Interweaving of two-dimensional hydrogen-bonded networks directed by chloride ions

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A novel mixed anion complex has been prepared in the course of crystal engineering studies of guanidinium organosulfonates. Bis(guanidinium) ethanesulfonate chloride, $\{[C(NH_2)_3]^+\}_2CH_3CH_2SO_3{}^-Cl^-$, assembles into a crystalline lattice which exhibits structural characteristics reminiscent of both of its monoanion counterparts guanidinium chloride and guanidinium ethanesulfonate. The structure nominally contains two-dimensional (001) hydrogen-bonded sheets resembling those found in guanidinium organosulfonates, but in which chloride ions replace half of the sulfonate ions. The (001) sheets consist of alternating guanidinium-sulfonate and guanidinium-chloride hydrogen-bonded ribbons, linked together by guanidinium-sulfonate and guanidinium-chloride hydrogen bonds. The presence of chloride ions in the (001) sheets expands this network to enable interweaving of a second hydrogen-bonded sheet, consisting only of guanidinium and chloride ions, orthogonal to the (001) sheets. The interweaving also is made possible by the isotropic nature of the chloride ion with respect to hydrogen bonding.

The design and synthesis of molecular materials requires a thorough understanding, and ultimately control, of the assembly of constituent molecules into supramolecular motifs that define solid-state structures. The formation of ordered solid-state networks with a desired arrangement and dimensionality relies on appropriate 'topological directors,' that is, modules having well-defined functional groups that can recognize complementary functional groups on other like molecules (homomeric assembly) or different molecules (heteromeric assembly). A crucial property of a director is its ability to participate in noncovalent intermolecular interactions which are strong and highly directional relative to competing ones. Formation of extended networks also requires 'polyvalent' modules, that is, molecules having more than one bonding functionality. These capabilities are provided by molecules containing multiple hydrogen bonding functionalities.

Several examples of ordered, extended hydrogen-bonded networks have been reported that illustrate the important influence of hydrogen bonding on directing the organization of molecules during the crystallization of solid-state materials. These reports have demonstrated that the local supramolecular organization about each module can be predicted with reasonable confidence based on molecular topology. Flat molecules having one-dimensional hydrogen-bonding topologies form 'ribbon' or 'tape' networks,[1–5] while tetrahedral-like hydrogen-bonding topologies have afforded diamond-like networks.[6–10] However, control of packing in three dimensions can be elusive owing to the contribution of other intermolecular interactions in the crystal, many of which are nondirectional, resulting in a multiplicity of structural possibilities. A reasonable strategy for surmounting these obstacles is to use *robust* supramolecular 'modules'[11,12] or 'synthons,'[13] where robust is defined as the ability of the module to maintain its dimensionality and general structural features upon changes in ancillary functional groups or inclusion of other molecular species in the lattice. Robust *n*-dimensional modules can reduce the crystal engineering problem to $3 - n$ dimensions, thereby simplifying materials design.

Recently we reported molecular layered materials based on a two-dimensional hydrogen-bonded (**HB**) network composed of guanidinium cations (**G**) and the sulfonate groups of alkane- and arene-substituted monosulfonate anions (**S**).[11,14–18] The topological equivalence of the guanidinium ions and sulfonate groups and strong (guanidinium)N—H···O(sulfonate) hydrogen bonds favored the formation of quasihexagonal two-dimensional **GS** networks in over thirty different crystalline phases containing various sulfonate functionalities (Fig. 1). All the hydrogen-bonding capacity is fulfilled within this network, which is important in forming robust networks.[19] The networks assembled in the third dimension *via* van der Waals interactions between sulfonate R groups extending from the **GS** sheets, either as densely packed bilayers or continuously interdigitated single layers. The pervasiveness of the **GS** sheets was attributed to their ability to form 'accordion' or 'pleated' sheets by puckering about (**G**)N—H···O(**S**) HB 'hinges' joining adjacent one-dimensional hydrogen-bonded ribbons in order to accommodate the different steric requirements of various sulfonate functionalities. The degree of puckering can be described by the interribbon dihedral angle, θ_{IR}.

