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Supramolecular assemblies and modes of binding of the 1,6-hexanedipyridinium ion and the HCl salt of *N,N'*-bis(3-pyridylmethyl)-diaminoethane, with the symmetrically substituted tetramethylcucurbit[6]uril

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Supramolecular assemblies and modes of binding of the 1,6-hexanedipyridinium ion and the HCl salt of *N*,*N*′-bis(3-pyridylmethyl)-diaminoethane, with the symmetrically substituted tetramethylcucurbit[6]uril

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The molecular binding behaviour of the symmetrically substituted tetramethylcucurbit[6]uril (TMeQ[6]) was examined in relationship to the two pyridine-based molecular guests 1,6-hexanedipyridinium dication ($Hdipy^{2+}$) and the HCl salt of *N*,*N*′-bis(3-pyridylmethyl)-diaminoethane (Ediamp). The interactions and binding modes of each guest with TMeQ[6] are discussed using solution results (^{1}H NMR spectroscopy) and solid-state findings (single-crystal X-ray diffraction), to evaluate interactions in common. Supramolecular structures are formed that rely on a combination of the now typical driving forces associated with Q[*n*] as a molecular host, which are dipole–ion, hydrophobic, H-bonding and in the present examples include π···π and C—H···π interactions.

Keywords: tetramethylcucurbit[6]uril; 1,6-hexanedipyridinium dication; *N*,*N*′-bis(3-pyridylmethyl)-diaminoethane; self-assembled; binding modes

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Introduction

A number of solid-state supramolecular assemblies based on cucurbit[*n*]uril, Q[*n*], as building blocks have been reported (*1–24*). Many of these assemblies have been derived from Q[*n*] where metals ions are involved (*1–15*). The metal ions are either coordinated directly with the oxygen atoms of the portals of Q[*n*] or indirectly through secondary components such as water molecules. In some cases, metal ion coordination is to an organic component and this unit is then threaded through or associated with Q[*n*]. Solid-state assemblies involving organic components and Q[*n*] without the presence of metal ions are less common (*1a*, *16–24*). The intrinsic feature of these metal-free constructs is that the organic components are usually salts that have a cationic part that interacts favourably with Q[*n*] electronegative portals. These metal-free supramolecular assemblies as solids facilitate an understanding of the chemical interrelationship between the various organic components relative to Q[*n*], and these interrelationships are complementary in some respects to the findings in solution. Variations in Q[*n*] such as the introduction of alkyl substitution into Q[*n*] add another dimension to the range of possibilities for supramolecular assemblies (*16–22*). We have recently reported observations which indicate that the alkyl substitution has an effect on the chemical and physical properties of the portals and cavities of Q[*n*] that modify their binding behaviour (*14*, *17*). Given that the extent of these effects has yet to be thoroughly explored, it is important to investigate a variety of potential guests with alkyl-substituted Q[*n*].

Here, we report our findings in relationship to the self-assembly of the hosts 1,6-hexanedipyridinium ion ($Hdipy^{2+}$) and the HCl salt of *N*,*N*′-bis(3-pyridylmethyl)-diaminoethane [Ediamp·2HCl; (*25*)] with the molecular host tetramethylcucurbit[6]uril (TMeQ[6]) which is symmetrically substituted (Figure 1). The interactions of the host TMeQ[6] with the two guests were determined using ^{1}H NMR spectroscopy in solution and using single-crystal X-ray diffraction in the solid state.

Experimental

Materials

TMeQ[6] was prepared and purified according to the method established in our laboratories (*26*). Reagents and solvents were used without further purification.

Synthesis of $Hdipy^{2+} \subset$ TMeQ[6]

The dication $Hdipy^{2+}$ as the bromide salt was prepared by methods similar to those previously described (*25*).

