Crystal Engineering

Cubic, Hydrogen-Bonded (10,3)-*a* Networks in the Family $[C(NH_2)_3][N(CH_3)_4][XO_4]$ (X = S, Cr, and Mo)**

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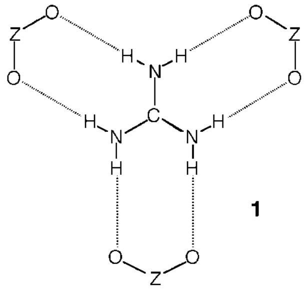
The guanidinium cation $C(NH_2)_3^+$ serves as a powerful structure-determining component in a number of networks, both metal/ligand-bonded and hydrogen-bonded. The six hydrogen atoms of the cation are nicely disposed to form a pair of hydrogen bonds to each of three oxyanions, as shown in the generalized representation **1**. In an extensive family of carbonate-bridged coordination polymers reported recently, the guanidinum cation plays the crucial structural role represented in **1** (Z = C), thus promoting the formation of highly symmetrical metal/carbonate networks with cubic symmetry and sodalite-like topology.[1] The arrangement seen in **1** (Z = B) is present in some highly symmetrical cubic guanidinium borate derivatives we discovered recently which have the boracite topology.[2] A closely related hydrogen-bonding mode, again as in **1** (Z = S), is seen in a range of guanidinium sulfonates in which the sulfonate units, as well as the guanidinium components, act as 3-connecting nodes, each being attached to three guanidinium units as in **2**. In some of the nicest examples of true crystal engineering, Ward and co-workers have elegantly exploited this complementarity between the guanidinium cation and various sulfonate anions to generate an extensive family of solids having a common, predictable, yet pliable, underlying hydrogen-bonded 3-connected sheet structure with the (6,3) topology or hexagonal grid topology.[3] We report here a new family of hydrogen-bonded frameworks related to these guanidinium sulfonates in which the guanidinium cation again acts as in **1** (Z = S) and a sulfur oxyanion (in this case SO_4^{2-}) again acts as a second type of 3-connecting node; however, the network generated is the most symmetrical 3-connected 3D network possible, namely the (10,3)-*a* net,[4] rather than the most symmetrical 3-connected 2D network possible that was seen by Ward and co-workers.



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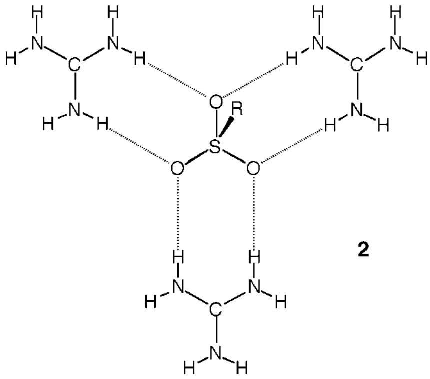

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Solvent-free crystalline products of composition $[C(NH_2)_3][N(CH_3)_4][XO_4]$, (X = S, Cr and Mo) suitable for single-crystal X-ray diffraction studies were obtained directly from mixtures containing the component ions in the following solvents or solvent mixtures: X = S, from methanol; X = Cr, from aqueous DMSO; X = Mo, from methanol/DMF.[5] All our attempts to generate the analogous tungsten derivative $[C(NH_2)_3][N(CH_3)_4][WO_4]$ have failed. In all cases, the crystals appear almost exclusively as well-formed tetrahedra, space group $P2_13$, $a = 10.5828(6)$ Å (X = S), 10.7589(5) Å (X = Cr), or 10.8802(4) Å (X = Mo).[6] The three compounds are isostructural and the following observations pertaining to the sulfate apply equally well to the chromate and molybdate, except for minor differences in some distances and angles. All the guanidinium cations in $[C(NH_2)_3][N(CH_3)_4][SO_4]$ are equivalent and act as 3-connecting nodes, each being attached to three sulfate anions by hydrogen-bond pairs as represented in **1** (Z = S). Each sulfate unit is attached by hydrogen-bond pairs to three guanidinium cations (Figure 1), and therefore acts as a second type of 3-connecting node. Figure 2a shows the extended 3D network and Figure 2b shows the net generated by linking together the carbon centers of the