In our attempt to prepare guanidinium ethanesulfonate from guanidinium chloride and ethanesulfonic acid, we discovered a crystalline phase with an atypical two-dimensional HB network in which a chloride ion was incorporated, in addition to the sulfonate ion. This mixed anion complex, bis(guanidinium) ethanesulfonate chloride (**GEC**), $\{[C(NH_2)_3]^+\}_2CH_3CH_2SO_3{}^-Cl^-$, exhibited characteristics common to both guanidinium ethanesulfonate and guanidinium chloride. The structure of **GEC** contains the typical **GS** HB ribbon motif as well as guanidinium-chloride (**GC**) HB ribbons, both linked to each other to form a sheet motif resembling the typical quasihexagonal **GS** sheet network. The retention of the sheet motif in spite of the substitution of chloride ions for half of the sulfonate ions in the **GS** structures illustrates the robustness of hydrogen bonding. Another type of sheet composed of only **GC** hydrogen bonding is interwoven with the **GS**/**GC** sheets. We describe here the solid-state structure of **GEC**, including detailed analysis of its hydrogen-bonding and layering motifs, and comparison with

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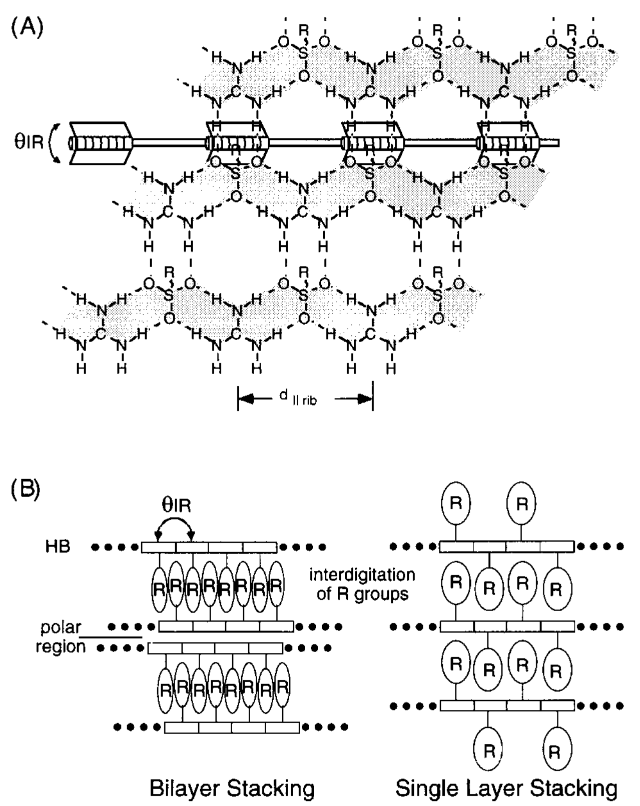
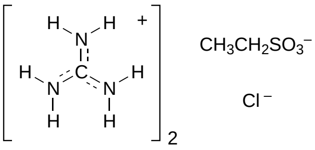


Fig. 1 Schematic illustrations of molecular packing modes commonly observed in the solid-state structures of guanidinium organosulfonates. (A) Quasihexagonal HB sheet motif composed of **GS** HB ribbons (shaded and oriented horizontally). The sheets are flexible and may pucker about HB 'hinges' between ribbons. The degree of puckering can be described by the interribbon dihedral angle, θ_{IR}. The repeat distance of ion pairs parallel to the ribbon, $d_{\parallel rib}$, is indicated. (B) Edge-on views to the HB sheets. The sheets assemble in the third dimension into either bilayer or single layer stacking motifs depending on the nature of the sulfonate R group



GEC

the structures of guanidinium sulfonates and guanidinium chloride.

