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# 1. Introduction

Hydrogen bonding has long been known to be a useful tool for crystal engineering, allowing molecular chemists to design important physical properties into crystalline solids.<sup>1-10</sup> One particularly desirable structural characteristic is noncentrosymmetry. Noncentrosymmetric, or acentric crystals, those without a center of symmetry in their lattice, can possess a number of very useful properties such as nonlinear optical behavior, piezoelectricity, and optical activity, among others.<sup>11-13</sup> They also have a very important subgroup, namely crystals with a polar axis, that can specifically display pyroelectric and ferroelectric properties.<sup>14-16</sup> Hydrogen bonded crystals have proven to be an ideal workspace for crystal engineering and the preparation of single crystals with interesting properties, including those that are acentric or polar.<sup>17–22</sup>

The guanidinium ion has been shown by Ward and coworkers to react readily with an enormous range of organosulfonates  $(RSO_3^{-})$  to form crystals whose structures are predominantly driven by extensive two-dimensional

# Guanidinium sulfates as directors of noncentrosymmetric structures†

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The structures of seven compounds based on guanidinium cations, isolated sulfate anions, and additional organic cations and solvent molecules are reported. All seven compounds,  $(C(NH_2)_3)_2(SO_4)$  (1),  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$  (2),  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2 \cdot H_2O$  (3),  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2 \cdot CH_3OH$  (4),  $(C(NH_2)_3)_{11}(C_5H_6N)(SO_4)_6 \cdot 2.5C_2H_5OH$  (5),  $(C(NH_2)_3)_3(C_6H_{16}N)(SO_4)_2$  (6), and  $(C(NH_2)_3)_2(C_{20}H_{26}N_2O_2)(SO_4)_2$  (7) crystallize without a center of symmetry, and are built of related motifs of six-membered rings *via* hydrogen bonding of three guanidinium cations and three sulfate anions. These six-membered rings form extended sheets and frameworks through additional hydrogen bonding interactions. The presence of additional cations and solvent molecules in varying ratios add structural diversity by modifying the guanidinium sulfate frameworks, but retaining the acentricity of the structures. The study reveals a remarkable tendency for these guanidinium sulfate frameworks to crystallize without a center of symmetry, and furthermore, in polar or chiral space groups. This provides a potential pathway for the use of hydrogen bonding interactions to design structures having interesting physical or nonlinear optical properties.

hydrogen bonding.<sup>23–26</sup> The crystals can be engineered to adopt many useful properties and in some cases the hydrogen bonding can be used to design the formation of acentric crystals.<sup>27</sup> We were able to follow the lead of Ward and exploit this extensive network of hydrogen bonding to selectively grow high quality single crystals of guanidinium salts of chiral organosulfates ( $ROSO_3^-$ ) for simple unambiguous chiral identification.<sup>28</sup> However, it is estimated that less than 10% of compounds that are not derived from resolved chiral solutions will spontaneously crystallize in acentric space groups.<sup>29–31</sup> Thus it becomes an important aspect of crystal engineering to identify candidate classes of compounds that fall into this minority category of structures that lack a center of symmetry and do not contain a chiral center.

In this paper we examine the structure of several new guanidinium salts based on isolated sulfate dianions, beginning with the simple parent guanidinium sulfate salt itself,  $Gu_2(SO_4)$ . This explores the use of two building blocks that are acentric, but not chiral (a trigonal plane and a tetrahedron). The guanidinium ions present rich possibilities for structural assembly in that every hydrogen atom in the cation can and does engage in hydrogen bonding, while every oxygen atom on the sulfate anions can likewise engage in hydrogen bonding. Such systems with isolated sulfate groups present an interesting contrast to the systems studied in such great detail by Etter, Ward, and others, who generally use organic moieties on either the donor or acceptor, or both, to

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#### Paper

act as scaffolding for the rings and chains of hydrogen bonding. The lack of an appendage on the isolated sulfates can enable the extension of hydrogen bonding motifs into the third dimension. We further expand upon this by introducing other cationic species or cocrystallizing solvent molecules with hydrogen bonding capability, such as triethylammonium, to examine pyridinium or how guanidinium sulfate hydrogen bonding networks are modified. Herein we examine the hydrogen bonding networks found in seven guanidinium sulfate compounds containing various other small molecule cations and solvents of crystallization. In this way such systems can be thought of as a host-guest relationship between the guanidinium sulfate host frameworks and the guest cations and solvent molecules 1). All were found crystallize (Scheme to in noncentrosymmetric space groups, distinguishing this as an especially promising class for the growth of new crystals for nonlinear optical applications or other applications relying on acentric or polar features.

#### 2. Materials and methods

#### 2.1 Synthesis

Crystals in the present study were generally obtained serendipitously as side products from one-pot reactions targeting organosulfate salts of guanidinium.28 In this process, an organic alcohol (1 mmol) was treated with 1.3 equivalence of technical grade ( $\geq 45\%$  SO<sub>3</sub> basis) sulfur trioxide/pyridine in 5 mL of dry dichloromethane (DCM) to afford the organosulfate pyridinium complex in solution. After the suspension was stirred for 24 hours under N2, the mixture was filtered and concentrated in vacuo or directly used in the subsequent guanidinium salt crystallization. To the sulfate pyridinium complex, guanidinium chloride was added, and an alcohol solvent was dropped in until the solution became homogenous. Slow evaporation of the solution will typically give crystals of the guanidinium organosulfate salt. However, when sulfation of the organic substrate is unsuccessful (i.e. for tertiary alcohols) or the rate of the reaction is slow, at the end of the 24 h reaction there remains a significant amount of the unreacted SO<sub>3</sub>-pyridine in solution that is available to react directly with the guanidinium chloride once it is added. These circumstances led to the formation of the compounds in the present study.



