

Supramolecular Rosette Ribbon Constructed from Guanidinium and Hydrogen Carbonate Ions in the Crystal Engineering of Hydrogen-Bonded Networks

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The design and construction of hydrogen-bonded “supramolecular rosettes” from guanidinium/organic sulfonate,¹ trimesic acid,² or cyanuric acid/melamine³ depend on utilization of their topological equivalence, i.e., equal numbers of donor and acceptor hydrogen-bonding sites and C_3 symmetry of the component moieties. Here we depart from this strategy by exploring a new kind of “fused-rosette ribbon” built of the guanidinium cation¹ (GM^+) **1** and hydrogen carbonate dimer⁴ (HC^-)₂ **2** in the ratio of 1:1 (see Scheme 1).

Each supramolecular rosette **3** comprises a quasi-hexagonal assembly of two GM^+ and four HC^- units connected by strong $\text{N}_{\text{GM}}-\text{H}\cdots\text{O}_{\text{HC}}$ ($\text{N}\cdots\text{O}$ distances in the range 2.793 to 2.990 Å) and $\text{O}_{\text{HC}}-\text{H}\cdots\text{O}_{\text{HC}}$ ($\text{O}\cdots\text{O}$ distances 2.554 to 2.827 Å) hydrogen bonds. The (HC^-)₂ dimer is shared as a common edge of adjacent rosettes and makes full use of its remaining acceptor sites in linking with GM^+ . On the other hand, each GM^+ in the resulting linear ribbon (or tape) still possesses a pair of free donor sites, and it is anticipated that some “molecular connector” with suitable acceptor sites may be used to bridge an array of parallel ribbons to form a sheetlike network. Our design objective has now been realized in the synthesis and characterization of new inclusion compounds⁵ $5[\text{C}(\text{NH}_2)_3^+]\cdot 4(\text{HCO}_3^-)\cdot 3[(n\text{-Bu})_4\text{N}^+]\cdot 2[1,4\text{-C}_6\text{H}_4(\text{COO}^-)_2]\cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{C}(\text{NH}_2)_3^+]\cdot (\text{HCO}_3^-)\cdot (n\text{-Bu})_4\text{N}^+ \cdot [1,4\text{-C}_6\text{H}_4(\text{COO}^-)(\text{NO}_2)]\cdot \text{H}_2\text{O}$ (**2**) with either the terephthalate (TPA^{2-}) **4** or the 4-nitrobenzoate (NB4^-) **5** anion functioning as a connector.

As shown in Figure 1, each HC^- in (**1**) provides one donor and one acceptor site to form a planar dimer motif [**A**, $N_2 = R_2^2(8)$].⁶ The remaining eight acceptor sites of each (HC^-)₂ dimer are topologically complemented by four GM^+ units, such that each GM^+ connects two (HC^-)₂ dimers through two pairs of $\text{N}-\text{H}_{\text{syn}}\cdots\text{O}$ hydrogen bonds [**B**, $N_2 = R_2^2(8)$]. Thus two GM^+ and two (HC^-)₂ dimers constitute a planar, pseudocentrosymmetric, quasi-hexagonal supramolecular rosette [**C**, $N_6 = R_6^4(12)$] with inner and outer diameters of ca. 5.5 and 9.5 Å, respectively. In the resulting fused-rosette ribbon, the remaining two *exo*-orientated donor sites of each GM^+ unit form a pair of

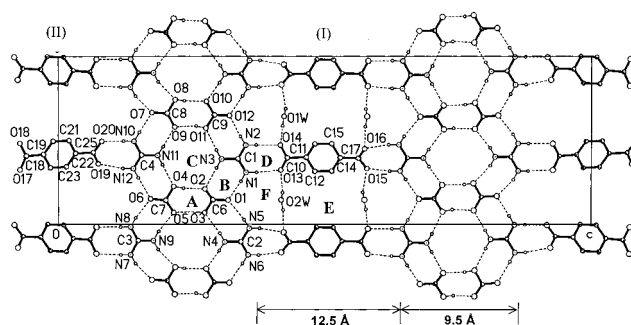
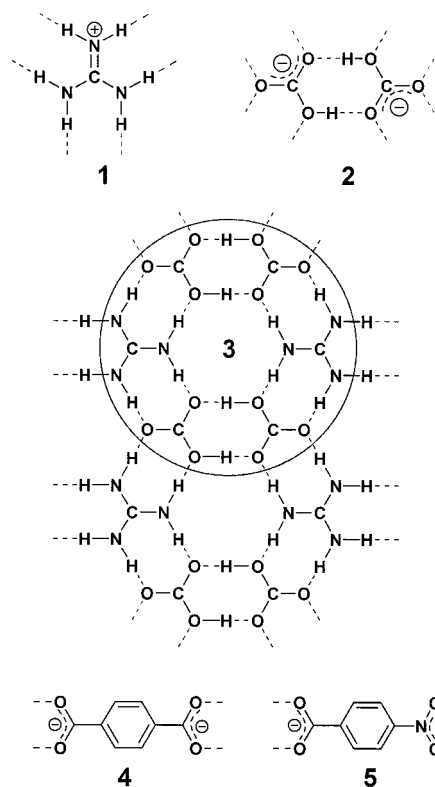