Experimental

Preparation and characterization

Guanidinium chloride and ethanesulfonic acid were purchased from Aldrich Chemical Co. and used as received. The 2 : 1 : 1 salt bis(guanidinium) ethanesulfonate chloride (**GEC**) was crystallized, by slow evaporation of a methanol solution containing equimolar quantities of guanidinium chloride and ethanesulfonic acid, as colorless needles: Thermal analysis (differential scanning calorimetry): 144–146 °C (m.p.); IR (Nujol mull) 3408, 3338, 3259, 3184, 1665, 1584, 1563, 1461, 1378, 1297, 1246, 1179, 1040, 745, 722 cm^{-1}; ^1H NMR $[(CD_3)_2SO]$ δ 7.07 {s, 6 H, $[C(NH_2)_3]^+$}, 2.48 (q, 2 H, CH_3CH_2), 1.10 (t, 3 H, CH_3CH_2). Anal: calc (%) for $C_4ClH_{17}N_6O_3S$: C, 18.15; H, 6.47; N, 31.75; S, 12.11. Found: C 18.94; H, 6.77; N, 31.11; S, 13.50. **GEC** was typically isolated when using guanidinium chloride as the guanidinium source. Note, however, that the potential for isolating guanidinium ethanesulfonate[14] (colorless hexagonal plates, m.p. 159–162 °C) exists.

Crystal structure determination

Experimental details of the X-ray structural determination for **GEC** are given in Table 1. The structure was determined using an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation at $\lambda = 0.71069$ Å. Intensities were corrected for Lorentz and polarization effects, absorption,[20] and secondary extinction. The structure was solved by direct methods with MITHRIL[21] and DIRDIF.[22] Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at idealized positions. All calculations used TEXSAN[23] with scattering factors from ref. 24. Positional parameters are given in Table 2.

CCDC reference number 440/006.

Results and Discussion

Molecular structure

GEC crystallizes in the orthorhombic space group $Cmc2_1$. The asymmetric unit (Fig. 2) contains half of each of two crystallographically inequivalent guanidinium ions, half of an ethanesulfonate anion, and half of a chloride anion, with the remainder of the ions generated by mirror symmetry $(-x, y, z)$. The terminal methyl group of the ethanesulfonate is disordered across the mirror plane. Intramolecular bond geometries are given in Table 3.

Hydrogen bonding

Analysis of the molecular organization in the crystal structure of **GEC** reveals that the ions are held together by extensive hydrogen bonding in three dimensions (Fig. 3). All six of the guanidinium proton donors and all six of the sulfonate lone electron-pair acceptor sites are used in hydrogen bonding and the chloride ion participates in several weak hydrogen bonds. Hydrogen-bond and close contact distances and angles for **GEC** are given in Table 4. The guanidinium-sulfonate N—H···O hydrogen-bond lengths and angles compare well with those observed previously in the structures of guanidinium organosulfonates.[14,15,18] The guanidinium-chloride N—H···Cl interactions were generally longer than those

Table 1 Crystallographic data for **GEC**

Formula	$C_4ClH_{17}N_6O_3S$
FW	264.73
Crystal color, habit	Colorless prism
Crystal size/mm^3	0.60 × 0.30 × 0.20
Crystal system	Orthorhombic
Space group	$Cmc2_1$
a/Å	7.286(4)
b/Å	21.434(5)
c/Å	8.571(2)
U/Å^3	1339(1)
Z	4
d_{calc}/g cm^{-3}	1.314
F(000)	560
μ(Mo-Kα) cm^{-1}	4.34
T/°C	24
$2\theta_{max}$/°	56.0
Index range	$0 \leqslant h \leqslant 9, 0 \leqslant k \leqslant 26, 0 \leqslant l \leqslant 10$
Reflections collected	1730
Unique reflections	933
R_{int}	0.033
$R(F)^a$	0.037
$R(wF)^b$	0.039
Indep refl obs$[F_o > 2\sigma(F_o)]$	727
N_o/N_v	8.55
G.o.f.	1.35

^{a} $R(F) = \Sigma \| F_o| - |F_c\| / |F_o|$. ^{b} $R(wF) = [\{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2\}]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$.