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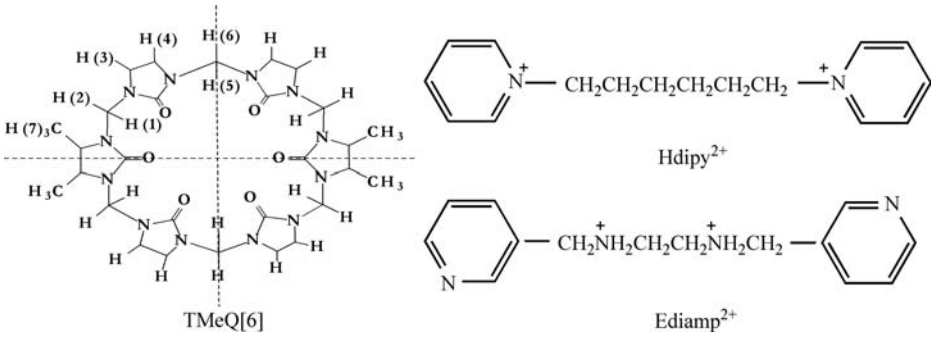

Figure 1. Structures of TMeQ[6] and the guests $Hdipy^{2+}$ and $Ediamp^{2+}$ dications.

$Hdipy^{2+}$(0.12 g, 0.30 mmol) was dissolved in H_2O (50 ml) and, to this solution, TMeQ[6] (0.24 g, 0.20 mmol) was added. The mixture was heated to dissolve the host and the guest and then filtered. The filtrate was set aside for 3 weeks, which resulted in the deposit of colourless crystals of $Hdipy^{2+} \subset TMeQ[6]{\cdot}2Cl^-$. TMeQ[6] often has HCl of crystallisation, which is the likely source of Cl^- replacing Br^-.

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Synthesis of $Ediamp^{2+} \subset TMeQ[6]{\cdot}2Cl^-$

Following a method similar to a reported procedure (*27*), a solution of 3-pyridine carboxaldehyde (2.12 g, 20 mmol) in $CHCl_3$ (20 ml) was added to a stirred solution of ethylenediamine (0.6 g, 10 mmol) in $CHCl_3$ (40 ml) in an ice bath over a period of 1 h. The solvent was removed by evaporation, which yielded a solid. This solid was dissolved in ethanol (30 ml), cooled to 0°C and a solution of $NaBH_4$ (1.5 g, 40 mmol) in ethanol (50 ml) was added dropwise over 5 h. The mixture was filtered, and the filtrate was neutralised with HCl to pH 6–7 and filtered again. Concentrated HCl (10 ml) was added to the filtrate and the mixture was allowed to stand at 4°C overnight to afford colourless crystals of Ediamp·4HCl. Ediamp·4HCl (0.078 g, 0.20 mmol) was dissolved in H_2O (50 ml) and to this solution, TMeQ[6] (0.24 g, 0.20 mmol) was added. The mixture was heated to dissolve the host and the guest and then filtered. Slow evaporation of the filtrate over a period of 4 weeks provided rod-shaped colourless crystals of $Ediamp^{2+} \subset TMeQ[6]{\cdot}2Cl^-$.

Instrumentation and measurements

The solution studies were carried out using 2.0–2.5 mmol samples of the guest in 0.5–0.7 g of D_2O and the concentrations of TMeQ[6] were gradually increased. Their ^1H NMR spectra were recorded at 20°C on a Varian INOVA-400 spectrometer.

