# Self-assembly of Guanidinium Hexagonal Carboxylate: How Many H-bonds and H-bonding Pattern between $ArCOO^-$ and $C(NH_2)_3^+$?

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In guanidinium hexacarboxylate, $\mathbf{H}\cdot G_6\cdot 2H_2O$ (**2**, G = $C(NH_2)_3$, the guanidinium cations and the side pyridinecarboxylate rings are self-assembled *via* multiple H-bonds into zigzag-like ribbons which located between the hexahost **H** core plane layers. The H-bonds graph set present in the *zigzag* ribbons are $R_2^2(8)$, $R_2^1(6)$, $R_2^2(10)$, $R_1^2(6)$, $R_2^4(12)$, $R_5^3(10)$, $R_8^6(24)$, and $R_8^4(24)$.

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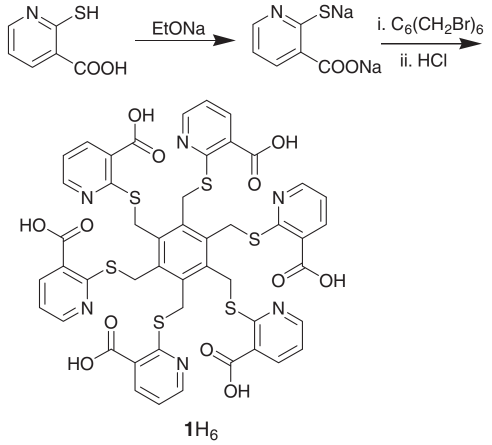
Functional hexahost tailored with rigid polar groups at the side arms have been explored to build supramolecular networks with potential specific enclanthration properties by using intermolecular hydrogen bonding or metal ion coordination interactions.[1–6] The guanidinium cation as a good hydrogen bonding donor units with $C_3$ symmetry have been used to a number of hydrogen-bonded supramolecular networks together with organic sulfonate,[7] hydrogen carbonate dimer,[8] or aromatic carboxylic acid.[9] The topological equivalence between guanidinium cation (G) and the sulfonate group ($SO_3^-$) or $(HCO_3)_2$ moieties favor the formation of 2-D rosettes-like networks. However, the hydrogen-bonding pattern between guanidinium cation and carboxylic acid is more complexing because of the non equivalence of symmetry and the different numbers of donor and acceptor hydrogen-bonding sites. Report of the crystal structure for the guanidinium aromatic polycarboxylate is rare.[7,9] We report here the first synthesis and structural analysis of a guanidinium salt of a new hexagonal carboxylate, hexakis(carboxyl-3-pyridine-2-thiolmethyl)benzene **1** (Scheme 1).



$1H_6$

**Scheme 1.** Synthesis of **1** ($\mathbf{H}\cdot H_6$).

Synthesis of the new hexahost **1** ($\mathbf{H}\cdot H_6$) is straightforward and of high yield. Refluxing of hexakis(bromomethyl)benzene with the disodium salt of 2-mercaptopyridine-3-carboxylic acid, proceeds remarkably cleanly to afford the hexagonal carboxylic acid $\mathbf{H}\cdot H_6$ in ≈87% yield (Scheme 1). The guanidinium salt of **1**, $\mathbf{H}\cdot\mathbf{G}_6\cdot 2H_2O$ (**2**, **G** = $C(NH_2)_3^+$) was prepared by reaction of **1** with excess of guanidinium hydrogen carbonate in hot water in 96% isolated yield.

The X-ray crystal structure of **2** ($\mathbf{HG}_6\cdot 2H_2O$) possesses a center of symmetry (Figure 1).[10] The side aromatic rings of pyridine-3-carboxylate arms (marked as A, B, and C) are directed alternately above and below the central benzene plane, with the dihedral angles to the core plane of 66.0(1), 73.8(2), and 81.7(1)°, respectively. The carboxylic acid group of the side arm B is remarkably twisted from the corresponding aromatic plane with the dihedral angle of 60.8(2)°, while the COO groups of side ring A and C arms tilt to the corresponding plane of 4.6(8) and 18.5(5)°, respectively. The guanidinium cations (marked as G1, G2, and G3) with a orthorgonal arrangement are connected to the **H** molecule as donor sites through multiple hydrogen bonds to the side aromatic carboxylate groups (Figure 1).