Scheme 1 Structural building block ions in the present study

Since the primary interest in these specific compounds at this time is solely structural in nature, no efforts have been made to optimize their synthesis or gauge their purity. All reagents and chemicals were obtained from commercial sources and used without further purification unless stated otherwise. Dichloromethane (DCM) was dried by refluxing over phosphorous pentoxide  $(P_2O_5)$  and distilling under nitrogen prior to use.

2.1.1 (C(NH<sub>2</sub>)<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>) (1). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq$ 45% SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N2 and (-)-carveol was added dropwise (1 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, after which the unreacted SO<sub>3</sub>·Pyr was filtered off. The filtrate was then concentrated in vacuo and guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added. Isopropyl alcohol (IPA) was added until the solution became homogenous. Solvent layering with hexanes produced large block-like crystals of 1.

2.1.2 (C(NH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>6</sub>N)(SO<sub>4</sub>)<sub>2</sub> (2). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq 45\%$ SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N2 and 1,3-butanediol was added dropwise (0.5 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, after which the unreacted SO<sub>3</sub>·Pyr was filtered off. Guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added directly to filtrate and methanol (MeOH) was added until the solution became homogenous. Slow evaporation of the solution produced large plate-like crystals of 2.

2.1.3 (C(NH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>(C<sub>5</sub>H<sub>6</sub>N)(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (3). To a flame dried 10 mL round bottom flask with a stir bar, technical grade  $(\geq 45\% \text{ SO}_3 \text{ basis})$  sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N2 and (-)-Corey lactone benzoate was added dropwise (1.0 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, after which the unreacted SO3·Pyr was filtered off. Guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added directly to filtrate and MeOH was added until the solution became homogenous. Slow evaporation of the solution produced block-like crystals of 3. Formation of the water solvate appears to be assisted by adventitious water from the ambient atmosphere.

2.1.4  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2 \cdot CH_3OH$  (4). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq$ 45% SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N<sub>2</sub> and (-)-linalool was added dropwise (1.0 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, and after completion the unreacted SO<sub>3</sub>·Pyr was filtered off. Guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added directly to filtrate and MeOH was added until the solution became

homogenous. Slow evaporation of the solution produced block-like crystals of **4**.

**2.1.5**  $(C(\mathbf{NH}_2)_3)_{11}(\mathbf{C}_5\mathbf{H}_6\mathbf{N})(\mathbf{SO}_4)_6\cdot 2.5\mathbf{C}_2\mathbf{H}_5\mathbf{OH}$  (5). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq$ 45% SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N<sub>2</sub> and (–)-carveol was added dropwise (1 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, and after completion the unreacted SO<sub>3</sub>·Pyr was filtered off. The filtrate was then concentrated *in vacuo* and guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added. Ethanol (EtOH) was added until the solution became homogenous. Slow evaporation of the solution produced block-like crystals of 5.

**2.1.6** (C(NH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>16</sub>N)(SO<sub>4</sub>)<sub>2</sub> (6). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq$ 45% SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.), triethylamine (1.0 mmol, 0.101 grams, 1.0 equiv.), and dry DCM (5 mL) was added. The suspension was stirred under N<sub>2</sub> and D-phenylalanine was added dropwise (1.0 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, after which the unreacted SO<sub>3</sub>·Pyr was filtered off. Guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added directly to filtrate and MeOH was added until the solution became homogenous. Slow evaporation of the solution produced large block-like crystals of 6.

**2.1.7**  $(C(NH_2)_3)_2(C_{20}H_{26}N_2O_2)(SO_4)_2$  (7). To a flame dried 10 mL round bottom flask with a stir bar, technical grade ( $\geq 45\%$  SO<sub>3</sub> basis) sulfur trioxide/pyridine complex (1.3 mmol, 0.207 grams, 1.3 equiv.) and dry DCM (5 mL) was added. The suspension was stirred under N<sub>2</sub> and (+)-quinidine was added dropwise (1 mmol, 1 equiv.). The resulting solution was stirred for 24 hours, and after completion the unreacted SO<sub>3</sub>-Pyr was filtered off. The filtrate was then concentrated *in vacuo* and guanidinium chloride (1.0 mmol, 0.095 grams, 1.0 equiv.) was added. MeOH was added until the solution became homogenous. Slow evaporation of the solution produced block-like crystals of 7.

#### 2.2 X-ray diffraction

Single crystal X-ray diffraction data were collected using a Bruker D8 Venture diffractometer with a Photon 100 detector and a Mo K $\alpha$  ( $\lambda = 0.71073$  Å) microfocus source. Crystals were mounted on low-background loops and quenched in a cold nitrogen stream. Data were collected using phi and omega scans with a width of 0.5°. Data collection and processing was performed through the Apex 3 software suite (SAINT and SADABS).<sup>32</sup> Space group determinations based on the systematic absences were made using the XPREP module of SHELXTL. Structure solution was achieved using intrinsic phasing (SHELXT) with subsequent refinement by full matrix least squares on  $F^2$  (SHELXL).<sup>33</sup>

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon atoms were placed in

geometrically-optimized positions and refined using appropriate riding models. Hydrogen atoms attached to nitrogen and oxygen atoms were first identified from the difference electron density map, and their positions and thermal parameters fully refined. In some circumstances, more reasonable hydrogen atom positions were obtained by incorporating distance fixing restraints into the model. When the parent atom was on a special position or the hydrogen bonding arrangement subject to disorder, geometricallyoptimized positions were found to be preferable, and these positions remained consistent with residual electron density in the difference map. All of the structures in the present study were refined in noncentrosymmetric space groups with acceptable Flack parameters indicating the proper absolute structure (given the presence of sulfur in all the structures to enhance anomalous dispersion). All bond lengths were found to be within the typical ranges. Crystallographic data are given in Tables 1 and 2. Further details may be obtained in CIF form from the Cambridge Crystallographic Data Centre, upon quoting deposition numbers 2012777-2012783.