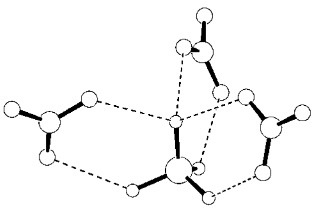

Figure 1. Three guanidinium cations each provide a pair of hydrogen bonds to a sulfate ion in the structure of $[C(NH_2)_3][N(CH_3)_4][SO_4]$. The three equivalent hydrogen bonds to the oxygen atom at the apex of the SO_4 tetrahedron are slightly longer (N–H···O, 2.899 Å) than the other three (2.792 Å); this expands the C-S-C angle to 97.5°.

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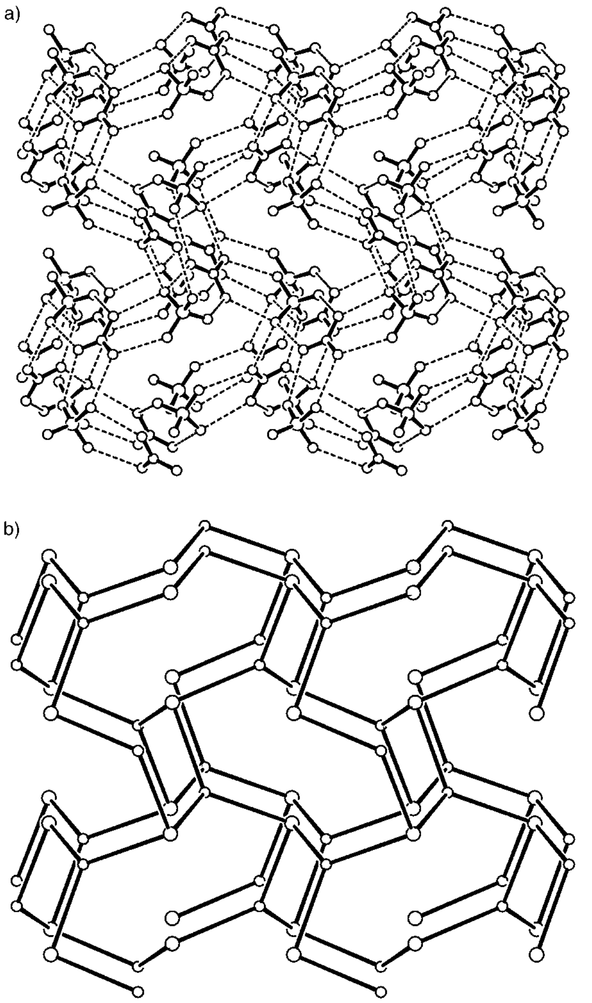


Figure 2. a) The extended 3D hydrogen-bonded $[C(NH_2)_3]/[SO_4]$ network in $[C(NH_2)_3][N(CH_3)_4][SO_4]$. b) The underlying (10,3)-*a* connectivity of the network showing only the sulfur atoms and the carbon atoms of the guanidinium units.

guanidinium units and the sulfur centers of the sulfate units that are hydrogen-bonded to them. The net has the intrinsically chiral (10,3)-*a* topology.[4] The guanidinium nodes are slightly pyramidal (S-C-S angle 118.6°) but the sulfur nodes are much more so (C-S-C angle 97.5°). We have noted previously that it is possible to construct strain-free (10,3)-*a* nets and still retain the cubic symmetry not only when all the nodes are trigonal planar but also when all the nodes are trigonal pyramidal;[7] the present case brought to our attention the fact, previously unrecognized we believe, that it is also possible to construct strain-free (10,3)-*a* nets, again conserving cubic symmetry, in which half the nodes are trigonal planar and the other half are pyramidal, provided the latter retain a threefold axis of symmetry. These variants on the (10,3)-*a* net highlight the distinction that should be drawn (in considerations of networks in general) between geometry and topology: from the geometrical point of view, the three variants—1) all nodes trigonal planar, 2) all nodes trigonal pyramidal, and 3) alternate nodes trigonal planar and trigonal pyramidal—appear to be very different, but from a topological point of view they are of course identical.