Table 2 Positional parameters for **GEC** (with estimated standard deviations in parentheses). Hydrogen atoms were placed at idealized positions

Atom	*x*	*y*	*z*
S1	0.5	0.09285(6)	0.2588
O1	0.3339(3)	0.1145(1)	0.3357(4)
O2	0.5	0.0257(1)	0.2361(5)
C2	0.5	0.1269(3)	0.072(1)
C3	0.351(2)	0.1079(5)	−0.025(1)
H4	0.4940	0.1708	0.0831
H5	0.6116	0.1159	0.0209
H6	0.3601	0.1292	−0.1230
H7	0.3593	0.0642	−0.0432
H8	0.2394	0.1178	0.0234
Cl1	0	0.1858(6)	0.5844(2)
N11	0.5	0.1899(2)	0.5868(7)
N12	0.3426(4)	0.2576(2)	0.7396(5)
C11	0.5	0.2356(2)	0.6884(7)
H11	0.3871	0.1734	0.5515
H12	0.2311	0.2403	0.7029
H13	0.3418	0.2905	0.8134
N1	0	0.0455(2)	0.2742(8)
N2	0.1557(4)	−0.0383(1)	0.1752(6)
C1	0	−0.0107(3)	0.2074(8)
H1	0.1597	0.0646	0.2965
H2	0.2696	−0.0176	0.1986
H3	0.1586	−0.0780	0.1268

Table 3 Intramolecular bond geometries for **GEC** (distances in Å, angles in °)

S1—O1	1.454(3)	N1—C1	1.334(7)
S1—O2	1.453(3)	N2—C1	1.309(4)
S1—C2	1.759(8)	N11—C11	1.312(7)
C2—C3	1.43(1)	N12—C11	1.315(4)
O1—S1—O1	112.7(2)	N1—C1—N2	119.9(3)
O1—S1—O2	112.1(1)	N2—C1—N2	120.3(5)
O1—S1—C2	106.3(2)	N11—C11—N12	119.3(2)
O2—S1—C2	106.8(3)	N12—C11—N12	121.4(5)
S1—C2—C3	114.3(6)		

observed in the structure of guanidinium chloride,[25] in which N···Cl lengths range from 3.25 to 3.36 Å (average 3.30 Å) and deviate about 15° from linearity. Nearly all of the N—H···Cl contacts for **GEC** listed in Table 4 are longer than the generally accepted hydrogen-bond distance (less than the sum of the van der Waals radii of the donor and acceptor atoms, 3.30 Å[26]), ranging from 3.26 to 3.65 Å, but nonetheless appear to play a role in directing the crystal packing. The chloride ion in **GEC** is located in a position which provides for a maximum number of (**G**)N—H···Cl$^-$ intermolecular interactions, while accommodating (**G**)N—H···O(**S**) hydrogen bonds within the structure.

GEC exhibits structural features observed in both guanidinium ethanesulfonate (**GEtS**) and guanidinium chloride (Fig. 4, see also Fig. 3). Several HB motifs and regions in **GEC**

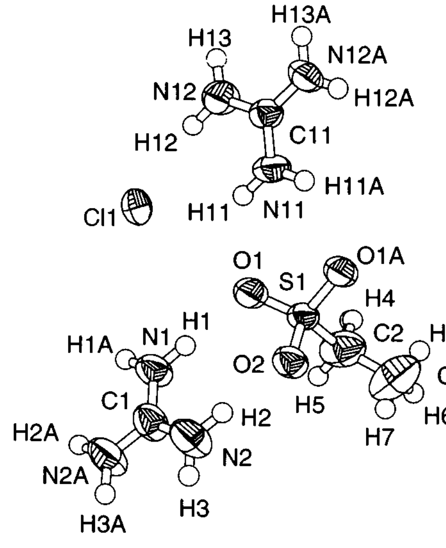


Fig. 2 View of the asymmetric unit of **GEC** showing the labelling scheme (atoms labeled 'A' were generated by mirror symmetry). Non-hydrogen atoms are drawn as thermal ellipsoids (50% probability)