### 3. Results and discussion

#### 3.1 Synthesis and occurrence

The guanidinium cation has demonstrated great versatility in establishing a rich structural chemistry in organic sulfonate chemistry.<sup>5,6,23-27</sup> The extensive hydrogen bonding capabilities of the guanidinium cation combined with the stability of the R-SO<sub>3</sub> functionality has led to a great variety of complex structures, including framework-, pore-, pillar-, and channel-based architectures. Far less-studied than the sulfonates are the organic sulfates, having R-O-SO3 functionality. In principle, the same hydrogen bonding capabilities of these guanidinium sulfates should present a similarly vast potential for crystal engineering and structural studies. We are focusing on preparing organic sulfates from alcohols to accomplish chiral identification,<sup>28</sup> and chiral resolution via the growth of enantiopure, large single crystals.

Our approach is to use the SO<sub>3</sub>-pyridine complex as a reagent to convert organic alcohols to organic sulfates. Once the organic sulfate has been formed as a pyridinium complex in solution, guanidinium chloride can be added to displace the pyridinium and form crystals of the guanidinium salt of the organic sulfate, driven by the formation of extensive hydrogen bonding networks. While developing that synthetic methodology we observed several instances where the SO3pyridine complex itself reacted directly with guanidinium chloride to form guanidinium sulfates, including sulfate salts having mixtures of guanidinium and pyridinium cations. This often occurred when attempting the sulfation of highly functionalized secondary alcohols or stubborn tertiary alcohols, situations where sulfation of the alcohol substrate was apparently disfavored. In another instance, a triethylammonium cation from an attempted optimization reaction was paired with the guanidinium cation and sulfate

Table 1 Crystallographic data for compounds 1-4

	1	2	3	4
Formula	$C_2H_{16}N_6O_4S$	$C_8H_{24}N_{10}O_8S_2$	$C_8H_{26}N_{10}O_9S_2$	$C_9H_{28}N_{10}O_9S_2$
Space group	<i>P</i> 4 <sub>3</sub> 32 (no. 212)	<i>R</i> 32 (no. 155)	C2 (no. 5)	$P2_1$ (no. 4)
a (Å)	17.8273(6)	10.0469(10)	12.3826(9)	7.4737(6)
b (Å)	17.8273(6)	10.0469(10)	11.1225(7)	11.8491(11)
<i>c</i> (Å)	17.8273(6)	17.3180(17)	7.7723(5)	13.0179(13)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	90	90	102.385(2)	93.723(3)
γ (°)	90	120	90	90
Cell volume (Å <sup>3</sup> )	5665.7(6)	1513.9(3)	1045.53(12)	1150.39(18)
Z	20	3	2	2
Formula weight	216.24	452.49	470.51	484.53
Density (calc, mg $m^{-3}$ )	1.268	1.489	1.495	1.399
Temp (K)	100	100	100	140
Size (mm)	$0.21 \times 0.12 \times 0.09$	$0.30 \times 0.27 \times 0.04$	$0.19 \times 0.18 \times 0.14$	$0.16 \times 0.11 \times 0.07$
Abs. coeff. $(mm^{-1})$	0.286	0.322	0.318	0.291
$\Theta$ range (deg.)	3.23-26.41	2.62-27.47	2.49-28.50	2.33-25.50
Reflections	131 432	11748	11 289	25 166
Unique reflections	1952	774	2640	4270
R <sub>int</sub>	0.0616	0.0373	0.0277	0.0578
No. of parameters	131	54	179	352
$R_1$ , w $R_2$ (all data)	0.0371, 0.1163	0.0257, 0.0629	0.0216, 0.0550	0.0297, 0.0680
$R_1$ , w $R_2$ (obs. data)	0.0384, 0.1178	0.0265, 0.0632	0.0223, 0.0554	0.0340, 0.0701
Goodness of fit on $F^2$	1.200	1.092	1.076	1.056
Flack param.	0.013(14)	0.01(3)	-0.018(18)	0.07(3)
Larg. diff. peak (e $Å^{-3}$ )	0.738	0.195	0.169	0.379
Larg. diff. hole (e $Å^{-3}$ )	-0.283	-0.337	-0.333	-0.250
CCDC deposition no.	2012777	2012778	2012779	2012780

 $R_1 = \left[\sum ||F_0| - |F_c||\right] / \sum |F_0|; \ \text{w}R_2 = \left\{\left[\sum w[(F_0)^2 - (F_c)^2]^2\right]\right\}^{1/2}.$ 

#### Table 2 Crystallographic data for 5–7

	5	6	7
Formula	$C_{21}H_{87}N_{34}O_{26.5}S_6$	$C_9H_{34}N_{10}O_8S_2$	$C_{22}H_{38}N_8O_{10}S_2$
Space group	<i>Pna</i> 2 <sub>1</sub> (no. 33)	<i>P</i> 4 <sub>1</sub> (no. 76)	$P2_1$ (no. 4)
<i>a</i> (Å)	26.0251(8)	10.8776(4)	7.1728(4)
b (Å)	22.0693(6)	10.8776(4)	11.1002(7)
c (Å)	12.5545(4)	20.4184(7)	19.3610(12)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90	90	100.265(2)
γ (°)	90	90	90
Cell volume (Å <sup>3</sup> )	7210.7(4)	2415.9(2)	1516.84(16)
Ζ	4	4	2
Formula weight	1432.60	474.58	638.72
Density (calc, mg $m^{-3}$ )	1.320	1.305	1.398
Temp (K)	140	100	140
Size (mm)	$0.17 \times 0.15 \times 0.14$	$0.44 \times 0.40 \times 0.35$	$0.38 \times 0.10 \times 0.10$
Abs. coeff. $(mm^{-1})$	0.278	0.272	0.240
$\Theta$ range (deg.)	2.02-26.00	2.65-26.50	2.12-26.50
Reflections	59 324	22 103	46 918
Unique reflections	13 979	4984	6243
R <sub>int</sub>	0.0558	0.0264	0.0527
No. of parameters	945	341	440
$R_1, WR_2$ (all data)	0.0482, 0.1309	0.0254, 0.0620	0.0336, 0.0762
$R_1$ , w $R_2$ (obs. data)	0.0642, 0.1420	0.0268, 0.0628	0.0390, 0.0785
Goodness of fit on $F^2$	1.095	1.090	1.025
Flack param.	0.07(2)	0.000(14)	-0.007(17)
Larg. diff. peak (e $Å^{-3}$ )	0.680	0.168	0.388
Larg. diff. hole (e $Å^{-3}$ )	-0.541	-0.282	-0.277
CCDC deposition no.	2012781	2012782	2012783