Figure 1. Projection on (010) showing the 2D network in (**1**). Atom types are differentiated by size and shading, and hydrogen bonds are represented by broken lines. Various hydrogen-bonding motifs as discussed in the text are labeled by bold capital letters **A** to **E**, and similar labels are used in Figure 3.

Scheme 1



$\text{N}-\text{H}_{\text{anti}}\cdots\text{O}$ hydrogen bonds [**D**, $N_2 = R_2^2(8)$] with a TPA^{2-} carboxylate group. Thus two types of ladders are developed: type

(5) Crystals of each compound were obtained in nearly quantitative yield from slow evaporation of the reactants at room temperature. X-ray measurements were made on a Rigaku AFC7R diffractometer at $T = 294$ K using Mo K α radiation ($\lambda = 0.71013$ Å). Crystal data for (**1**), $5[\text{C}(\text{NH}_2)_3^+]\cdot 4(\text{HCO}_3^-)\cdot 3[(n\text{-Bu})_4\text{N}^+]\cdot 2[1,4\text{-C}_6\text{H}_4(\text{COO}^-)_2]\cdot 2\text{H}_2\text{O}$ ($\text{C}_{73}\text{H}_{154}\text{N}_{18}\text{O}_{22}$): $M = 1636.14$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 13.785(1)$ Å, $b = 15.874(1)$ Å, $c = 43.754(3)$ Å, $V = 9574.4(11)$ Å³, $Z = 4$, 10248 unique, 2787 observed with $I > 2\sigma(I)$; final $R = 0.0605$ (observed), 0.3182 (all), $wR(F^2) = 0.1115$ (observed), 0.1320 (all). Crystal data for (**2**), $[\text{C}(\text{NH}_2)_3^+]\cdot (\text{HCO}_3^-)\cdot (n\text{-Bu})_4\text{N}^+ \cdot [1,4\text{-C}_6\text{H}_4(\text{COO}^-)(\text{NO}_2)]\cdot \text{H}_2\text{O}$ ($\text{C}_{25}\text{H}_{49}\text{N}_5\text{O}_8$): $M = 547.69$, triclinic, space group $P1$ (No. 2), $a = 8.472(1)$ Å, $b = 13.770(1)$ Å, $c = 27.944(3)$ Å, $\alpha = 92.58(1)^\circ$, $\beta = 96.78(1)^\circ$, $\gamma = 102.08(1)^\circ$, $V = 3157.3(6)$ Å³, $Z = 4$, 11109 unique, 4231 observed with $I > 2\sigma(I)$; final $R = 0.0714$ (observed), 0.1994 (all), $wR(F^2) = 0.1973$ (observed), 0.2193 (all). Hydrogen atoms of the H_2O and HCO_3^- groups were located from difference maps, and those belonging to the remaining ions were placed in their idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-137917 for (**1**) and CCDC-137918 for (**2**).

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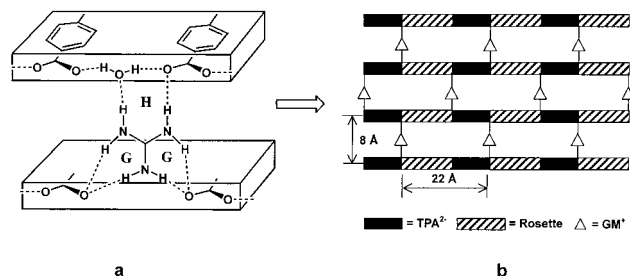


Figure 2. (a) Hydrogen-bonding motifs involving linkage of the free guanidinium ion to neighboring rosette ribbon-terephthalate layers in **(1)**. (b) Schematic presentation of the pillared layer structure.