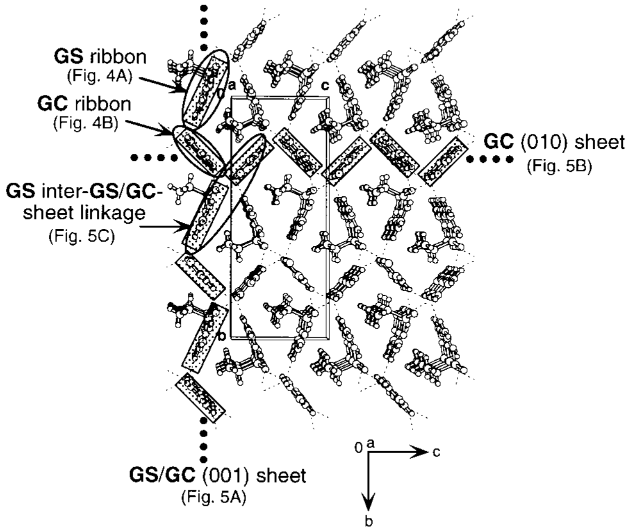


Fig. 3 Three-dimensional crystal packing viewed along the *a* axis in **GEC**. **GS**/**GC** HB sheets parallel to the (001) plane (oriented vertically) are composed of alternating **GS** and **GC** ribbons (protruding out of the plane of the paper). The **GS**/**GC** (001) sheets are interwoven with **GC** (010) sheets (oriented horizontally). Neighboring 2_1-screw-related **GS**/**GC** (001) sheets are also linked by **GS** hydrogen bonding.

Table 4 Hydrogen-bond and close contact geometries for **GEC**[a]

Interaction	N—H···A	$d_{N\cdots A}$/Å	$d_{H\cdots A}$[b]/Å	$\theta_{N-H\cdots A}$[b]/°
GS dimer in ribbon	N1—H1···O1	2.896(4)	1.95	173.7
GS dimer in ribbon	N2—H2···O2	2.906(4)	1.96	176.4
GC dimer in ribbon	N11—H11···Cl1	3.647(4)	2.84	143.4
GC dimer in ribbon	N12—H12···Cl1	3.264(4)	2.33	166.8
GS/**GC** ribbon linkage within (001) sheet	N2—H3···Cl1	3.366(3)	2.52	149.0
GS/**GC** ribbon linkage within (001) sheet	N12—H13···O1	3.138(4)	2.41	133.7
inter-**GS**/**GC**-sheet [**GC** (010) sheet]	N12—H13···Cl1	3.428(4)	2.66	137.8
inter-**GS**/**GC**-sheet	N11—H11···O1	2.951(5)	2.26	128.5

[a] Note that a second N—H···A interaction exists for each N—H···A given and is generated by mirror symmetry of the given interaction (−*x*, *y*, *z*). [b] Note that hydrogen atoms were placed at idealized locations, resulting in uncertainty in these values.