The crystal structures of $Hdipy^{2+} \subset TMeQ[6]{\cdot}2Cl^-$ and $Ediamp^{2+} \subset TMeQ[6]{\cdot}2Cl^-$ were determined using a Bruker SMART Apex-II CCD diffractometer with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected at 223 K in the range $1.50 \leq \theta \leq 25.01$ for TMeQ[6]–$Hdipy^{2+}$ and $1.49 \leq \theta \leq 25.00$ for TMeQ[6]–$Ediamp^{2+}$. The structures were solved by direct methods and refined using full-matrix least squares on F2 (SHELXTL, Bruker, 2000). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined as reading, with U ~ iso ~ (H) = 1.2–1.5 U ~ eq ~ (C, N). Both structures were well defined but many of the water molecules within the crystal were in a state of disorder. The crystals derived from $Hdipy^{2+}$ and TMeQ[6] had a formula of $Hdipy^{2+} \subset TMeQ[6]{\cdot}2Cl^- \cdot HCl{\cdot}20H_2O$; formula weight: 1762.98, monoclinic, space group: *C* 2/*c*, $a = 22.687(3)$ Å, $b = 12.2937(18)$ Å, $c = 28.528(4)$ Å, $\alpha = 90°$, $\beta = 108.324(2)°$, $\gamma = 90°$, $V = 7553.2(18)$ Å^3, $Z = 4$, $D_{calcd} = 1.514$ g cm^{-3}, temp. 223 K, $\mu = 0.226$, $F(000) = 3564$, reflns measured = 4133, unique reflns = 6575, $R(\text{int}) = 0.0516$, $R_1[I > 2\sigma(I)] = 0.0841$, $wR_2[I > 2\sigma(I)] = 0.2699$, R_1(all data) = 0.1289, wR_2(all data) = 0.2975, GOF = 1.141. The crystals derived from Ediamp·4HCl and TMeQ[6] had a formula of $[Ediamp^{2+} \subset 2(TMeQ[6])\ Ediamp^{2+}]{\cdot}4Cl^-{\cdot}35H_2O$; formula weight: 3369.91, triclinic, space group: *P*-1, $a = 12.8085(19)$ Å, $b = 14.745(2)$ Å, $c = 21.664(3)$ Å, $\alpha = 81.428(2)°$, $\beta = 78.349(2)°$, $\gamma = 68.228(2)°$, $V = 3709.1(10)$ Å^3, $Z = 1$, $D_{calcd} = 1.476$ g cm^{-3}, temp. 223 K, $\mu = 0.190$, $F(000) = 1708$, reflns measured = 9446, unique reflns = 12835, $R(\text{int}) = 0.0320$, $R_1[I > 2\sigma(I)] = 0.0841$, $wR_2[I > 2\sigma(I)] = 0.2641$, R_1(all data) = 0.1053, wR_2(all data) = 0.2866, GOF = 1.952. Crystallographic data for structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos CCDC 685527 and 685528.

Results and discussion

We have previously investigated the host–guest binding of unsubstituted Q[6] and the pyridinium salt $Hdipy^{2+}$ in solution and found that the binding appeared to be consistent with the Q[6] cavity situated over the six-carbon methylene chain but with a slight anomaly (*25a*). With the

molecular host TMeQ[6] and the pyridinium salt, $Hdipy^{2+}$ in D_2O, the ^1H NMR spectra indicated a similar conclusion with the same anomaly. However, in this report, we also have the solid-state supramolecular structure of the $Hdipy^{2+} \subset$ TMeQ[6] to help draw plausible conclusions.

By ^1H NMR, it was established that TMeQ[6] forms a 1:1 association complex with $Hdipy^{2+}$, showing slow exchange kinetics on the NMR time scale. The ratio of association was found to be unaffected by an excess of the guest or, on the contrary, where the host was in excess (see Figure 2). Compared to the unbound guest $Hdipy^{2+}$, the methylene proton resonances all shift upfield, with H^4, H^5 and H^6 having chemical shift differences of 0.17, 0.73 and 0.84 ppm, respectively. These shifts in their direction and magnitude suggest that the methylene protons of the guest are located within the interior cavity of TMeQ[6]. Consistent with this argument, the pyridinium aromatic proton resonances of H^1 experience a large downfield shift of 0.51 ppm, indicating that these protons are located at or near the portal of Q. However, an apparent conflict of arguments arises when considering the chemical shift directions of the aromatic proton resonances of H^2 and H^3, which were shifted upfield slightly by 0.09 and 0.08 ppm, respectively. It is also noted that the magnitude of the downfield chemical shift difference of the protons of H^1 is unusually large.

The single-crystal X-ray diffraction of the association adduct $Hdipy^{2+} \subset$ TMeQ[6] reveals in the solid state that a supramolecular assembly is formed where the guest $Hdipy^{2+}$ forms a pseudorotaxane with TMeQ[6]. The six-carbon chain is entirely encapsulated and the pyridinium rings sit just outside the portals. Each pseudorotaxane, as a unit, is arranged in a linear fashion with the neighbouring units and each of the neighbouring pyridinium rings is stacked in pairs with their aromatic rings exactly situated face to face, a possible $\pi\cdots\pi$ interaction. The ring pairs are slightly tilted, which facilitates the optimal occupation of interstitial space created by the two Q portals (Figure 3). The centroid–centroid distance between the pyridinium pairs is 3.60 Å (Figure 3c). The ion–dipole interactions between the charge on the guest and the electronegative Q portals are also optimised at an average distance of 3.80 Å from the quaternised N^+ to the portal carbonyl O (Figure 3a,b).