(1) [TPA²⁻ composed of C(10) to C(17) and O(13) to O(16)] is consolidated by two independent water molecules that alternately bridge carboxylate oxygen atoms of neighboring steps by pairs of donor O_w-H...O hydrogen bonds, generating a centrosymmetric ring motif [E, $N_2 = R_4^4(22)$] and a pentagon pattern [F, $N_6 = R_6^3(12)$]. In the type **(II)** ladder [TPA²⁻ composed of C(18) to C(25) and O(17) to O(20)], carboxylate oxygen atoms O(18') and O(19) belonging to adjacent steps are connected by the remaining GM⁺ ion, which is not involved in rosette formation, via two pairs of donor hydrogen bonds [G, $N_2 = R_1^1(6)$] (Figure 2a). The remaining two donor sites of each free GM⁺ ion are linked to a carboxylate oxygen atom and a water molecule of TPA²⁻ column **(I)** of an adjacent layer to form a pentagon motif [H, $N_3 = R_3^2(8)$], thus yielding a 3D pillared-layer structure (Figure 2b). The large voids in the pillar region generate nanoscale channels extending along the [100] direction. The dimensions of the cross section of each channel are ca. $8 \times 22 \text{ \AA}^2$, within which three independent [(*n*-Bu)₄N]⁺ cations are aligned in separate columns in a well-ordered manner.

The rosette ribbon of **(2)** bears a strong resemblance to that of **(1)**, except that the hydrogen-bonding pattern C is centrosymmetric and the spacing between neighboring parallel ribbons is increased to ca. 18.5 Å (Figure 3). The independent GM⁺ cations, **C(1)** and **C(2)**, form a pair of N-H_{anti}...O hydrogen bonds [D, $N_2 = R_2^2(8)$] with the carboxylate groups of NB4⁻ ions **N(7)** and **N(8)**, respectively. As in the case of **1**, two independent water molecules secure the hydrogen-bonded network by bridging the oxygen atoms of neighboring NB4⁻ carboxylate groups alongside the rosette ribbon [E, $N_6 = R_6^3(12)$]. The resulting hemmed rosette ribbon-nitrobenzoate chains are organized into an undulated layer structure with the formation of weak C-H...O

(6) For details of the definition, terminology, and notation in the graph set approach, see: Bernstein, J.; Davis R. E.; Shimoni, L.; Chang, N.-L. *Angew. Chem., Int. Engl. Ed.* **1995**, *34*, 1555.

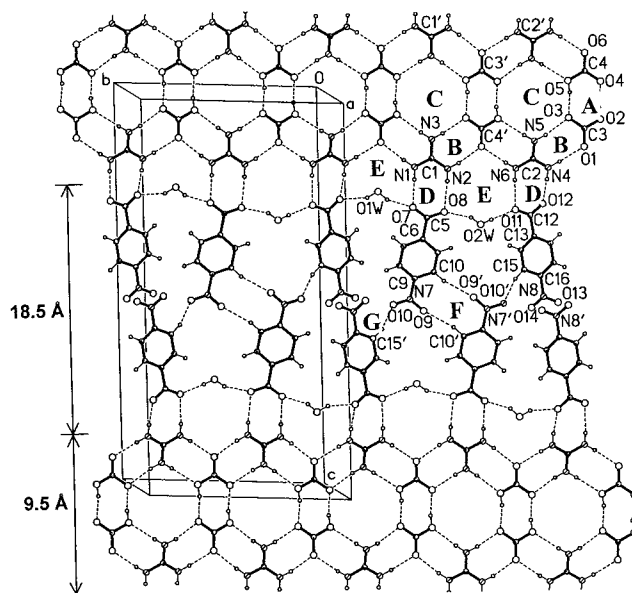


Figure 3. Perspective view of the hydrogen-bonded layer in **(2)** along the [110] direction. Linear ribbons of fused rosettes are interlinked by 4-nitrobenzoate ions through strong N-H...O(carboxylate) and weak C-H...O(nitro) hydrogen bonding.

interactions,⁷ leading to a centrosymmetric ring motif [F, $N_1 = R_2^2(10)$] plus a discrete motif [G, $N_1 = D$] in the interdigitated region. The two independent [(*n*-Bu)₄N]⁺ cations are sandwiched between adjacent layers; the interlayer separation is 8.2 Å, which is comparable to those in **(1)** and in other anionic host structures accommodating [(*n*-Bu)₄N]⁺ cations as guest moieties.⁸

The present study has shown that **(1)** and **(2)** are prototypes of a new class of host lattice featuring an uncharged, linear fused-rosette ribbon hemmed with multiple hydrogen-bonding donor sites, leading to nanoscale voids for the enclathration of moderately sized guests.

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