contain guanidinium ions and only one type of anion (*i.e.*, sulfonate or chloride); these features are described as homoanionic. The most common building block in guanidinium sulfonate structures, the **GS** eight-membered ring dimer [graph set[27] $R_2^2(8)$] formed between one guanidinium ion and one sulfonate group, is observed in **GEC**. The **GS** dimers propagate along the *a* axis by mirror symmetry to form a homoanionic **GS** HB ribbon (Fig. 4A). Hydrogen-bonded ribbons of this topology have been observed in *all* structures of guanidinium sulfonates that we have reported and also occur in related structures, for example, in compounds containing guanidyl and sulfonato functionalities.[28–31] Ions in the structure of **GEC** are also organized by guanidinium-chloride (**GC**) N—H···Cl hydrogen-bonded six-membered ring motifs [graph set $R_2^1(6)$]. One of the N—H···Cl interactions [$d_{N11\text{-}H11\cdots Cl1} = 3.65$ Å] in this $R_2^1(6)$ ring is longer than that generally accepted as a hydrogen bond and is longer than those observed in a database study of bridging amino···chloride $Cl^-\cdots H—N—H\cdots Cl^-$ hydrogen bonds.[32] However, the observation of topologically identical HB ring motifs as packing directors in the structure of guanidinium chloride strongly suggests that this motif also directs self-assembly in **GEC**. The **GC** dimers in **GEC** propagate by mirror symmetry along the *a* axis to form a homoanionic **GC** hydrogen-bonded ribbon (Fig. 4B). Interestingly, the structure of guanidinium chloride also consists of identical six-membered ring motifs, but the ribbon motifs in guanidinium chloride and **GEC** have a slightly different topology (Fig. 4C). The neighboring **G** ions within the ribbons in guanidinium chloride are related by 2_1-symmetry along the ribbon axis, whereas neighboring **G** ions within the ribbons in **GEC** are related by translation.

Sheet-like networks and three-dimensional packing

The two types of homoanionic hydrogen-bonded ribbons parallel to the *a* axis in **GEC** (**GS** and **GC** ribbons) join in an alternating fashion along the *b* direction to form a **GS**/**GC** HB sheet parallel to (001) (Fig. 5A). The ribbons are linked into a **GS**/**GC** double ribbon motif by **GC** (G)N—H···Cl hydrogen bonds with $R_2^1(6)$ and $R_6^3(12)$ ring motifs. The *C*-center-related **GS**/**GC** double ribbons are linked into the (001) **GS**/**GC** sheet by **GS** (G)N—H···O(S) hydrogen bonds with $R_4^2(10)$ and $R_4^3(10)$ ring motifs. In forming the **GS**/**GC** HB sheet, the **GS** and **GC** ribbons do not approach each other directly edge on, but instead link in a zig-zag fashion to form corrugated nominally two-dimensional sheets parallel to (001). The **GS**/**GC** HB sheet exhibits features similar to the quasihexagonal hydrogen-bonded sheet motif commonly observed in many guanidinium organosulfonates, including **GEtS** (see Fig. 1). The **GS**/**GC** HB double ribbon motif has a quasihexagonal arrangement of anions identical to that found in **GEtS** except for the substitution of chloride ions for half of the sulfonate ions. The linkage of neighboring **GS**/**GC** double ribbons through the **GS** $R_4^2(10)$ and $R_4^3(10)$ HB ring motifs to form the **GS**/**GC** sheet, however, breaks the quasihexagonal 'symmetry'.

