Hydrogen-bonded cubanes and ladder fragments by analogy with the inorganic solid state

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By application of an analogy with the structures of alkali-metal phosphinimides, two hydrogen-bonded cubanes, $[Ph_3CNH_3{}^+X^-]_4$ (X = Cl, Br), and one unprecedented four-rung ladder fragment, $[Ph_3CNH_3{}^+I^-]_4$, have been prepared in the organic solid state.

Controlled formation of supramolecular motifs in the organic solid state is one of the principal challenges of crystal engineering.[1] As one approach within this area, we have attempted to draw upon the experience of chemists working within the traditional boundaries of structural inorganic chemistry, where similar challenges are often encountered for controlled syntheses of metallo-organic complexes. It is generally recognised that the structures of such complexes reflect a competition between the Coulombic drive for aggregation of metal cations and organic anions, and the requirement that the organic molecules pack efficiently, usually within the confines of the solid state. In this area, Snaith's ring-laddering and ring-stacking principles provide intuitive guidelines,[2] although they are by no means rigorous predictive tools. Following an initial observation of analogous cubanes in $[2,6\text{-}Pr^i{}_2C_6H_3NH_3{}^+Cl^-]_4$ and $[M^{2+}(2,6\text{-}Pr^i{}_2C_6H_3N^{2-})]_4$ (M = Sn, Pb),[3] ring-laddering and ring-stacking principles have been applied to the organic solid state.[4] A specific analogy has been developed between organic ammonium halides and metallo-organic complexes such as alkali-metal amides or imides. We report here the first experimental exploitation of this analogy for targeted realisation of new hydrogen-bonded cubanes, $[Ph_3CNH_3{}^+X^-]_4$ (X = Cl, Br), together with an accompanying observation of an unprecedented hydrogen-bonded four-rung ladder fragment, $[Ph_3CNH_3{}^+I^-]_4$.

We targeted the cubane motif because it is relatively common in metallo-organic complexes, but rare in the organic solid state. Prior to this communication, only four $[RNH_3{}^+X^-]_4$ cubanes have been reported,[3,5,†] all of which are chlorides. In each case, the cubanes were obtained without intent, and the primary ammonium cations display considerable structural variety. On the basis of these four structures, it is not trivial to select a new $RNH_3{}^+$ cation that we would expect to crystallise with the cubane motif. To identify our target $RNH_3{}^+$ cation, we considered the crystal structures of metallo-organic complexes that met the following criteria: cubanes $[MA]_4$, where M^+ is a group 1 metal cation, A^- is a singly-charged organic anion bound to M^+ through an N atom, and M^+ forms only three bonds to N (*i.e.* no other ligands were bound to M^+). The restriction to group 1 cations was applied to ensure that there were no particular preferences for the coordination geometry around M^+, and also that the Coulombic interactions in the $[MA]_4$ complex were of comparable magnitude to those in our intended $[RNH_3{}^+X^-]_4$ cubane. In $[M^{2+}A^{2-}]_4$, for example, the Coulombic energy would be expected to become relatively more significant compared to the steric factors.[4c] The search[6] identified several candidates, including $[Li(NP(Bu^t)_3)]_4$,[7] $[K(NP(Cy)_3)]_4$,[8] and $[Cs(NPPh_3)]_4$.[9] Each of these cubane complexes are based on $R_3P\text{–}N^-$ (phosphinimide) anions, suggesting that suitable targets in the organic solid state would be $R_3C\text{–}NH_3{}^+X^-$. The Cs^+ complex seemed most promising of all, since the Cs–N distances in $[Cs(NPPh_3)]_4$ are *ca.* 3.0–3.1 Å, comparable to the $N^+\cdots Cl^-$ distances in a typical $N^+\text{–}H\cdots Cl^-$ hydrogen bond. We set out therefore to examine $Ph_3CNH_3{}^+X^-$.