 $R_1 = \left[\sum ||F_0| - |F_c||\right] / \sum |F_0|; \ wR_2 = \left\{\left[\sum w[(F_0)^2 - (F_c)^2]^2\right]\right\}^{1/2}.$ 

anion. In that case, triethylamine was added to the sulfation reaction in hopes that it would deprotonate the alcoholic proton and increase the rate of reaction. The quinidine substrate also resisted sulfation, but was protonated in situ, and having sufficient hydrogen bonding donor sites was able to crystallize as the mixed guanidinium-quinidinium sulfate. These are somewhat unique structures because in general, relatively few materials are reported based on isolated sulfate anions and guanidinium cations. The structures of guanidinium sulfate,<sup>34</sup> the methanol solvate of guanidinium sulfate,<sup>35</sup> guanidinium sulfate chloride,<sup>36</sup> a mixed guanidinium-tetramethylammonium sulfate,37 and several guanidinium sulfates with hydrated divalent<sup>38</sup> and trivalent<sup>39,40</sup> metal cations are reported in the literature and represent the few examples of isolated sulfate groups coordinated only through hydrogen bonding with the cation species. The serendipitous compounds of the present study significantly expand the scope of this structural class. Interestingly, all of these salts in the present study crystallize in noncentrosymmetric space groups, and in many cases in polar or chiral space groups.

#### 3.2 Guanidinium sulfate

The structure of parent guanidinium sulfate,  $(C(NH_2)_3)_2(SO_4)$ (1), is an example of the formation of a three-dimensional hydrogen bonded framework comprised of only guanidinium cations and sulfate anions, where every nitrogen and oxygen atom in the lattice is hydrogen bonded. The room



temperature structure of 1 was previously reported, though

that refinement resulted in a high  $R_1$  value ( $R_1 = 0.1026$ ),<sup>34</sup>

and an improved refinement of the structure based on low

temperature data is provided in the current study. The

structure of guanidinium sulfate (1) is based on a three

dimensional hydrogen bonding network between planar

guanidinium cations and tetrahedral sulfate anions (Fig. 1).

There are two unique sulfate anions, and each oxygen atom

of the sulfate molecules supports hydrogen bonds to three

different guanidinium molecules. Through these N-H···O

interactions, each sulfate anion is hydrogen bonded to six

guanidinium cations such that each guanidium chelates one

edge of the sulfate tetrahedron. Each guanidium cation is

hydrogen bonded to three sulfate anions. This results in a

complex framework primarily consisting of distorted six-

membered rings of three guanidinium cations and three

sulfate anions (Fig. 2). In the extended framework formed by

these distorted six-membered rings, distorted eight-

membered rings are also formed. We note that this motif of

six-membered guanidinium sulfate rings, and the occasional

formation of additional rings within the larger framework are

key components of all the structures reported herein.

Fig. 1 Hydrogen bonding interactions between guanidinium cations and sulfate anions (top) and packing diagram (bottom) for  $(\mathsf{C}(\mathsf{NH}_2)_3)_2(\mathsf{SO}_4)$  (1). Hydrogen atoms are omitted for clarity, and green dashed lines represent the N-H...O hydrogen bonds. The color scheme for atoms in the diagrams is: C: gray, N: blue, O: red, S: yellow.

Fig. 2 Six-membered guanidinium sulfate motif formed via hydrogen bonding observed throughout the present study (top). Guanidinium sulfate network in  $(C(NH_2)_3)_2(SO_4)$  (1) (bottom). Connections drawn between the center of guanidinium cations (gray) and sulfate anions (yellow) represent N-H···O hydrogen bonds forming the framework.

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#### 3.3 Family of mixed cation guanidinium-pyridinium sulfates

The differences in size and possible N-H...O hydrogen bonding patterns between pyridinium and guanidinium cations with sulfate anions dictates that introduction of pyridinium to the systems will add additional variety to the structures. Here, we observed four cases of mixed pyridinium and guanidinium cations with the isolated sulfate anions. In all cases, pyridinium is the minor component of the cationic mixture, incorporating into the structures as 3:1 and 11:1 ratios of guanidinium: pyridinium. Although SO3-pyridine was used in slight excess of 1.3 equivalence with respect to the alcohol in the sulfation step, the solid unreacted SO<sub>3</sub>pyridine was filtered off after the 24 h reaction. Therefore, it was never in a stoichiometric deficiency relative to guanidinium chloride, which was added in the subsequent step in 1.0 equivalence. Even so, the resulting crystals all exhibit a significant excess of guanidinium in their structures, suggesting that the increased hydrogen bonding capacity of the guanidinium cations to the sulfate anions is still the primary contributor to crystal growth. For those compounds crystallizing in the 3:1 cation ratio, the solventfree  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$  (2) and solvated  $(C(NH_2)_3)_3(C_5 H_6N)(SO_4)_2 \cdot H_2O$  (3) and  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2 \cdot CH_3OH$  (4) crystals were grown. The compound with the 11:1 cation ratio was obtained as the ethanol solvate,  $(C(NH_2)_3)_{11}(C_5H_6N)$  $(SO_4)_6 \cdot 2.5C_2H_5OH$  (5).

