Bis(5-amino-3-carboxy-1H-1,2,4-triazol-4-ium) sulfate dihydrate

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The crystal structure of the title compound, $2C_3H_5N_4O_2{}^+\cdot SO_4{}^{2-}\cdot 2H_2O$, displays a three-dimensional framework in which mixed infinite chains [oriented parallel to (510) and ($\bar{5}$10)] interfere, forming tunnels extending parallel to the c axis. Intermolecular O—H⋯O, N—H⋯O and O—H⋯N hydrogen bonds ensure the unity of the structure and generate centrosymmetric $R_4^4(14)$ and $R_4^2(8)$ rings. The S atom lies on a twofold axis.

Related literature

For uses of 1,2,4 triazole derivatives, see: Beckmann & Brooker, (2003); Bhargava *et al.* (1981); Fujigaya *et al.* (2003); Hirota *et al.* (1991); Li *et al.* (2004); Matulková *et al.* (2008). For related hybrid compounds, see: Berrah *et al.* (2011a,b,c). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Etter *et al.* (1990).
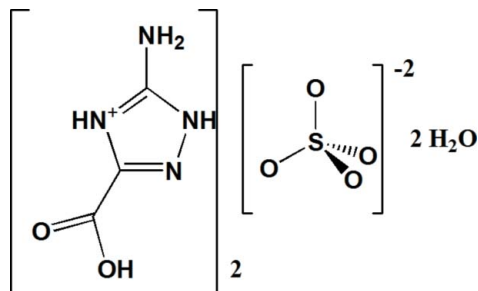
Experimental

Crystal data

$2C_3H_5N_4O_2{}^+\cdot SO_4{}^{2-}\cdot 2H_2O$
$M_r = 390.31$
Monoclinic, $C2/c$
$a = 19.4350\ (9)$ Å
$b = 5.8467\ (2)$ Å
$c = 13.3343\ (6)$ Å
$\beta = 109.981\ (2)°$

$V = 1423.98\ (10)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.31$ mm^{-1}
$T = 150$ K
$0.48 \times 0.08 \times 0.06$ mm

Data collection

Bruker APEXII diffractometer
11018 measured reflections
1620 independent reflections

1470 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.077$
$S = 1.08$
1620 reflections
121 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1W—H2W⋯N2	0.83 (2)	2.16 (2)	2.9774 (16)	169 (2)
O1W—H1W⋯O1[i]	0.89 (2)	1.93 (2)	2.7941 (17)	163 (2)
O2—H2⋯O1W[ii]	0.82	1.74	2.5403 (16)	165
N1—H1⋯O4[iii]	0.86	1.94	2.7107 (16)	149
N3—H3⋯O4[iv]	0.86	1.79	2.6436 (15)	171
N4—H4A⋯O3[v]	0.86	2.17	2.8452 (17)	136
N4—H4B⋯O3[vi]	0.86	2.08	2.9255 (16)	168

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, y-1, -z+\frac{3}{2}$; (v) $-x+1, -y, -z+1$; (vi) $x, y-1, z$.

Data collection: *APEX2* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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organic compounds

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supporting information

Bis(5-amino-3-carboxy-1*H*-1,2,4-triazol-4-ium) sulfate dihydrate

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S1. Comment

1,2,4-triazole derivatives are remarkable substances exhibiting a wide range of properties; while several compounds incorporating 1,2,4-triazole moieties show pharmacological and biological activities (antidepressants, anti-inflammatory, fungicides) (Bhargava *et al.*, 1981; Hirota *et al.*, 1991; Li *et al.*, 2004), a number of them find use in material field and coordination chemistry (magnetic and non-linear optics properties, multidentate ligands) (Beckmann & Brooker, 2003; Fujigaya *et al.*, 2003; Matulková *et al.*, 2008).

Our recent investigation on some N-heterocycle compounds with inorganic acids (Berrah *et al.*, 2011*a,b,c*), has revealed their ability to generate original networks stabilized in particular by hydrogen bonds; we report herein the structure of a new hybrid compound obtained from a disubstituted 1,2,4-triazole derivative (5-amino-1,2,4 triazol-1*H*-3-carboxylic acid hydrate) and the sulfuric acid.