Given that $Hdipy^{2+} \subset$ TMeQ[6] in the solid state has pyridinium $\pi\cdots\pi$ stacked pairs, it is tempting to conclude that this may be reflected in solution resulting in the apparent anomalous chemical shift differences of the pyridinium proton resonances compared to the free guest. This conclusion, however, cannot be supported for two reasons: (1) dilute solutions or high proportions of the host (TMeQ[6]) have no influence upon the chemical shift difference and (2) the protons H^1, H^2 and H^3 of these rings should be uniformly affected and they are not. A likely explanation is that the apparent anomaly is the summing effect of the deshielding of the portal environment and the localisation of the positive charge near N in the polarising environment of the electronegative portal region. This type of charge localisation has also been observed with protonated bipyridines encapsulated unsymmetrically within the cavities of Q (*17*, *26*). The polarisation of the pyridinium rings would also facilitate the $\pi\cdots\pi$ interaction observed in the solid state due to the complementary charges that would develop on the paired rings in the portal environments.

In contrast to a single binding interaction of the guest $Hdipy^{2+}$ with TMeQ[6], the HCl salt of Ediamp exhibits two different binding states with this host. The HCl salt of Ediamp adopts both portal and cavity binding modes. These two binding modes have been found in the solid state and are observed in solution. The ^1H NMR spectrum in D_2O of the combined host (TMeQ[6]) and the guest (Ediamp as the HCl salt) in a ratio of 1.4:2 best shows the two binding modes in solution, both of which have relatively slow exchange kinetics (Figure 4b). Cavity binding is obvious by the upfield shift of the four-pyridyl

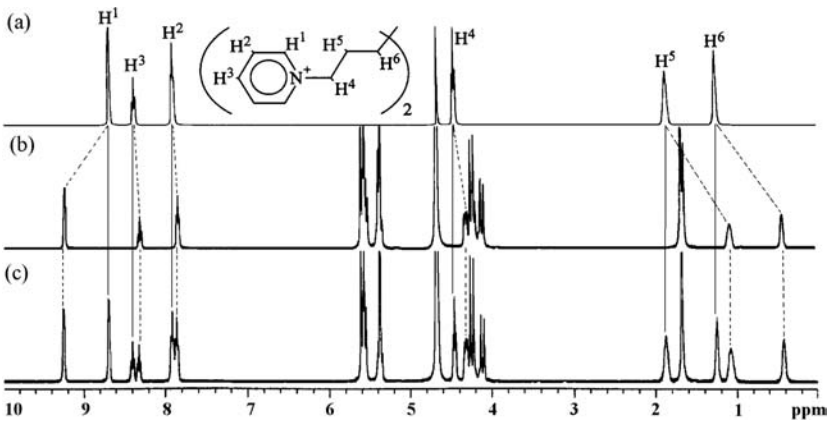

Figure 2. ^1H NMR spectra (400 MHz, D_2O) of (a) the guest $Hdipy^{2+}$ alone, (b) in the presence of 1.5 and (c) 0.5 equiv. of TMeQ[6].