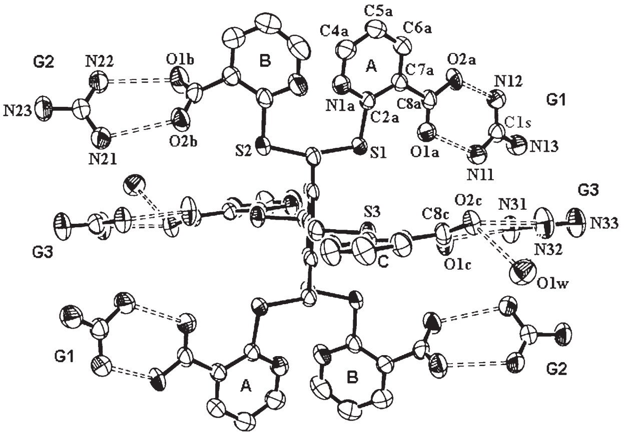


**Figure 1.** ORTEP drawing of **2** showing atomic numbering scheme: the side arms are marked as A, B, and C, and the corresponding guanidinium cations marked as G1, G2, and G3, respectively. Dashed line: H-bonds.

The H-bonds present in crystal **2** are listed in Table 1. The guandinium cations G1, G2, and G3 are connected to side aromatic rings of A, B, and C of **H** molecule through two pairs of $N–H_{syn}\cdots O$ hydrogen bonds [$\boldsymbol{\alpha}$, $N_2 = R_2^2(8)$],[11] i.e. G1 to ring A with a dihedral angle of 18.4(3)°, G2 to ring B of 50.6(2)°, and G3 to ring C of 9.7(3)°, thus forming quasi planar AG1, BG2, and CG3 pairs, respectively (Figure 1). Beside to ring A, the remaining donor sites of G1 connect to ring B (via two $N–H\cdots O$ hydrogen bonds [$\boldsymbol{\beta}$, $N_2 = R_2^1(6)$] and ring C (one $N–H\cdots O$ bond) belong to adjacent two H molecules, and one water molecule. Similarly, in addition to ring C, the remaining donor sites of G3 connect A and B arms belong to adjacent two H molecules [$\boldsymbol{\beta}$, $N_2 = R_2^1(6)$]. G2 cation is also H-bonded to one water molecule and arm A of the adjacent **H** molecule along *c* axis via a strong N–H···O bond and one weak N–H···S bond [$\boldsymbol{\gamma}$, $N_2 = R_2^2(10)$]. G2 cation is located close to the central benzene core with the short contact to the core plane about 3.04(5) Å. Thus, G2 can be regarded as a guest encapsulated in the cavity formed by ABC arms located at the same side of the central benzene plane. The peculiar location and connectivity of G2 cation results in the large distortion of COO group from the corresponding aromatic ring plane of arm B. Each water molecule links two guanidinium cations (G1 and G2) as hydrogen bonding acceptors, and as donors links two COO groups of C arms belong to adjacent two **H** molecules along [1,−1,1] direction. The O1w–H···O1c and the weak O1w–H···S3 bonds form a hexagonal motif [$\boldsymbol{\delta}$, $N_2 = R_1^2(6)$] (Figure 2).

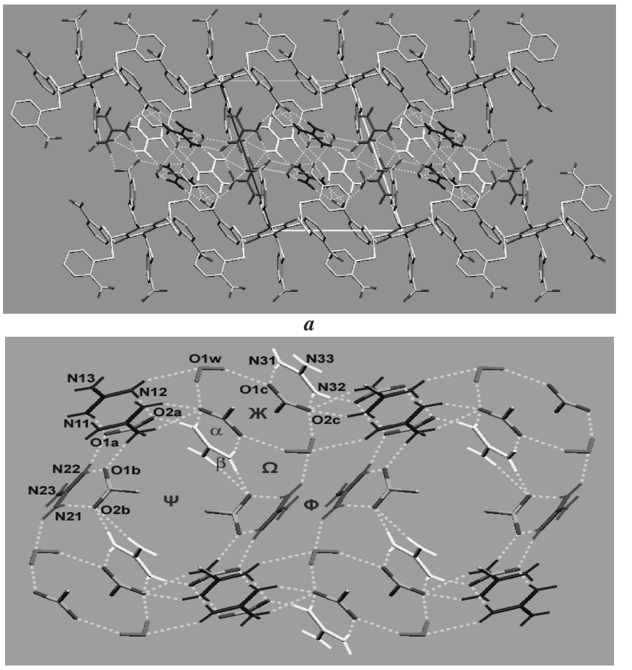
**Table 1.** Specified hydrogen bonds in **2**