The tetramethylammonium cations, all of which are equivalent, are snugly accommodated in cavities within the framework (Figure 3). In the imaginary transition from a (10,3)-*a* net in which all the nodes are trigonal planar (Figure 4a) to one in which every other node is made trigonal pyramidal (Figure 4b), half the cavities centered on the threefold axes are increased in size (A in Figure 4b) and the others (B) are contracted: the $[N(CH_3)_4]^+$ units are found in the expanded cavities of type A and the sites on the threefold axes at the centers of the contracted cavities are empty. One C–N bond of the tetramethylammonium cation is oriented along one of the threefold axes with its carbon atom very

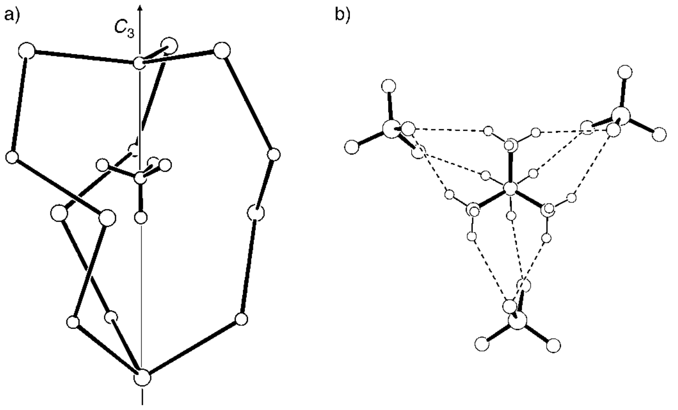


Figure 3. a) The environment of the tetramethylammonium ion showing only the guanidinum carbon atoms and the sulfur atoms of the surrounding hydrogen-bonded (10,3)-*a* net. b) View down the threefold axis showing the nine C–H···O interactions in which each $[N(CH_3)_4]^+$ ion participates.

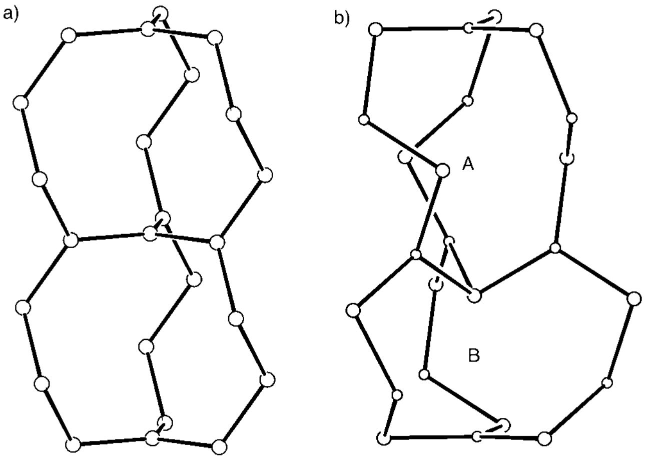
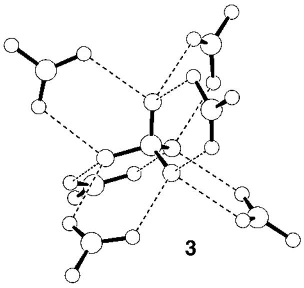