Preparation of the cubanes proved to be straightforward: bubbling HX (X = Cl or Br) gas through a toluene solution of Ph_3CNH_2 (tritylamine) produced an immediate precipitate, which could be dissolved by addition of $CHCl_3$. Slow evaporation of the mixed solvent system provided single crystals of $[Ph_3CNH_3{}^+Cl^-]_4\cdot\frac{1}{2}C_7H_8$ (**1**) or $[Ph_3CNH_3{}^+Br^-]_4\cdot CH_3Cl$ (**2**) (Fig. 1).‡ The cubanes in **1** and **2** are closely comparable, although **2** contains two independent conformations in the solid state that vary in the relative rotations of the phenyl groups about the C(*ipso*)–C(sp^3) bonds. From the distributions of the $N^+\text{–}H\cdots Cl^-$ or $N^+\text{–}H\cdots Br^-$ distances, it is not possible to distinguish a "ring-stacking direction" within the cubanes, as is commonly defined in archetypal ring-stacked metallo-organic systems.[10]

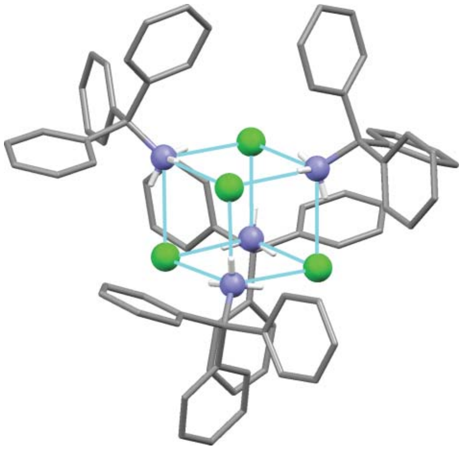

Fig. 1 Hydrogen-bonded cubane $[Ph_3CNH_3{}^+Cl^-]_4$ in the crystal structure of **1** (H atoms bound to C atoms are omitted). The $[Ph_3CNH_3{}^+Br^-]_4$ cubane in **2** is comparable.

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The gross crystal structures of **1** and **2** are different, and neither of them are isostructural with $[Cs(NPPh_3)]_4$. The observation of cubanes in each case—that is, the fact that the analogy operates at all—demonstrates that the principal factors governing self-assembly of the cubanes in the organic and inorganic systems must be comparable. In each case, cubanes appear to represent optimal Coulombic aggregation within the constraints of efficient packing of the organic cations. The specific directional features of the $N^+–H\cdots X^-$ hydrogen bonds are compatible with cubane formation, although the existence of the analogy suggests that Coulombic aggregation rather than directional hydrogen bonding should be viewed as the principal "structure-directing" factor in these charged systems.[11]

The interactions *between* cubanes are quite different in the organic and inorganic structures. This is shown clearly by comparison of **1** with $[Cs(NPPh_3)]_4$. Both crystallise as toluene solvates. In $[Cs(NPPh_3)]_4$, toluene molecules cap Cs^+ corners of the cubane through cation–π interactions (Fig. 2(a)). In **1**, the toluene molecules lie within pockets between phenyl rings, and the shortest inter-cubane contacts to Cl^- are made by C–H bonds of adjacent phenyl rings (Fig. 2(b)). The distinction is also revealed on closer inspection of the cubanes themselves: in **1** and **2**, the phenyl rings of $Ph_3C–NH_3^+$ are oriented so that their C–H bonds point directly towards Cl^- or Br^- (Fig. 2(b)). In $[Cs(NPPh_3)]_4$, the phenyl rings of $Ph_3P–N^-$ are aligned to form cation–π type interactions (Fig. 2(a)). These contacts demonstrate that the organic parts of the ammonium cations cannot simply be considered to be "innocent" space fillers, and that their electrostatic properties are significant for determining the gross crystal structure. This being the case, we would never expect to observe truly isostructural systems by application of the present analogy: while the electrical polarity of the central ionic core of the cubane can be inverted, the polarity of the atomic nuclei and electrons in the organic portions of the molecules cannot. The difference between the crystal structures of **1** and **2**, which we might reasonably expect to be isostructural, could be attributable to more subtle metric differences between the cubanes on account of the differing $N^+–H\cdots Cl^-$ and $N^+–H\cdots Br^-$ distances. The delicate nature of this particular balance is highlighted by an unexpected outcome for the $Ph_3NH_3^+I^-$ system.