Compound 2,  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$  crystallizes in the rather high symmetry acentric space group *R*32. The tetrahedral sulfate group has a sulfur atom at a 6c Wyckoff position with trigonal symmetry, a unique apical oxygen atom O1 also at a 6c site, and one unique basal oxygen atom O2 at an 18f general position. Each sulfate group is surrounded by six guanidinium and three pyridinium cations, and each oxygen atom has three hydrogen bonding interactions to the cations (Fig. 3). There is only one half of a guanidinium molecule in the asymmetric unit, with the cation formed by the C1 atom at a 9d site, N1 at a 9d site, and N2 at an 18f site. The apical O1 site of the sulfate anion supports three hydrogen bonds from N2 atoms of the guanidinium cations. The basal O2 sites support two hydrogen bonds from guanidinium cations (one from N1 and one from N2) and one hydrogen bond from pyridinium. In this way, the three basal edges of the sulfate tetrahedra are chelated by guanidinium cations. All six of the hydrogen atoms of the guanidinium cation are committed to hydrogen bonding with sulfate anions. The pyridinium cation is formed from one unique atom at a general position. The nitrogen atom is disordered over the six resulting equivalent positions on the pyridine ring, and thus each position has on average a weaker N/C-H···O hydrogen bonding interaction with a sulfate oxygen acceptor compared to the N-H…O interactions from the guanidinium nitrogen atoms. The hydrogen bonding interactions between the guanidinium and sulfate units alone form a three dimensional framework (Fig. 4), which is decorated by the additional pyridinium contributions. The structure has a distinct layered nature along the *c*-axis, with alternating layers of guanidinium and pyridinium/sulfate ions.

In the mixed cation water solvate,  $(C(NH_2)_3)_3(C_5H_6N)$  $(SO_4)_2 \cdot H_2O$  (3), the asymmetric unit in space group *C*2 consists of one sulfate anion with all atoms at general positions, one guanidinium cation at general positions, one guanidinium cation having two-fold symmetry, one pyridinium cation having twofold symmetry, and a halfoccupied water molecule at a general position. Here, the sulfate group is coordinated by six guanidinium cations and one water molecule *via* hydrogen bonding. The pyridinium cation is well ordered in this case, and participates in N– H…O hydrogen bonding with the water molecule, opposite the O–H…O hydrogen bonding from the water molecule to the sulfate. The immediate guanidinium coordination about



**Fig. 3** Hydrogen bonding interactions between guanidinium cations, pyridinium cations, solvent molecules, and sulfate anions (top row) and packing diagrams (bottom row) for the 3:1 guanidinium : pyridinium cation family:  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$  (2),  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$ ·H<sub>2</sub>O (3), and  $(C(NH_2)_3)_3(C_5H_6N)(SO_4)_2$ ·CH<sub>3</sub>OH (4). Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity, and green dashed lines represent the N-H…O hydrogen bonds that occur. The color scheme for atoms in the diagrams is: C: gray, N: blue, O: red, S: yellow; disordered C/N sites of the pyridinium cation in **2** are shown in black.





Fig. 4 Guanidinium sulfate frameworks of 2–4 visualized by connections between the central carbon and sulfur atoms of the guanidinium cations and sulfate anions, including the positions of the pyridinium cations and solvent molecules. In 2, the nitrogen atom of the pyridinium cation is disordered evenly over all sites in that molecule.

the sulfate group is identical to that in anhydrous 2, and the two compounds form similar guanidinium sulfate frameworks, though 3 is distorted from the ideal three-fold symmetry of 2 (Fig. 3). Honeycomb-like nets form in the bc plane, with eight-membered rings forming in the ac plane to create a framework with hexagonal channels. The distortion of the channel structure of 3 compared to 2 occurs to accommodate the water molecules in the channels of 3, enabling the associated O-H…O interactions with the sulfate groups. Since the primary interaction of the pyridinium cation in 3 is with the water molecule, its position is also affected by the solvent, and it is forced off the pseudo-three fold symmetry of the guanidinium sulfate framework (Fig. 4). This interaction likely also facilitates a well-ordered pyridinium cation to allow for the formation of pyridinewater-sulfate hydrogen bonding as N-H···O-H···O-S chains. The polar nature of the structure is apparent in all of the structural units, but most dramatically in the cooperative alignment of the C1-N1 bonds of the guanidinium cations, the N6 atoms of the pyridinium cations (and thus the N-H…O hydrogen bonds), and the orientation of the water molecules along the *b*-axis of the structure. The sulfate groups are of course also co-aligned, with the S1-O4 bond most closely corresponding to the polar b-axis. A similar layered nature to the structure occurs in 3 as in 2, where there are layers of guanidinium cations alternating with layers containing both the pyridinium cations and sulfate anions. Here the layers are oriented diagonally in the ac plane.