Figure 4. The imaginary transformation of a (10,3)-*a* net in which all nodes are trigonal planar (a) to one in which alternate nodes are trigonal planar and trigonal pyramidal (b). In the latter net, which retains cubic symmetry, half the cavities centered on the threefold axes are expanded (site A) and the others (site B) are contracted.

close to the center of an equilateral triangle of sulfur atoms (Figure 3a). Each of the C–H bonds of this methyl group located on the threefold axis is directed towards a sulfate oxygen atom (C···O 3.324 Å; angle at hydrogen atom ca. 168°; Figure 3b), thus indicating significant directional C–H···O hydrogen-bonding interactions in addition to the electrostatic attraction. Desiraju has drawn attention to the significance of C–H···O hydrogen bonding as a supramolecular motif in a variety of crystalline solids and to its importance in crystal engineering.[8] As can be seen in Figure 3b, two hydrogen atoms on each of the other three methyl groups are also directed towards a sulfate oxygen atom (C···O, 3.447 and 3.455 Å), thus providing additional C–H···O hydrogen-bonding interactions. All but three of the twelve C–H atoms of the $N(CH_3)_4^+$ ion are therefore involved in this hydrogen-bonding arrangement. Every sulfate ion is associated in this way with three tetramethylammonium ions by three trios of C–H···O hydrogen bonds and every tetramethylammonium ion is likewise associated with three sulfate ions. A 3-connected, 3D network of C–H···O interactions can therefore be envisaged in which the sulfur atoms and the nitrogen centers of the tetramethylammonium ions provide the nodes. This net also has the chiral (10,3)-*a* topology, but it is of the opposite sense to that of the primary (10,3)-*a* net composed of guanidinium and sulfate nodes. The C–H···O interactions between the tetramethylammonium cation and the sulfate anion are very likely much weaker than the N–H···O interactions that support the primary (10,3)-*a* network. In discussions of many networks it is convenient for simplicity to focus on certain selected interactions as constituting "the net" and to set aside other weaker interactions, whilst recognizing that these may nevertheless be structurally important. Such is the case here—the (10,3)-*a* net involving the stronger $[C(NH_2)_3]^+/[SO_4]^{2-}$ interactions is conveniently regarded as the primary net, but the secondary $[N(CH_3)_4]^+/[SO_4]^{2-}$ (10,3)-*a* net of the opposite chirality is of undoubted, possibly crucial, structural importance.[9]

In guanidinium sulfate itself,[10] every cation is attached by pairs of hydrogen bonds, again as in **1** (Z = S), to three sulfate anions. However, since in this case there are twice as many guanidinium cations as sulfate anions, each anion is connected to six guanidinium cations in the manner represented in the idealized form shown in **3**. The environment of the sulfate ion in guanidinium sulphate, as seen in **3**, can be envisaged in terms of guanidinium cations associated by a pair of hydrogen bonds at each of the six edges of the sulfate O_4 tetrahedron. In the guanidinium sulfonates, as represented in **2**, a cation provides a pair of hydrogen bonds at each of the three edges of an O_3 triangle, thus disposing the system to form a 2D network, since the CN_3 planes of the three guanidinium cations surrounding any sulfonate are close to coplanar with the plane that includes all three guanidinium carbon centers. In the case of $[C(NH_2)_3][N(CH_3)_4][SO_4]$ reported here the $[C(NH_2)_3]^+$ and $[SO_4]^{2-}$ ions are present in equal numbers and only three of the six edges of the O_4 tetrahedron are required to participate in the hydrogen-bonding network and, as can be seen in Figure 1, the particular edges used are those that share an apex of the O_4 tetrahedron. This arrangement disposes the system to form a 3D network, rather than the 2D network seen in the sulfonates because, as can be seen in Figure 1, the CN_3 planes of the three guanidinium units are now close to perpendicular to the plane containing the three carbon atoms. If the two N–H···O hydrogen bonds in any particular $[C(NH_2)_3]^+/[SO_4]^{2-}$ association had been equal in length the C-S-C angles would have been 90°. The observed C-S-C angle of 97.5° is achieved by slightly stretching the three equivalent hydrogen bonds to the apex oxygen atom (to N–H···O = 2.899 Å) relative to the other three hydrogen bonds (2.792 Å). The C-S-C angle dictates the size of the cavity where the tetramethylammonium cation is located and presumably the inequality in the two hydrogen-bond lengths is such as to optimize the fit of the tetramethylammonium cation therein. It is significant in our view that guanidinium sulfate, itself a relatively stable, multiple hydrogen-bonded crystal lattice and therefore relatively insoluble, can be converted in the presence of $[N(CH_3)_4]^+$ into $[C(NH_2)_3][N(CH_3)_4][SO_4]$: this presumably reflects the snug fit of the $[N(CH_3)_4]^+$ ion into the expanded cavities within the $[C(NH_2)_3]^+/[SO_4]^{2-}$ (10,3)-*a* framework, with the formation of nine C–H···O interactions.



