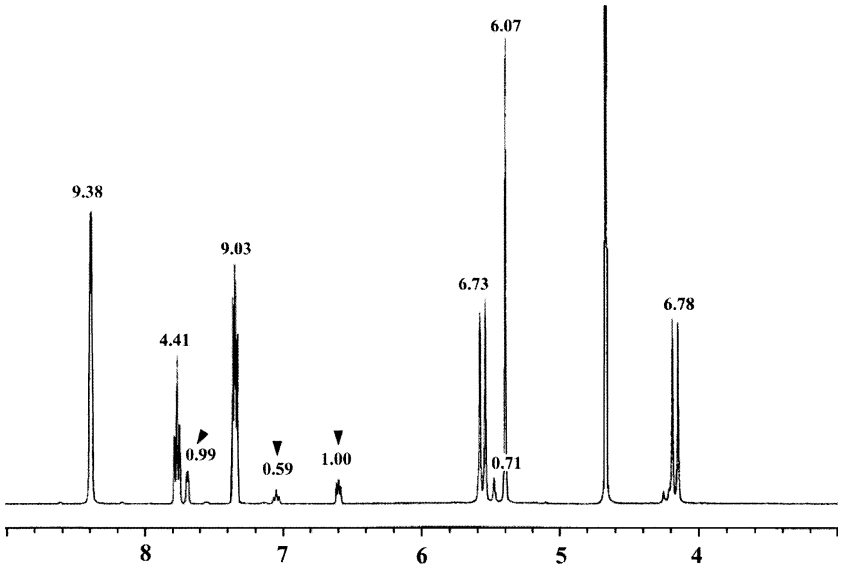

Figure 6. ^{1}H NMR spectrum in D_2O of pyridine HCl salt and Q[6]. Wedges indicate bound proton resonances. The integrals are indicated above each set of resonances.

shift of **aepy·1HCl** in the absence of Q[6] (and decrease in broadness).

Q[7] and Q[8] with ortho substituted pyridines and pyridineammonium ions

Given the increased portal size of Q[7] and Q[8], 5.4 and 6.9 Å in diameter, respectively, ingress and egress would be facile. This was observed to be the case in the ^{1}H NMR spectra of Q[7] or Q[8] (together with guests **ampy, aepy**, **bpy** and **bampy** and their HCl salts), which showed broadened proton resonances for the guests. This indicated binding with fast exchange. In addition, and of particular note, was the increased solubility of Q[8] in 0.2 M solutions of **bpy·1HCl**; ~50 times compared to water. This indicates a likely ion–dipole interaction between Q[8] and **bpy·1HCl**. The ability to increase the solubility of Q[8] under moderate pH conditions is significant as Q[8] normally has low solubility.

Conclusion

We have been able to demonstrate, using ^{1}H NMR spectroscopy, either portal binding or the combination of portal and cavity binding in Q[5–8] for the aminopyridines **ampy**, **aepy** and **bampy,** and bispyridine **bpy**, which are all ortho substituted pyridine systems. Portal binding of the free bases of **ampy**, **aepy** and **bampy** was demonstrated through changes in the magnetic environment of the Q[5] protons or, in the latter example, the Q[6] protons. These changes were observed in their ^{1}H NMR spectra, in most cases as sharp signals. Cavity binding in Q[5] with the range of guests used in this study was excluded due to the limitation of the portal size, but these guests enabled the demonstration of a distinctly different mode of binding of an organic substrate by Q[*n*]. With Q[6], both cavity and portal binding were demonstrated with **ampy, ampy·1HCl** and **bpy·1HCl**, and only portal binding with **bampy·2HCl**. A strong 1:1 deep cavity inclusion complex was formed between Q[6] and **bpy·1HCl** and an unusual 1:2 inclusion complex was formed, as much as 70%, between Q[6] and **ampy**.

Acknowledgements

We thank P. Newitt for assistance in the preparation of this manuscript. H.-Y.F, S.-F.X, Q.-J.Z, Z.T and J.-X.Z acknowledge the support of the International Collaborative Project of Guizhou Province (ICPGP), the Key Project of the Natural Science Foundation of Guizhou Province (KPNSFGP) and the Natural Science Foundation of China (NSFC).

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