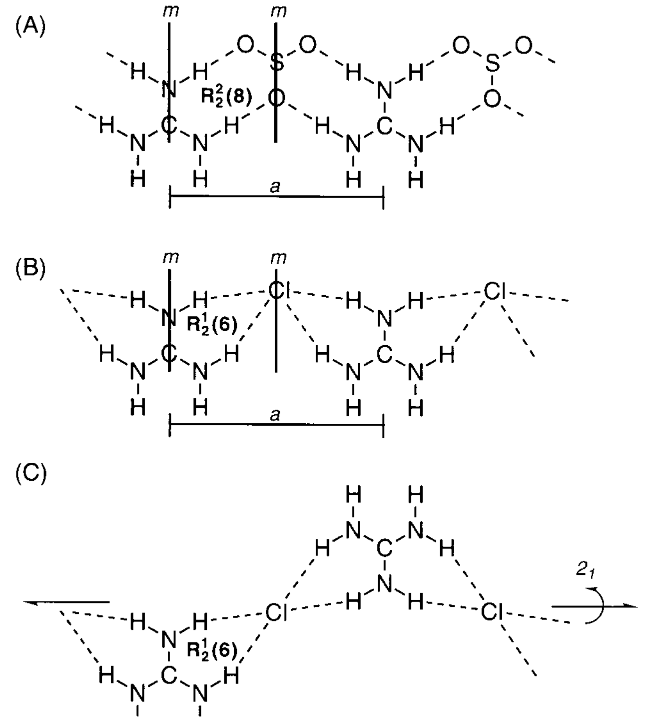


Fig. 4 Schematics illustrating **GS** and **GC** dimer and ribbon topologies. Ribbons are oriented horizontally. (A) **GS** ribbon composed of $R_2^2(8)$ dimers observed in the structures of **GEC**, guanidinium organosulfonates, and other compounds containing guanidyl and sulfonato groups. Neighboring dimers comprising the ribbon in **GEC** are related by mirror symmetry normal to the ribbon axis. (B) **GC** ribbon composed of $R_2^1(6)$ dimers observed in the structure of **GEC**. Neighboring dimers comprising the ribbon are related by mirror symmetry normal to the ribbon axis. (C) **GC** ribbon composed of $R_2^1(6)$ dimers observed in the structure of guanidinium chloride. Neighboring dimers comprising the ribbon are related by 2_1-screw symmetry along the ribbon axis

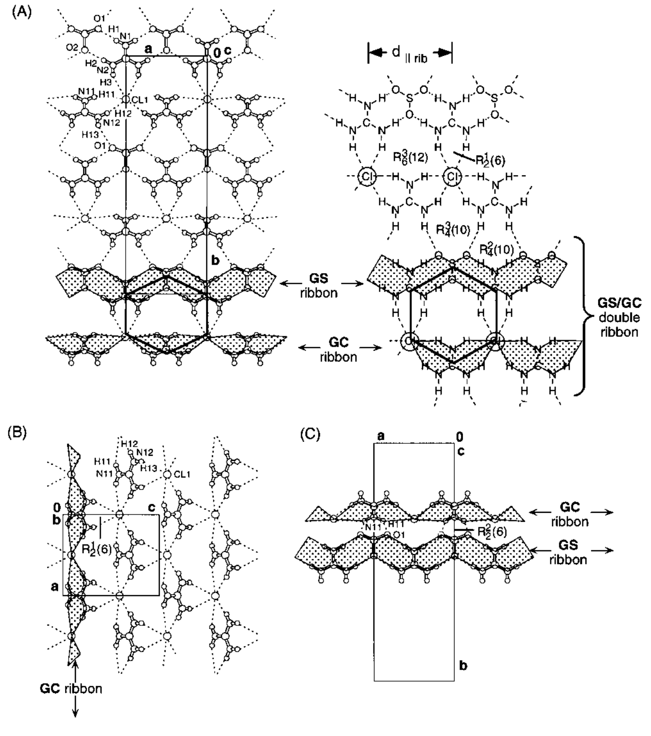


Fig. 5 Views of the specific hydrogen bonding interactions in the structure of **GEC**. See Fig. 3 for a view of these interactions projected onto (100). (A) View of one **GS**/**GC** (001) HB sheet composed of **GS** and **GC** ribbons (sulfonate ethyl groups removed for clarity), projected onto (001). The **GS** and **GC** ribbons are oriented horizontally. The corresponding schematic shows the connection of adjacent **GS** and **GC** ribbons into a double ribbon motif. A hexagon is drawn onto each diagram to illustrate the structural similarity of the double ribbon to the quasihexagonal sheet motif found in guanidinium sulfonates (*cf.* with Fig. 1). (B) View of one homoanionic **GC** (010) HB sheet [interwoven with and oriented orthogonal to the (001) **GS**/**GC** HB sheets], projection onto (010). (C) View of the **GS** hydrogen bonds linking neighboring 2_1-related (001) **GS**/**GC** HB sheets, projection onto (001). The sheets are linked by **GS** $R_2^2(6)$ ring motifs

The **GS**/**GC** HB sheets are puckered in **GEC**, with an inter-ribbon dihedral angle, θ_{IR}, of $\approx 115°$, whereas they are planar in **GEtS** ($\theta_{IR} = 180°$). Although the **GS** ribbons of **GEC** have the identical topology as in **GEtS**, the repeat distance parallel to the ribbon, $d_{\|rib}$ (see Fig. 1), in **GEC** contracts slightly to accommodate the N—H···Cl interactions in the neighboring **GC** ribbons that comprise the sheet, with $d_{\|rib}$ values of 7.29 Å and 7.40 Å for **GEC** and **GEtS**, respectively. The N—H···Cl contacts within the **GC** ribbons in **GEC** are longer than typical hydrogen bonds due to elongation of the **GC** ribbon to provide an optimum separation for the **G** and **S** hydrogen bonding in the neighboring **GS** ribbons within the sheet.