In the mixed cation methanol solvate,  $(C(NH_2)_3)_3(C_5H_6N)$  $(SO_4)_2$ ·CH<sub>3</sub>OH (4), all atoms are located at general positions in space group  $P2_1$ . Here the connectivity differs significantly from the other 3:1 structures. The S1 sulfate group is coordinated by five guanidinium cations. Each of these guanidinium molecules chelates one edge of the tetrahedron. If the polar *b*-axis of the structure is chosen to define the apices of the sulfate tetrahedra, then the three apical edges of the S1 tetrahedron are all chelated, and the basal O1–O2 edge of the tetrahedron is doubly-chelated. The O1–O3 and O2–O3 edges are not chelated since O3 only supports one hydrogen bond to a guanidinium molecule. This occurs because a pyridinium cation in the vicinity of O3, though not in a proper orientation to hydrogen bond to O3, causes the guanidinium cation to rotate away from a chelating position. The S2 sulfate anion participates in hydrogen bonding with four guanidinium molecules, the pyridinium cation, and the methanol solvent molecule. The guanidinium cations are again chelating edges of the sulfate tetrahedron, with one apical edge and two basal edges chelated, with one of the basal edges (O5-O6) is doubly-chelated. The pyridinium and methanol molecules have hydrogen bond interactions to single oxygen atoms at O7 and O8, respectively (Fig. 3). The three-dimensional framework formed by the guanidinium and sulfate ions is much different in 4 than in 2 and 3. In 4 the framework is built of six- and eight-membered rings of the ions (Fig. 4) with the pyridinium cations aligned in channels.

The structure of  $(C(NH_2)_3)_{11}(C_5H_6N)(SO_4)_6 \cdot 2.5C_2H_5OH$  (5) is somewhat more complex, consisting of six unique SO4 groups (two of which are subject to disorder of the basal oxygen atoms), eleven unique guanidinium cations, one pyridinium cation disordered over two positions, one fullyoccupied ethanol solvent molecule, one half-occupied ethanol solvent molecule, and one ethanol solvent molecule disordered over the same two areas as the pyridinium cation, providing the balance of that occupancy. The coordination to the sulfate anions is shown in Fig. 5. Each of the six unique sulfate groups has a different coordination pattern through hydrogen bonding. The S1 sulfate anion is coordinated by six guanidinium cations, five of which chelate edges. The basal O3-O4 edge is chelated by two guanidinium cations approaching from opposing directions. The apical O1 oxygen atom is bifurcated by the sixth guanidinium cation, accepting hydrogen bonds from the N5 and N6 donors. The S2 sulfate is coordinated by six guanidinium cations and one ethanol molecule (the fully occupied EtOH) via hydrogen bonding. Here, four of the guanidinium cations chelate edges, with one of the edges of the SO<sub>4</sub> tetrahedron (O5-O7) again doubly chelated. The fifth guanidinium cation is bifurcated toward the O8 oxygen atom, while the sixth guanidinium cation makes only one hydrogen bond to the sulfate, also to O8. The ethanol molecule completes the coordination through O-



Fig. 5 Hydrogen bonding interactions between guanidinium cations, pyridinium cations, ethanol solvent molecules, and sulfate anions (top) and packing diagrams (bottom) for the 11:1 guanidinium:pyridinium sulfate:  $(C(NH_2)_3)_{11}(C_5H_6N)(SO_4)_6\cdot 2.5C_2H_5OH$  (5). Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity, and green dashed lines represent the N-H···O hydrogen bonds that occur. Only one of the disordered arrangements for the pyridinium, ethanol, and sulfate disorder is shown. The color scheme is the same as in previous figures.

H…O hydrogen bonding to O7, giving that oxygen atom a total of four hydrogen bonds. The S3 sulfate group is coordinated by five guanidinium cations, all chelating edges of the tetrahedron, with one of the sulfate (O9-O10) edges being doubly-chelated. The S4 sulfate tetrahedron is chelated by five guanidinium cations on its edges, again with one edge (O13-O14) doubly chelated. The half-occupied ethanol solvent molecule maintains a rather weak hydrogen bond interaction to O16 of this sulfate group. The S5 and S6 sulfate groups are subject to basal oxygen atom disorder, so only the major components of the disorder will be discussed. The S5 sulfate anion is coordinated by five edge-chelating guanidinium cations, however none of the edges are doubly chelated. The disordered pyridinium/ethanol entities are involved here. The pyridinium cation maintains a N-H…O hydrogen bond to the ethanol oxygen atom, which in turn is the hydrogen bond donor for the O-H…O interaction to the sulfate group. The final sulfate group, S6, is coordinated by six guanidinium cations, four of which chelate edges of the tetrahedron and two of which form bifurcated coordination at oxygen corners. The O21-O24 edge is doubly chelated.

As a result, an extensive, complex framework of distorted six- and eight-membered rings of guanidinium cations and





**Fig. 6** Guanidinium sulfate framework of **5** visualized by connections between the central carbon and sulfur atoms of the guanidinium cations and sulfate anions, including the positions of the pyridinium cations and solvent molecules.

sulfate anions is generated with the pyridinium cations and solvent molecules occupying voids in the framework (Fig. 6).



Fig. 7 Hydrogen bonding interactions between guanidinium cations, triethylammonium cations, and sulfate anions (top) and packing diagram (bottom) for the 3:1 guanidinium:triethylammonium sulfate:  $(C(NH_2)_3)_3(C_6H_{16}N)(SO_4)_2$  (6). Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity, and green dashed lines represent the N-H…O hydrogen bonds that occur. Only one of the disordered arrangements for the pyridinium, ethanol, and sulfate disorder is shown. The color scheme is the same as in previous figures.

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As in the structure of parent guanidinium sulfate, the sixmembered rings exhibit varying conformations and degrees of distortion. An interesting component in the structure of 5 here, however, is the presence of honeycomb-type layers in the bc plane, similar to what was observed in the structures of 2 and 3.