Application of the same preparative procedure using HI gas gave single crystals of $[Ph_3NH_3^+I^-]_4\cdot 2CH_3Cl$ (**3**),‡ in which the hydrogen-bonded motif comprises a four-rung ladder fragment with a centrosymmetric "stair" conformation (Fig. 3). The motif appears to be the first such fragmented ladder in an RNH_3X system, and it provides a further link to the inorganic solid state by analogy with fragmented ladder complexes such as $[Li(Dipp)NCH_2CH_2N(Dipp)Li]_2$ (Dipp = 2,6-$Pr^i_2C_6H_3$).[12] The $[Ph_3NH_3^+I^-]_4$ motif is unusual in that it is "unsaturated" with respect to its potential for formation of $N^+–H\cdots I^-$ hydrogen bonds. At the NH_3^+ centres of the terminal ladder rungs, the $N^+–H$ groups not involved in $N^+–H\cdots I^-$ hydrogen bonds point towards adjacent phenyl rings, forming $N^+–H\cdots\pi$ interactions (Fig. 3). Similar to **1** and **2**, the shortest additional contacts to the outer ("two-coordinate") I^- anions are made by C–H bonds of

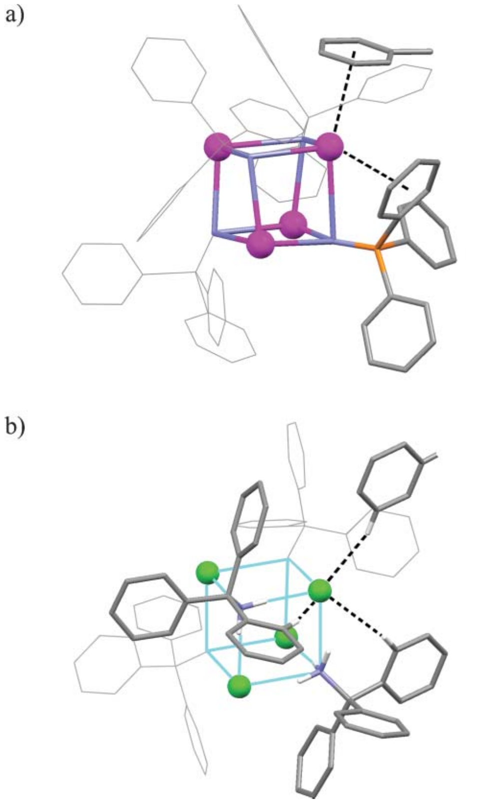

Fig. 2 (a) Environment of Cs^+ in $[Cs(NPPh_3)]_4\cdot 2C_7H_8$, showing cation–π contacts within the cubane and to a lattice toluene molecule. (b) Environment of Cl^- in **1**, showing C–H···Cl^- contacts within the cubane and from a phenyl group in a neighbouring cubane.

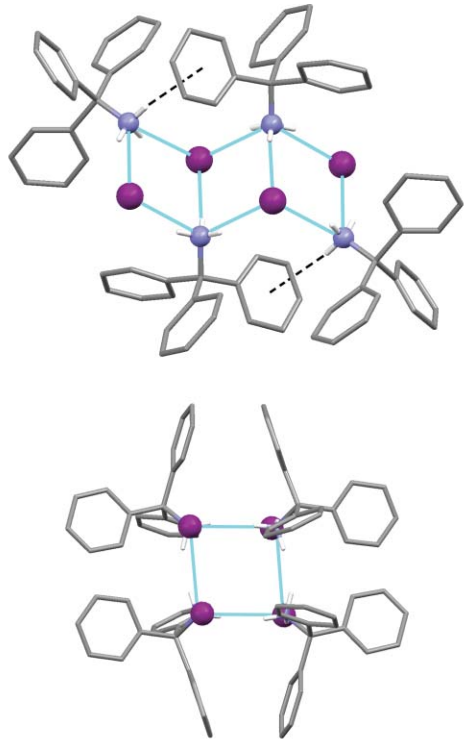

Fig. 3 Perpendicular views of the four-rung ladder fragment $[Ph_3CNH_3^+I^-]_4$ in the crystal structure of **3** (H atoms bound to C atoms are omitted). In the upper diagram, the $N^+–H\cdots\pi$ contacts from the terminal $Ph_3NH_3^+$ molecules are denoted by dashed lines.

adjacent phenyl groups within the ladder fragment, and also those in neighbouring ladder fragments.