The corrugated two-dimensional **GS**/**GC** sheets assemble in the third dimension along the *c* axis by stacking in a manner similar to that observed for guanidinium sulfonates (see Fig. 3). Neighboring 2_1-screw-related **GS**/**GC** (001) layers in **GEC** are held together by **GS** and **GC** hydrogen bonds. The stacking motif of **GEC** can be described neither as a bilayer nor as a single layer motif. However, the significant puckering observed is more characteristic of single layer structures than bilayer ones. Puckering of **GS** HB layers is frequently observed in the structures of guanidinium sulfonates containing sterically bulky sulfonate R groups and/or functional groups proximal to the **GS** sheet.[14,15,18] In the case of **GEC**, the **GS**/**GC** HB sheets pucker to fill void space resulting from the absence of alkyl groups in every other ribbon, which is a consequence of the spatially less demanding chloride ions substituting for half of the organosulfonate positions. The packing in **GEC** is noncentrosymmetric, although its constituent ions impose no symmetry restrictions.

The specific **GC** and **GS** hydrogen-bonding interactions that link the **GS**/**GC** (001) layers in the third dimension are shown in Fig. 5B and 5C. The **GEC** structure can be thought of as homoanionic segregated (010) layers, *i.e.*, regions containing **GC** hydrogen bonding (**G** and **C** ions only) and regions containing **G** and **S** ions (see Fig. 3). The **GC** inter-sheet interactions form a hydrogen-bonded sheet themselves, parallel to the (010) plane, composed of only (G)N—H···Cl hydrogen bonds with adjacent ribbon linkage *via* the $R_2^1(6)$ motif (Fig. 5B). This results in the **GC** (010) sheets and the **GS**/**GC** (001) sheets being interwoven orthogonally to one another, with connection nodes of hydrogen bonding at the chloride ions. The interweaving of the two different sheet motifs is a consequence of the isotropic nature of the chloride ion, which allows for hydrogen bonding in three dimensions, whereas the sulfonate ion in the previously reported **GS** salts restricts assembly to two dimensions. Aside from inter-**GS**/**GC**-sheet linkage *via* the interwoven **GC** (010) sheets, the neighboring 2_1-related **GS**/**GC** (001) layers are also linked by **GS** $R_2^2(6)$ HB dimer interactions (Fig. 5C). The numerous intra- and inter-**GS**/**GC**-sheet HB interactions result in an extensively hydrogen-bonded **GEC** structure.

Conclusion

The crystal structure of **GEC** reveals an unexpected motif that is a result of well-established supramolecular guanidinium-sulfonate ribbons crosslinked by guanidinium-chloride ribbons. These combined ribbon motifs generate a three-dimensional hydrogen-bonded structure in which the isotropic nature of the chloride ion hydrogen-bond acceptor permits interweaving of **GS** and **GC** networks. The quasihexagonal hydrogen-bonding motif observed previously for guanidinium organosulfonates is present in the double ribbon motif of **GEC**, within the **GS**/**GC** sheet, even though the chloride ion differs substantially in both size and chemical nature compared to the sulfonate ion. This observation illustrates the robustness and recurring nature of the **GS** network, providing further evidence of the reliability of **GS** modules for the design and synthesis of new crystalline materials.

Acknowledgements

The authors acknowledge Prof. Doyle Britton of the University of Minnesota for X-ray crystallographic services and the ONR for financial support.

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Received 5th May 1997; *Paper* 7/07638J