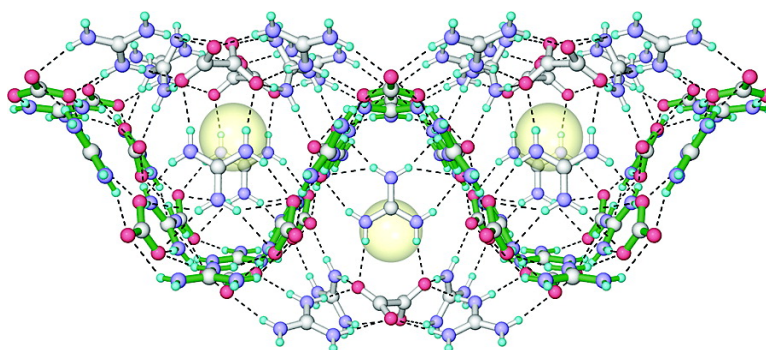## Communication

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# Hydrogen-Bonded Anionic Rosette Networks Assembled with Guanidinium and *C*₃-Symmetric Oxoanion Building Blocks

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In the realm of crystal engineering[1] of organic and organic–inorganic hybrid materials, the de novo self-assembly of hydrogen-bonded networks[2] that are topologically equivalent to the planar (6,3) honeycomb (or graphene) net[3] is a shining achievement in chemical creativity. The handful of known examples are hexagonal or quasihexagonal, single- or two-component, layer-type networks constructed with molecular building units possessing inherent 3-fold axial symmetry.[4] Notably, essentially planar rosette layers exist in all three crystalline phases of guanidinium nitrate, and the two structural phase transitions involve a delicate balance between N–H···O hydrogen bonds and electrostatic interactions.[5]

Drawing upon our previous studies on the design of a linear "fused-rosette ribbon" assembled from the hydrogen carbonate dimer and guanidinium ion in 1:1 molar ratio,[6] as well as the generation of urea/thiourea–anion host layers and their stabilization with bulky organic cations as interlayer spacers,[7] we set about the hydrogen-bond-mediated construction of two premeditated anionic rosette-layer architectures using guanidinium and ubiquitous *C*₃-symmetric oxoanions that carry *unequal* charges, namely, guanidinium–carbonate **I** and guanidinium–trimesate **II**, as illustrated in the following scheme.

Synthon D—A

Rosette Network	D	A
I	$[C(NH_2)_3]^+$	CO_3^{2-}
II	$[C(NH_2)_3]^+$	$1,3,5-C_6H_3(COO^-)_3$
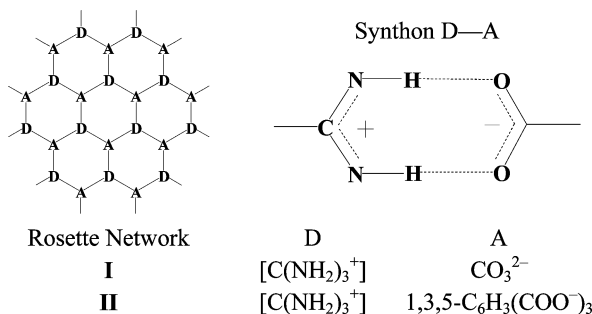
In principle, the negatively charged, presumably planar network **I** can be combined with 1 molar equiv of tetraalkylammonium ion R_4N^+ of the right size as interlayer template to yield a crystalline inclusion compound of stoichiometric formula (R_4N^+)-$[C(NH_2)_3^+]CO_3^{2-}$ that is reminiscent of the graphite intercalates.[8] Anionic network **II**, on the other hand, needs twice as many monovalent cations for charge balance and, furthermore, possesses honeycomb-like host cavities of ∼7 Å diameter that have to be filled by suitable guest species. The expected formula of the corresponding inclusion compound is $(R_4N^+)_2[C(NH_2)_3^+][1,3,5-C_6H_3(COO^-)_3]$·G, where G is an entrapped guest moiety with multiple hydrogen-bond donor sites to match the nearly planar set of six carboxylate oxygens that line the inner rim of each cavity.