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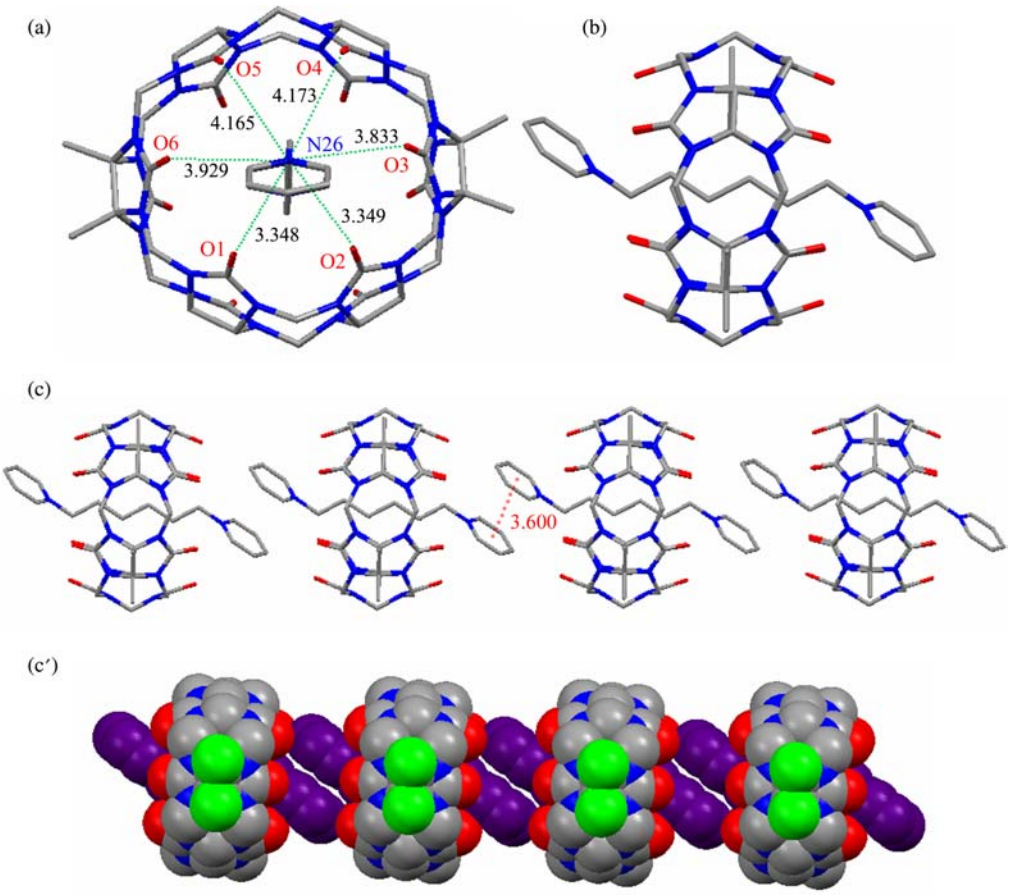

Figure 3. X-ray crystal structure of the pseudorotaxane: (a) top view, (b) side view and (c), (c′) the self-assembled arrangement and packing of the pseudorotaxane. All hydrogen atoms were omitted for clarity.

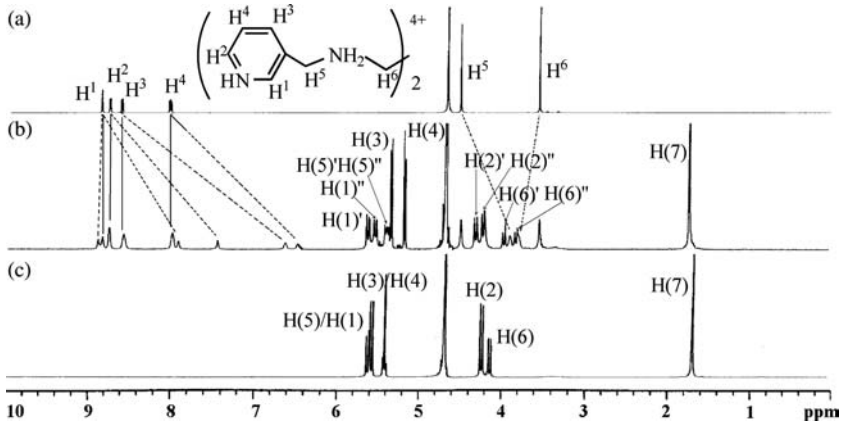

Figure 4. ^{1}H NMR spectra (400 MHz, D_2O) of (a) the guest Ediamp^{4+} alone, (b) the guest and TMeQ[6] in a ratio of 1.4:2 and (c) TMeQ[6] alone.

proton resonances (H^1 0.95, H^2 1.30, H^3 2.01 and H^4 1.58 ppm) and the α-pyridyl methlyene protons (0.61 ppm) of the guest. In addition, the remaining methylene proton resonances were shifted downfield by 0.23 ppm. The upfield shifts of the four-pyridyl protons and the α-pyridyl methlyene protons indicate that these parts of Ediamp are encapsulated within the cavity of TMeQ[6]. The single downfield shift of the remaining protons indicates that the linking ethane group is situated symmetrically between two portals. This suggests that Ediamp is bound symmetrically by two TMeQ[6], giving a structure resembling a dumbbell. Support for this type of structure