#### 3.4 Mixed cation guanidinium-triethylammonium sulfate

In certain reactions, triethylamine was used in the sulfation reaction of the alcohol to try to induce reactivity, again followed by the standard crystallization step using guanidinium chloride. This led to the formation of the mixed cation sulfate salt of (C(NH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>16</sub>N)(SO<sub>4</sub>)<sub>2</sub> (6), having a 3:1 ratio of guanidinium to triethylammonium cations (Fig. 7). The structure consists of two unique sulfate anions, three unique guanidinium cations, and one unique triethylammonium cation, with all atoms located on general positions in space group P41. Sulfate tetrahedron S1 is coordinated by four guanidinium cations chelating edges of the sulfate tetrahedron, while O1 serves as the hydrogen bond acceptor for the triethylammonium cation. Sulfate S2 is coordinated by five guanidinium cations. Four of these guanidinium cations chelate edges of the tetrahedron, while the fifth is positioned such that one of the hydrogen atoms is bifurcated, creating both circumstances of a chelated sulfate edge (the O5-O6 edge) and a bifurcated oxygen corner (O6). The hydrogen bonding interactions between guanidinium cations and sulfate anions result in two unique sixmembered rings that exhibit similar conformations, albeit differing in their degree of distortion. (Fig. 8). The triethylammonium cations reside in small channels of the framework extending along the a- and b-axes. The polar nature of the structure is evident in the cooperative alignment along the c-axis of N-H bonds (and thus the resulting N-H···O interactions) of the triethylammonium cation.

#### 3.5 Mixed cation guanidinium quinidinium sulfate

In one case, the target substrate (quinidine) did not undergo sulfation, but was incorporated structurally in the product,



**Fig. 8** Guanidinium sulfate framework of **6** visualized by connections between the central carbon and sulfur atoms of the guanidinium cations and sulfate anions, including the positions of the triethylammonium cations.



**Fig. 9** Hydrogen bonding interactions between guanidinium cations, quinidinium cations, and sulfate anions (top) and packing diagram (bottom) for  $(C(NH_2)_3)_2(C_{20}H_{26}N_2O_2)(SO_4)_2$  (7). Hydrogen atoms attached to carbon and nitrogen atoms are omitted for clarity, and green dashed lines represent the N-H···O hydrogen bonds that occur. The color scheme is the same as in previous figures.

leading to formation of a mixed cation guanidiniumquinidinium sulfate,  $(C(NH_2)_3)_2(C_{20}H_{26}N_2O_2)(SO_4)_2$  (7). Here, the quinidinium is a dication species formed *via in situ* protonation of the nitrogen atoms. Both of these sites participate in hydrogen bonding to sulfate anions, which differs from the pyridinium and triethylammonium cations of **2–6** that only had one available N–H donor site. The multiple hydrogen bond donors, including an O–H donor, allows the quinidinium cations to participate in the extension of the long range hydrogen bonding network like



**Fig. 10** Guanidinium sulfate layers of **7** visualized by connections between the central carbon and sulfur atoms of the guanidinium cations and sulfate anions, including the positions of the quinidinium cations.

guanidinium does (Fig. 9), rather than simply serving as a terminal decoration, as was the case for pyridinium and triethylammonium cations.

The three dimensional framework of 7 consists of guanidinium sulfate sheets in the *ab* plane, connected along the *c*-axis by the quinidinium cations. Hydrogen bonding of guanidinium cations to three of the available oxygen atoms of the sulfate tetrahedra enables the formation of the guanidinium sulfate sheets (Fig. 10). This is similar to what occurs in the organosulfates where three oxygen atoms are available as hydrogen bond acceptors and the fourth oxygen atom connects to the organic backbone.<sup>28</sup> In 7, there are two unique sulfate anions and two unique guanidinium cations. sulfate tetrahedron is coordinated by three Each guanidinium cations via chelated edges, creating two corrugated honeycomb-like layers of guanidinium and sulfate ions. Each sulfate group also forms hydrogen bonds to quinidinium cations (there is one unique quinidinium cation in the asymmetric unit). The sulfate group about S1 has one such interaction, occurring via N-H…O from the N1 donor of the quinidinium to the O3 acceptor at the corner of the sulfate tetrahedron. The S2 sulfate group has two hydrogen bonding interactions with two neighboring quinidinium cations, one from the OH donor (O2) of one quinidinium cation to the O7 corner of the sulfate group, and the other from the N2 donor of another quinidinium cation to the O9 corner of the sulfate tetrahedron. In this way, each quinidinium cation provides hydrogen bond donor sites to three sulfate anions, and provides pillared connections between guanidinium sulfate sheets.

#### 3.6 General observations

We report here a series of compounds based on sulfate anions hydrogen bonded to guanidinium or to mixtures of guanidinium with pyridinium, triethylammonium, or quinidinium cations. This work greatly expands the structural characterization of the general class of guanidinium salts with isolated  $[SO_4]^{2-}$  tetrahedral anions. The structures assemble *via* complex asymmetric hydrogen bonding networks (Table 3) that can be additionally templated by hydrogen bonding contributions of small organic cations (pyridinium, triethylammonium, quinidinium) and solvent molecules. These compounds crystallize in noncentrosymmetric space groups at an extraordinarily high frequency. All seven of the structures discussed here are noncentrosymmetric, as well as the previously reported examples of (C(NH<sub>2</sub>)<sub>3</sub>)((CH<sub>3</sub>)<sub>4</sub>N)(SO<sub>4</sub>) in  $P2_13$ ,  $(C(NH_2)_3)_2(SO_4) \cdot CH_3OH$  in  $P2_12_12_1$ , and  $(C(NH_2)_3)_4(SO_4)$  $Cl_2$  in  $Cmc2_1$  and  $I\overline{4}2m$ .<sup>34–36</sup> One reason for this may be the nature of the resultant hydrogen bonding networks that occur from the guanidinium and sulfate ions, which themselves both lack a center of symmetry. There is a broad favorability toward frameworks consisting of six-membered rings of three guanidinium cations and three sulfate anions, though sometimes the frameworks also assemble to create eight-membered rings. The six-membered rings exhibit varying conformations and degrees of distortion (Fig. 11). The puckering of the six-membered rings in these structures distinguishes them from those that occur in the organosulfates and organosulfonates, which are largely planar. This occurs since all four oxygen atoms of the sulfate group are engaged in the hydrogen bonding network here, whereas the organosulfate and sulfonate moieties only have three oxygen atoms available as acceptors (effectively only the base of the tetrahedron about sulfur), limiting the hydrogen bonding to only two dimensions. This also creates more opportunities for asymmetry of hydrogen bond interactions between the guanidinium cations and sulfate anions.