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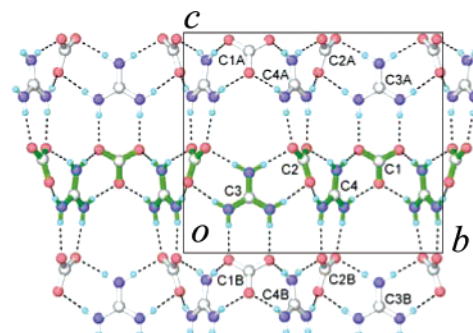
Figure 1. Projection diagram showing a portion of the nonplanar anionic rosette network **I** concentrated at $a = {}^1/_4$ in the crystal structure of **1**. The atom types are differentiated by size and color, and hydrogen bonds are indicated by dotted lines. For clarity, adjacent antiparallel $\{[C(NH_2)_3]^+ \cdot CO_3^{2-}\}_\infty$ ribbons are marked with differently colored bonds. Symmetry transformations: A $({}^1/_2 - x, 1 - y, {}^1/_2 + z)$, B $({}^1/_2 - x, y - {}^1/_2, z - {}^1/_2)$.

Our persistent attempt to crystallize $(R_4N^+)[C(NH_2)_3^+]CO_3^{2-}$ by variation of R, based on conceptual network **I**, was not successful. Mindful of the fact that the guanidinium ion can function as a pillar between layers[6] and the carbonate ion is capable of forming up to 12 acceptor hydrogen bonds, as observed in crystalline bis-(guanidinium) carbonate[9] and $[(C_2H_5)_4N^+]_2 \cdot CO_3^{2-} \cdot 7(NH_2)_2CS$,[10] a second guanidinium salt, $[C(NH_2)_3]X$, was used as an extra component. After much experimentation with various combinations of R and X, our targeted construction of network **I**, albeit in undulating form, was realized through the isolation of crystalline $4[(C_2H_5)_4N^+] \cdot 8[C(NH_2)_3^+] \cdot 3(CO_3)^{2-} \cdot 3(C_2O_4)^{2-} \cdot 2H_2O$ (**1**).

In the asymmetric unit of **1**, there are two independent carbonate anions and five independent guanidinium cations, which are henceforth conveniently referred to by their carbon atom labels in bold type. Carbonate **C(1)** and guanidinium **C(3)** each has one bond lying in a crystallographic mirror plane; together with carbonate **C(2)** and guanidinium **C(4)**, they form a nonplanar zigzag ribbon running parallel to the *b*-axis, neighboring units being connected by a pair of strong N^+–H···O$^-$ hydrogen bonds (Figure 1). Adjacent antiparallel $\{[C(NH_2)_3]^+ \cdot CO_3^{2-}\}_\infty$ ribbons are further cross-linked by strong N^+–H···O$^-$ hydrogen bonds to generate a highly corrugated rosette layer, which is folded into a plane-wave pattern by guanidinium **C(5)** (Figure 2). Guanidinium **C(6)** and **C(7)** protruding away from carbonate **C(1)** and **C(2)** are hydrogen-bonded to the 2-fold disordered oxalate ion containing **C(8)** and **C(9)** (Figure 2), forming a pouch that cradles the disordered $(C_2H_5)_4N^+$ ion. The carbonate ions **C(1)** and **C(2)** each forms 11 acceptor hydrogen bonds, only one fewer than the maximum number.[10] The resulting composite hydrogen-bonded layers at $a = {}^1/_4$ and ${}^3/_4$ are interconnected by $[(C_2O_4^{2-} \cdot (H_2O)_2]_\infty$ chains derived from centrosymmetric oxalate **C(10)** and water molecules O1w and O2w via strong $^+$N–H···O$^-$ hydrogen bonds to generate a complex
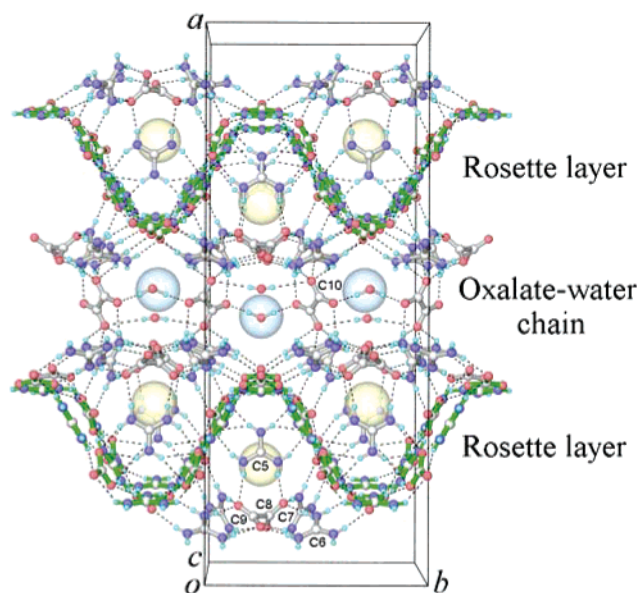
Figure 2. Perspective view of the crystal structure of **1** along [001]. The undulate guanidinium–carbonate rosette network **I**, seen as a sinusoidal cross-section, is highlighted in green. Adjacent composite hydrogen-bonded layers are interconnected by a $[C_2O_4{}^{2-}\cdot(H_2O)_2]_\infty$ chain. The disordered oxalate containing **C(8)** and **C(9)** is shown in one possible orientation, and the two different types of disordered Et_4N^+ ions (represented by large semi-transparent spheres of different colors) are included in the pouches and the zigzag channels running parallel to the [010] direction, respectively.
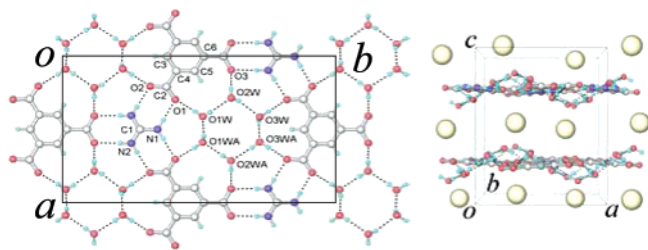
Figure 3. (Left) Projection diagram showing the hydrogen-bonding scheme in the infinite rosette layer **II** of **2**. Only one of the two cyclic arrangements of disordered H atoms lying on the edges of each $(H_2O)_6$ ring is displayed. Symmetry transformation: A $(1 - x, y, {}^1\!/_2 - z)$. (Right) Sandwich-like crystal structure of **2** viewed along the b-axis.