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is also evident in the doubling up of the methylene proton resonances of TMeQ[6] H(1), H(2), H(5) and H(6), which become H(1)′ 5.62, H(1)″ 5.53, H(5)′ 5.40, H(5)″ 5.36, H(2)′ 4.31, H(2)″ 4.21, H(6)′ 3.96 and H(6)″ 3.82 ppm (comparing Figure 4b,c). The doubling up of resonances arises as a consequence of a difference in the magnetic environments of the Q methylene protons, i.e. one portal is deshielded by the molecular guest's pyridyl ring and one remains virtually unaffected (*17*, *26*). The methyl proton resonances are unaffected as they lie in a plane of symmetry that is perpendicular to the plane or axis of change. However, H(3) and H(4), which are the methine protons on the same plane of symmetry as the Me, are affected and split into two doublets at 5.34 and 5.17 ppm. This is consistent with a preferred orientation of the guest within an ellipsoid cavity, a phenomenon which we have previously observed [Figure 5b; (*17*, *26*)]. The second mode of binding evident from the ^{1}H NMR spectrum appears to be portal. This is observed in the small downfield shift (0.02 ppm) in the resonance of a pyridyl H^1 proton to 8.90 ppm and a broadening and a slight upfield shift of the pyridyl resonances H^3 and H^4 (0.05 ppm). The portal binding is only observed when the HCl salt of Ediamp is in excess relative to TMeQ[6] (Figure 4b). At ratios of 1:2 (Ediamp to TMeQ[6]), the only chemical shifts observed are those consistent with the proposed dumbbell structure, which is supported by the solid-state structure discussed below.

A curious observation found with the ^{1}H NMR spectra of the free HCl salt of Ediamp and its encapsulation into TMeQ[6] was that the chemical shift differences were unusually large between the proton resonances of the pyridyl protons under the two conditions. The pyridyl protons H^3 and H^4 have the largest upfield shifts of 2.01 and 1.58 ppm, respectively. To account for this unusually large shift, the degree of protonation needs to be considered. The crystallisation of the base Ediamp from an ethanol solution using concentrated HCl furnishes Ediamp·4HCl, as there are four protonatable N (*27*). However, the large shift difference may be explained by the deprotonation of the pyridinium N during the process of cavity encapsulation, hence the upfield shifts are then a combination of shielding from the TMeQ[6] cavity and the removal of the cation by deprotonation. Given that there is a propensity for cations to reside at the portals and not in the cavities, the chemical shifts found for the encapsulated guest indicate that Ediamp is only protonated on the two ethylene diamine N and it is the ammonium ion that sits at the portal. This implies that the pyridinium ion loses its ability to remain protonated upon encapsulation. The pK_a of the ammonium ion (~8.8) of the ethylene diamine linking group is three units larger than the pyridinium ion (~5.7); therefore, if deprotonation is required for encapsulation, then pyridine would be more favourable (*28*). The modification of pK_a following encapsulation has recently been reported (*29*). The ^{1}H NMR solution of the free guest (Figure 4a) had a pH of 3.2 and, at this pH, the pyridine N would be protonated. As discussed previously, portal binding was also evident as a second mode of binding in the presence of excess guest. However, it appears that the pyridinium salt is portal bound in solution and not the pyridine as indicated by the small chemical shift differences of H^1, H^3 and H^4 protons (Figure 4b).

The binding behaviour of the HCl salt of Ediamp and TMeQ[6] in solution is also reflected in the solid-state structures obtained from the crystals derived from solutions where the salt was in excess (Figure 6). A striking feature of the crystal structure is the dumbbell configuration where two TMeQ[6] molecular 'beads' are threaded onto the pyridine ends of the dication $Ediamp^{2+}$ with complete inclusion, $Ediamp^{2+} \subset 2(TMeQ[6])$ (Figure 5a and 6). The ammonium ion (N103) of the ethylene diamine linking group forms the axis of the dumbbell, sitting just outside the portal of each of the TMeQ[6] at an average distance of 3.53 Å. In addition to cavity encapsulation of the pyridine rings, there is also a portal association of a second $Ediamp^{2+}$. The second $Ediamp^{2+}$ component is arranged in strings linked through