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Only very minor differences are seen between the sulfate, chromate, and molybdate structures, consequences presumably of the different bond lengths within the anion (S–O, 1.449(2) and 1.486(4) Å; Cr–O, 1.631(4) and 1.657(7); Mo–O, 1.752(3) and 1.780(4) Å). For each of the structures, the longer Z–O bond corresponds to the unique bond lying on the threefold axis. Given the fact that this oxygen atom is involved in three hydrogen bonds to guanidinium ions this is not surprising. Differences in hydrogen-bonded N···O separations are very minor (sulfate: 2.792(3), 2.899(4) Å; chromate: 2.790(6), 2.887(5) Å; molybdate: 2.790(5), 2.914(4) Å).

The (10,3)-*a* net, being the most symmetrical of all possible 3-connected 3D nets, should occupy a position comparable in importance and significance to that of its better known 4-connected counterpart, the (6,4) diamond net; both are cubic in their undistorted forms and Wells long ago drew attention to their close relationship.[4] No doubt the (10,3)-*a* net has been accorded less significance by chemists than its topology warrants simply because the number of examples known is not large, but, with the current burgeoning interest in the generation of new 3D networks, this situation is likely to change. Although numbers of metal/ligand-bonded frameworks with the (10,3)-*a* topology are now increasing, hydrogen-bonded examples such as the ones reported here remain rare.[11] The results presented here, together with others,[1,2] indicate the potential of the guanidinium cation as a structure-directing ion for the generation of new networks of high symmetry. These are possibilities we are actively pursuing.

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[5] $[C(NH_2)_3][N(CH_3)_4][SO_4]$: A solution of guanidinium chloride (110 mg, 1.15 mmol) in hot methanol (10 mL) was added to a solution of tetramethylammonium chloride (1.52 g, 13.9 mmol) and tetramethylammonium sulfate (225 mg, 0.93 mmol) in hot methanol (40 mL) on the steambath. The crystals of $[C(NH_2)_3][N(CH_3)_4][SO_4]$ that separated on cooling were collected after 3 h and washed with methanol. Yield: 80 mg, 38 %. The X-ray powder pattern of the bulk solid was in good agreement with that calculated on the basis of the single-crystal data. Elemental analysis calcd for $C_5H_{18}N_4O_4S$ (%): C 26.1, H 7.9, N 24.4; found: C 26.1, H 7.9, N 24.3. $[C(NH_2)_3][N(CH_3)_4][CrO_4]$: Na_2CrO_4 (150 mg, 0.925 mmol) together with excess guanidinium chloride and tetramethylammonium chloride were dissolved in hot water (2 mL) on the steambath. Hot dimethylsulfoxide (4.5 mL) was added on the steambath. The yellow crystals of $[C(NH_2)_3][N(CH_3)_4][CrO_4]$ which formed upon cooling were collected after 5 h and washed with a minimal amount of water. Yield: 70 mg, 30 %. The X-ray powder pattern of the bulk solid was in good agreement with that calculated on the basis of the single crystal data. Elemental analysis calcd $C_5H_{18}N_4O_4Cr$ (%): C 24.0, H 7.2, N 22.3; found: C 23.9, H 7.3, N 22.2. $[C(NH_2)_3][N(CH_3)_4][MoO_4]$: MoO_3 (130 mg, 0.925 mmol) and guanidinium chloride (160 mg, 1.85 mmol) were dissolved in a hot solution of tetramethylammonium hydroxide (1 mL of 25 % w/w in methanol, 2.4 mmol) and water (1 mL). Hot dimethylformamide (4 mL) was added and colorless crystals, which were deliquescent, separated after one day at room temperature. A single crystal was removed, immersed in oil and cooled as quickly as possible prior to collecting X-ray diffraction data.