Many of these hydrogen bonded networks also have a defined polarity or chirality, as five of the seven examples in this study crystallize in polar space groups and six of the seven crystallize in chiral space groups. This reveals an apparent tendency toward coalignment of sulfate tetrahedra and trigonal planar guanidinium ions. Since the edge lengths of the sulfate tetrahedra closely match the span of the hydrogen atoms on the guanidinium ion, the oxygen edges of the sulfate units are often chelated by hydrogen bonds from the guanidinium units, allowing the building blocks to mutually adopt a noncentrosymmetric, often polar sense naturally imposed by the tetrahedron (Fig. 12). The edgechelation of tetrahedra may also lead to the screw sense apparent in many of the structures, and thus the high frequency of chiral space groups. Identifying polar and corkscrew motifs such as these may have implications in the development of useful structural building blocks including molecular propellers.<sup>41</sup> With the exception of the

Table 3 Diversity of hydrogen bonding interactions in 1–7. Acceptor oxygen atoms are part of the sulfate anions, except where specified<sup>a,b</sup>

Compound	N…O range (guanidinium donor) (Å)	N…O range (minor cation donor) (Å)	O…O range (solvent or minor cation donor) (Å)
1	2.857(3) to 3.048(3)		_
2	2.860(2) to $2.8957(17)$	3.239(2)	_
3	2.849(2) to $2.948(2)$	$2.635(4)^a$	2.681(9) to 2.723(8)
4	2.827(4) to $3.032(4)$	2.721(4)	2.853(4)
5	$2.815(7)$ to $3.216(7)^{c}$	$2.595(18)^{b}$	2.820(4) to $3.197(14)$
6	2.815(3) to $3.058(3)$	2.713(2)	_
7	2.782(3) to 3.002(4)	2.637(4) to 2.701(3)	2.952(3)

<sup>*a*</sup> Oxygen acceptor is on a solvent water molecule. <sup>*b*</sup> Oxygen acceptor is on a solvent ethanol molecule. <sup>*c*</sup> Oxygen acceptors on disordered sulfate groups excluded.





Fig. 11 Six-membered guanidinium sulfate motifs comprising the hydrogen bonded frameworks of 1–7.

quinidinium dication, none of the other structures have chiral centers as building blocks, and thus the chirality is a characteristic of the resulting framework, rather than local stereochemistry.<sup>42</sup> In this way, the polar alignment of building blocks and the expression of helical chains (propagated by hydrogen bonding) as substructures of the larger three dimensional frameworks is akin to design



Fig. 12 Assembly of guanidinium cations about a sulfate anion to form polar and chiral structures, with the propeller-like substructure of 3 as a representative example.

principles observed in the guanidinium sulfonates,  $^{18,19}$  and in inorganic and metal–organic systems.  $^{43-50}$ 

In general, the non-guanidinium cations and solvent molecules tend to occupy voids in the larger guanidinium sulfate networks and typically connect to the network only through single hydrogen bond interactions to the sulfate groups. It is clear that the predominant driving force for the structural formation in all these cases is the extensive favorable hydrogen bonding between the guanidinium ion and the sulfate while the presence of the other ions is mostly incidental and they merely occupy voids generated by the guanidinium sulfate networks. Sometimes this occurs in a chain-like fashion, where the cation will hydrogen bond to the solvent molecule, which in turn hydrogen bonds to a sulfate group of the network. The relatively small size and singular hydrogen bonding capability of the pyridinium and triethylammonium cations allows them to reside in gaps or channels in the guanidinium sulfate frameworks, essentially as decorations. Thus they are not responsible for the continuation of the framework, but their presence likely

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influences or templates the surrounding guanidinium sulfate framework. For the quinidinium dication, having two available N–H hydrogen bond donors, we observe a different behavior, where the extra cation does play a role in connecting two-dimensional guanidinium sulfate sheets into a three-dimensional framework. While this product was clearly not the desired guanidinium organosulfate salt, the retention of the quinidinium moiety in the structure does enable the determination of the stereochemistry of the (+)quinidine substrate, with carbon stereocenters C11, C12, C14, and C15 identified as S, R, S, and R, respectively.

# 4. Conclusions

Seven compounds having varying compositions based on guanidinium cations, sulfate anions, and other organic cations including pyridinium, triethylammonium, and quinidinium were obtained as large single crystals serendipitously from reactions targeting guanidinium organosulfate salts. These compounds primarily form threedimensional guanidinium sulfate frameworks through extensive hydrogen bonding interactions. Additional organic cations and solvent molecules can incorporate into these frameworks via hydrogen bonding, but do not generally propagate the frameworks by bridging between sulfate groups and are not responsible for the overall framework structure (the exception to this in the present study being the quinidinium cation, having multiple hydrogen bond donor sites). A remarkable feature of these frameworks is their tendency to crystallize in noncentrosymmetric space groups, as all seven examples here do. Furthermore, six of the examples crystallize in chiral space groups, while five are polar. Such structure types are enabled through co-aligned building blocks as well as hydrogen bonding interactions such as edge-chelation of sulfate tetrahedra and formation of screw- or propeller-like substructures. The variety of the identity and stoichiometry of the guest molecules/cations to the host guanidinium sulfate frameworks observed in the present study suggests the host framework (and its associated hydrogen bonding interactions) largely drive the formation of these noncentrosymmetric structures. The inordinately high frequency with which these space groups occur within this family of compounds suggests such guanidinium sulfate frameworks may be of interest in the design of materials with interesting physical or optical properties.

# Conflicts of interest

The authors have no conflicts of interest to declare.

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