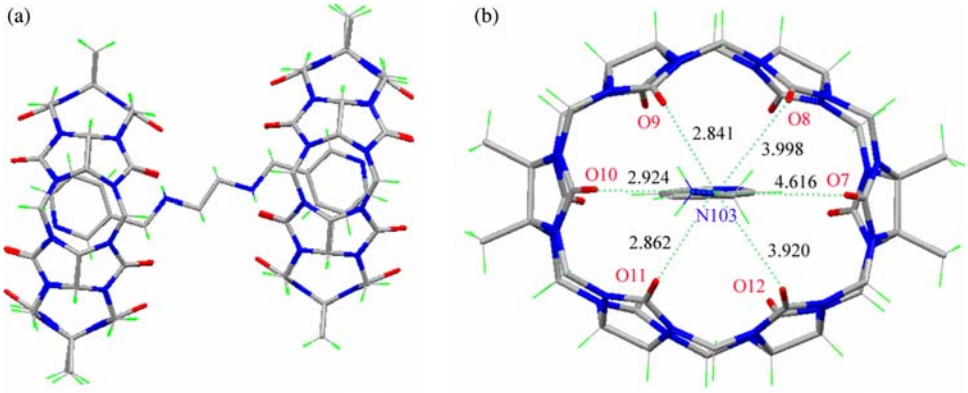

Figure 5. X-ray crystal structure of the dumbbell: (a) side view and (b) top view.