Viewed in projection perpendicular to the central N_2I_2 ring (Fig. 3), the ladder fragment in **3** is clearly closely related to the cubanes in **1** and **2**. Why **3** should form the fragmented ladder in preference to the cubane is likely to reflect the overall packing efficiency in the solid state. For **1** and **2**, the packing coefficients of 63.4 and 62.7%, respectively,[13] are considerably lower than 66.6% for **3**. One source of the packing inefficiency in **1** and **2** is the internal void of the cubane, which increases in volume from Cl^- to Br^-, and would be larger still for a cubane containing I^-. The packing coefficients suggest that the cubane motif in **1** and **2** is not an especially good solution to the packing problem for $Ph_3CNH_3^+X^-$, even with incorporation of solvent molecules in the crystal lattice. Further evidence of this appears in the ease with which hydrogen-bonding solvents intervene to prevent crystallisation of the cubanes: dimeric ring structures of the type $[Ph_3CNH_3^+X^-]_2Y_2$, in which one N–H bond of each ammonium centre is employed in a hydrogen bond to a solvent molecule Y, have been reported previously with Y = acetone[14] or dioxane,[15] and we have obtained comparable structures during this work with Y = H_2O or THF.‡ In terms of the analogy with metallo-organic complexes, this aspect resembles the common intervention of coordinating solvents, although coordination in the inorganic systems takes place at the metal centre rather than at the N atom of the amide/imide anion.

In summary, we have employed information from the traditional arena of "inorganic solid-state chemistry" to prepare in a targeted manner rare hydrogen-bonded cubanes in the organic solid state. The unexpected hydrogen-bonded ladder fragment **3** provides a further link between the structural chemistry of organic ammonium halides and that of inorganic amide/imide complexes, strengthening the assertion that the principal factors governing self-assembly of the organic and inorganic systems are genuinely comparable. More importantly, this work shows that the established link can be exploited successfully to prepare new compounds in the organic solid state.

Notes and references

† One secondary ammonium bromide cubane has also been reported (see M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695), in which each NH_2^+ centre forms three $N^+\cdots Br^-$ contacts. The ammonium cation is positioned so that one of its N^+–H bonds forms an almost linear N^+–$H\cdots Br^-$ hydrogen bond, while the other points between two Br^- anions. Our search here was restricted to primary ammonium cations.

‡ *Crystal data*: **1**: $C_{19}H_{18}NCl\cdot\frac{1}{8}C_7H_8$, M = 307.31, monoclinic, space group $C2/c$, a = 34.700(2), b = 14.7258(9), c = 28.107(2) Å, β = 103.850(3)°, U = 13944.7(15) Å^3, T = 180(2) K, Z = 32, μ(Mo-Kα) = 0.215 mm^{-1}, 61797 reflections measured, 9983 unique (R_{int} = 0.084), $R1$ [$I > 2\sigma(I)$] = 0.066, $wR2$ (all data) = 0.200. **2**: $C_{19}H_{18}NBr\cdot\frac{1}{4}CHCl_3$, M = 370.10, trigonal (on hexagonal axes), space group $P3$, a = b = 14.3387(3), c = 20.4479(8) Å, U = 3640.82(18) Å^3, T = 180(2) K, Z = 8, μ(Mo-Kα) = 2.364 mm^{-1}, 58037 reflections measured, 9521 unique (R_{int} = 0.035), $R1$ [$I > 2\sigma(I)$] = 0.063, $wR2$ (all data) = 0.183, Flack parameter 0.081(15). **3**: $C_{19}H_{18}NI\cdot\frac{1}{2}CHCl_3$, M = 446.93, triclinic, space group $P\bar{1}$, a = 11.7438(4), b = 11.9457(4), c = 14.9678(5) Å, α = 71.057(2), β = 69.997(2), γ = 85.534(2)°, U = 1864.97(11) Å^3, T = 180(2) K, Z = 4, μ(Mo-Kα) = 1.931 mm^{-1}, 31828 reflections measured, 7767 unique (R_{int} = 0.040), $R1$ [$I > 2\sigma(I)$] = 0.065, $wR2$ (all data) = 0.208. Crystallographic data also provided for $[Ph_3CNH_3^+Cl^-]_2\cdot 5H_2O$ and $[Ph_3CNH_3^+Cl^-]_2\cdot 2THF$. CCDC 645313–645317. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706422e

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