| D···A | <(DHA) | D–H···A | Comments |
|---|---|---|---|
| 2.883(5) | 168(5) | N11–H11A···O1A | G1. . .A |
| 2.917(5) | 169(5) | N12–H12A···O2A | G1. . .A |
| 3.066(5) | 149(4) | N11–H11B···O2C_$7 | G1. . .C |
| 2.970(6) | 150(4) | N13–H13A···O2C_$7 | G1. . .C |
| 3.338(6) | 148(5) | N12–H12B···O1W_$4 | G1. . .W |
| 2.841(5) | 174(5) | N13–H13B···O1B_$3 | G1. . .B |
| 2.836(5) | 159(4) | N22–H22A···O1A_$6 | G2. . .A |
| 3.502(5) | 174(4) | N23–H23A···S1_$6 | G2. . .S1(A) |
| 2.880(5) | 176(4) | N22–H22B···O1B | G2. . .B |
| 2.890(5) | 158(4) | N21–H21A···O2B | G2. . .B |
| 2.978(6) | 147(5) | N21–H21B···O1W_$2 | G2. . .W |
| 3.086(6) | 138(6) | N33–H33A···O2A_$4 | G3. . .A |
| 2.869(5) | 162(5) | N32–H32A···O2A_$4 | G3. . .A |
| 3.023(6) | 144(5) | N33–H33B···O2B_$5 | G3. . .B |
| 2.995(5) | 153(5) | N31–H31A···O2B_$5 | G3. . .B |
| 2.775(5) | 172(4) | N31–H31B···O1C | G3. . .C |
| 2.872(5) | 167(6) | N32–H32B···O2C | G3. . .C |
| 2.831(5) | 145(8) | O1W–H1W···O2C | W. . .C |

*Symmetry operators: $1 $-x+1$, $-y$, $-z$; $2 $-x+1$, $-y-1$, $-z$; $3 $-x$, $-y+1$, $-z$; $4 $-x$, $-y$, $-z+1$; $5 $x$, $y$, $z+1$; $6 $x$, $y$, $z-1$; $7 $x$, $y+1$, $z$.

The AG1, BG2, and CG3 pairs are self-assembled via H-bonding into a zigzag arrangement with hydrogen bonded ribbons located between the core plane layers of **H** molecules (Figure 2). In the ribbon, the strong N–H···O hydrogen bonding between the adjacent AG1, BG2, CG3 pairs and $H_2O$ molecules results in several large H-bonding graphs (Figure 2b). The binary graph Ж [$N_2 = R_2^4(12)$] comprises assembly of two water molecules and two COO groups of ring C belong to two adjacent **H** molecules along [1,−1,1] direction, which is connected by strong O1w–H···O2c (2.84 Å) and O1w–H···O1c (3.11 Å) hydrogen bonds. Two edges of adjacent BG2 and CG3 pairs are linked to a water molecule to form a pentagon motif, $\boldsymbol{\Omega}$ [$N_5 = R_5^3(10)$]. Six G-COO pairs [2 × (AG1 + BG2 + CG3)] are assembled in face-to-face mode, with N–H···O hydrogen bonds connecting the adjacent G-COO pair, thus forming a large cavity encapsulating the side aromatic ring of B [$\boldsymbol{\Psi}$, $N_4 = R_8^6(24)$]. Finally, two water molecules (as acceptor), AG1 and BG2 pair [2 × (AG1 + BG2)] are connected via N–H···O hydrogen bonds to form a long ring [$\boldsymbol{\Phi}$, $N_4 = R_8^4(24)$]. Because of the strong multiple hydrogen bonds between molecules, the crystal of **2** is quite stable and conversely packed with the calculated density of 1.43 g·cm$^{-3}$.

In summary, we have demonstrated the synthesis and crystal structure of guanidinium hexacarboxylate. The following H-bonds garph set are present in the crystal **2**: $R_2^2(8)$ [$\alpha$], $R_2^1(6)$ [$\beta$], $R_2^2(10)$ [$\gamma$], $R_1^2(6)$] [$\delta$], $R_2^4(12)$ [Ж], $R_5^3(10)$ [$\Omega$], $R_8^6(24)$ [$\Psi$], and $R_8^4(24)$ [$\Phi$] (Figure 2).



*a*

*b*

**Figure 2.** Perspective view of the crystal packing showing the hydrogen bonding pattern in the crystal **2**: a) along *a* axis and b) along *c* axis. The COO groups of **H** molecule is depicted, other atoms is deleted for clarity in figure b; color scheme: G1 in blue, G2 in red, G3 in yellow, and water molecule in pink.

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10 Crystal data for **2**: $C_{54}H_{70}N_{24}O_{14}S_6$; $M = 1471.7$, triclinic, space group $P-1$ (No. 2), $a = 11.853(6)$ Å, $b = 12.267(6)$ Å, $c = 13.764(7)$ Å, $\alpha = 80.438(8)^\circ$, $\beta = 84.799(11)^\circ$, $\gamma = 64.998(9)^\circ$, $V = 1706.2(11)$ Å$^3$, $Z = 1$, 8676 unique, 5076 observed with $I > 2\sigma(I)$; final $R = 0.070$ (observed), 0.094 (all), $wR(F^2)$ ) 0.197 (observed), 0.223 (all), final GooF = 1.066. All hydrogen atoms were located from difference maps and refined isotropically using SHELXL 97. CCDC-226197.
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