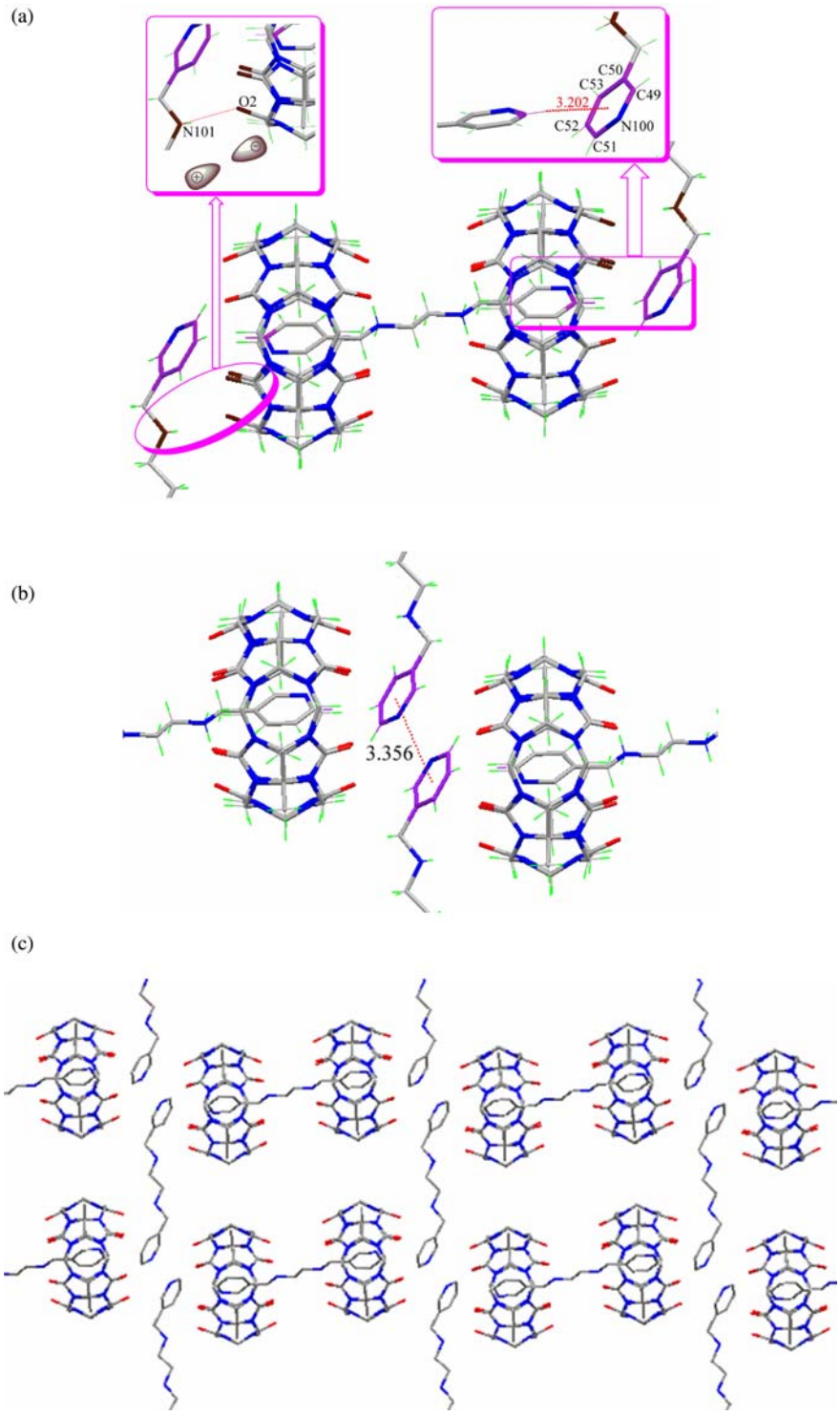

Figure 6. (a) The sandwich structure of the dumbbell and the excluded Ediamp^{2+} dications, (b) the offset pyridine rings stacks and (c) the self-assembly of the supramolecular structure as a whole showing the arrangement of TMeQ[6] and Ediamp^{2+}.

or associated with the end of a dumbbell at the otherwise vacant portal of TMeQ[6] (Figure 6c). There is a close arrangement of the pyridine rings, but are offset with no $\pi\cdots\pi$ stacking involved in the structural arrangement but instead a C—H$\cdots\pi$ link between the H^6 of the encapsulated dumbbell pyridine ring and the π region of one of the excluded pyridine rings of the Ediamp^{2+} string (Figure 6b). The ammonium ion (N101) of the excluded

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Ediamp^{2+} is in close proximity to the portal O1, O2 and O6 (2.85–3.60 Å), providing a partial ion–dipole interaction. The pyridine rings of the excluded Ediamp^{2+} are sandwiched between the two vacant portals of TMeQ[6] of two different dumbbell structures (Figure 6b,c). The closest point between the pyridine rings is at the edge of the ring between N100 (pyridine N) and C51 (pyridine C^{6}) ~2.95 Å. The empirical formula of the crystal structure $C_{108}H_{128}Cl_4N_{56}O_{24}{\cdot}35H_2O$ indicates that the cavity-bound and portal-bound guest is the dication Ediamp^{2+}, and that the ratio of the two organic components TMeQ[6] to Ediamp^{2+} is 1:1.

The most obvious forces at play in both solid-state structures appear to be hydrophobic, ion–dipole, H-bonding, π···π stacking and C—H···π interactions. The hydrophobic forces facilitated by the cavity of TMeQ[6] acted upon the hexane linking chain of Hdipy^{2+} and the neutral pyridine rings of Ediamp^{2+}. In the case of Ediamp^{2+}, a second likely hydrophobic site was between the portals of two TMeQ[6]. The ion–dipole interactions are obviously between the Q portals and the pyridinium cations of Hdipy^{2+} and the ammonium cations of Ediamp^{2+}. The ammonium cation protons also have the potential for H-bonding to the portals as well. Finally, the π···π interactions between the Hdipy^{2+} pyridinium rings and C—H···π interactions between the Ediamp^{2+} pyridines provide an additional stabilisation (*26*, *27*).

Conclusion

Two pyridine-based molecules, the dication Hdipy^{2+} and the HCl salt of Ediamp, have been investigated in the presence of the molecular host TMeQ[6] in both the solutions and the solid state. In both cases, a striking feature of encapsulation appears to be the effect that the cavity and the polarising environment of the portal have upon the localisation of cationic charges. This was evident in the anomalous chemical shifts found in the ^{1}H NMR spectra of Hdipy^{2+} ⊂ TMeQ[6] and Ediamp^{2+} ⊂ 2(TMeQ[6]) in D_2O and the solution structures are consistent with the major binding aspects of the crystal structures. It is clear that the driving forces for the association between the organic cations of this study and the host properties of the substituted TMeQ[6] are similar to the unsubstituted Q[6], in that the primary associations are made by a balance between ion–dipole interactions and hydrophobic forces and, where possible, contributions from smaller but energetically favoured interactions (*1*).

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