[6] Crystal data for $[C(NH_2)_3][N(CH_3)_4][SO_4]$: $0.50 \times 0.50 \times 0.50$ mm, cubic, space group $P2_13$, $a = 10.5828(6)$ Å, $V = 1185.2(1)$ Å^3, $\rho_{calcd} = 1.291\,g\,cm^{-3}$, $2\theta_{max} = 49.9°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 6294 (708), $\mu = 0.273\,mm^{-1}$, min./max. apparent transmission ratio: 0.867, no. of parameters: 50, $R1$ $[I > 2\sigma(I)] = 0.0476$, $wR2$ (all data) = 0.0899, max./min. residual electron density: 0.198/−0.159 e Å^{-3}. Crystal data for $[C(NH_2)_3][N(CH_3)_4][CrO_4]$: $0.08 \times 0.08 \times 0.08$ mm, cubic, space group $P2_13$, $a = 10.7589(5)$ Å, $V = 1245.4(1)$ Å^3, $\rho_{calcd} = 1.335\,g\,cm^{-3}$, $2\theta_{max} = 49.9°$, $\lambda = 0.71073$ Å, $T = 293$ K, no. of measured (and independent) reflections: 6547 (737), $\mu = 0.918\,mm^{-1}$, min./max. apparent transmission ratio: 0.837, no. of parameters: 49, $R1$ $[I > 2\sigma(I)] = 0.0673$, $wR2$ (all data) = 0.1399, max./min. residual electron density: 0.325/−0.19 e Å^{-3}4. Crystal data for $[C(NH_2)_3][N(CH_3)_4][MoO_4]$: $0.10 \times 0.10 \times 0.10$ mm, cubic, space group $P2_13$, $a = 10.8802(4)$ Å, $V = 1287.98(8)$ Å^3, $\rho_{calcd} = 1.517\,g\,cm^{-3}$, $2\theta_{max} = 55.0°$, $\lambda = 0.71073$ Å, $T = 130$ K, no. of measured (and independent) reflections: 8159 (996), $\mu = 1.018\,mm^{-1}$, min./max. apparent transmission ratio: 0.925, no. of parameters: 49, $R1$ $[I > 2\sigma(I)] = 0.0398$, $wR2$ (all data) = 0.0668, max./min. residual electron density: 0.591/−0.370 e Å^{-3}. In all cases all independent reflections were included in the refinement; multiscan absorption corrections were applied, all structures were solved by using direct methods and refined against F^2 using a full-matrix least-squares refinement;[12] hydrogen atoms were included at geometrically estimated positions. CCDC-247060–247062 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[9] If the tetramethylammonium centers along with the sulfate and guanidinium centers are all considered as nodes in a single network, then the result is a 3,6-connected net (S of sulfate being a 6-connecting node and C of guanidinium and N of tetramethylammonium being 3-connecting nodes). This 3,6-connected net has the same topology as cubic PdF_2. The relationship between the (10,3)-*a* net and the cubic PdF_2 net is considered in the Supporting Information.

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