three-dimensional host framework, within which the second kind of disordered $(C_2H_5)_4N^+$ ions are accommodated in a zigzag fashion within channels extending along the [010] direction. Owing to the presence of disordered groups in the structural model, the precision in the refinement of **1** is relatively low ($R_1 = 0.1013$).

The predicted assembly of guanidinium–trimesate network **II** was achieved through the crystallization of $[(C_2H_5)_4N^+]_2\cdot[C(NH_2)_3{}^+]\cdot[1,3,5\text{-}C_3H_3(COO^-)_3]\cdot6H_2O$ (**2**). The guanidinium and trimesate ions are connected together by pairs of strong charge-assisted $^+N-H\cdots O^-$ hydrogen bonds to generate an essentially planar rosette layer with large honeycomb cavities [Figure 3 (left)]. Three independent water molecules constitute a cyclic $(H_2O)_6$ cluster of symmetry 2, which is tightly fitted into each host cavity by adopting a flattened-chair configuration in an out-of-plane orientation, with $O\cdots O$ distances comparable to 2.759 Å in deuterated ice, I_h.[11] Each water molecule has its ordered hydrogen atom pointing outward to form a strong $O-H\cdots O^-$ hydrogen bond with a carboxylate oxygen on the inner rim of the cavity. The well-ordered $(C_2H_5)_4N^+$ guests, represented by large yellow spheres, are sandwiched between anionic rosette host layers with an interlayer spacing of ~7.5 Å [Figure 3 (right)].

The malleability of guanidinium–carbonate network **I**, rendered possible by the prolific hydrogen-bond accepting capacity of its carbonate building block, opens up opportunities for further exploration of supramolecular assembly. The flattened-chair $(H_2O)_6$ guest species, filling the cavity within robust guanidinium–trimesate layer **II** and being comparable to that in the host lattice of bimesityl-3,3′-dicarboxylic acid,[12] may conceivably be replaced by appropriate hydrogen-bond donor molecules. The present anionic rosette networks are unlike previously reported neutral honeycomb lattices of the same (6,3) topology, thus expanding the scope of de novo engineering of *charge-assisted* hydrogen-bonded networks using ionic modular components, from which discrete molecular aggregates bearing the rosette motif[13] may be derived.

Supporting Information Available: Preparative procedure for **1** and **2**, crystal data and X-ray analysis, additional figures (Figures 4–6) illustrating finer structural details, IR spectra, TGA and DSC measurement of **2**, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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