The molecular structure and the atom-numbering scheme of the title compound are shown in Fig. 1. The sulfur atom lies in the twofold axis and the sulfate anion shows a quite regular geometry compared with that seen in similar compounds (Berrah *et al.*, 2011*b,c*). The triazole ring exhibits a short distance of 1.3046 (18) Å revealing the double-bond character of the C2═N2 bond, two long distances 1.3648 (18) Å and 1.3774 (17) Å related to the single bonds C2—N3 and N1—N2, respectively. The C3—N1 and C3═N3 bonds lengths are respectively 1.3420 (18) Å and 1.3480 (18) Å which suggests the delocalization of the double bond (N1 ⋯C3 ⋯N3).
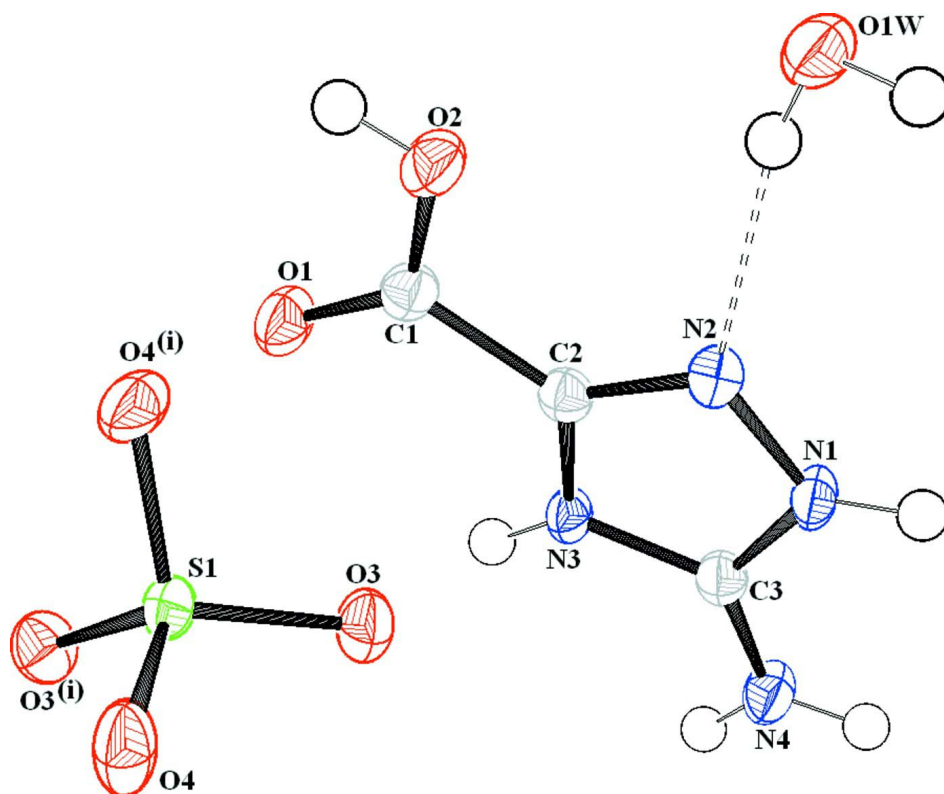
The crystal structure of the title compound (Fig. 2) displays a three-dimensional framework where mixed infinite chains interfere to form tunnels parallel the *c* axis. According to their orientation, we can distinguish two kinds of chains: the first one directed along the (510) plane and the second along the ($\bar{5}$10) plane (Fig. 2). In a mixed chain, the cations adopt a head to head configuration in a way that NH$_2$, of two adjacent cations, are linked (*via* N—H⋯O hydrogen bonds) to two sulfate anions and C—OH are linked (by O—H⋯O hydrogen bonds) to two water molecules (Fig. 3) (Table 1). Consequently, centro-symmetric $R^4_4(14)$ and $R^2_4(8)$ graph-set rings are created (Etter *et al.*, 1990; Bernstein *et al.*, 1995).

S2. Experimental

The title compound was synthesized by reacting 5-amino-1,2,4 triazol-1*H*-3-carboxylic acid hydrate with some excess of sulfuric acid in aqueous solution. Slow evaporation leads to well crystallized colorless needles.

S3. Refinement

The H atoms of the water molecules were located in difference Fourier maps and were refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The remaining H atoms were located in difference Fourier maps but introduced in calculated positions and treated as riding on their parent atoms (N or O) with, O—H = 0.82 Å and N—H = 0.86 Å with $U_{iso}(H) = 1.2 U_{eq}(N)$ and $U_{iso}(H) = 1.5 U_{eq}(O)$.

Figure 1

The molecular structure of the title compound with the atomic labeling scheme. Displacement are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.
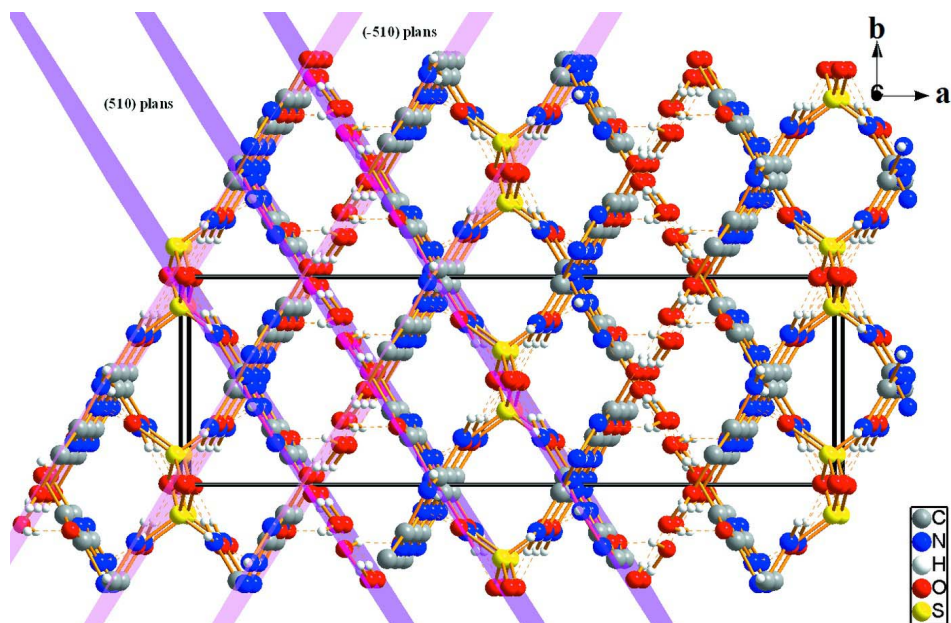
Figure 2

(Brandenburg & Berndt, 2001) A diagram of the three-dimensional packing of (I). (510) and (-510) planes have been presented to illustrate the mixed infinite chains. Hydrogen bonds are shown as dashed lines.
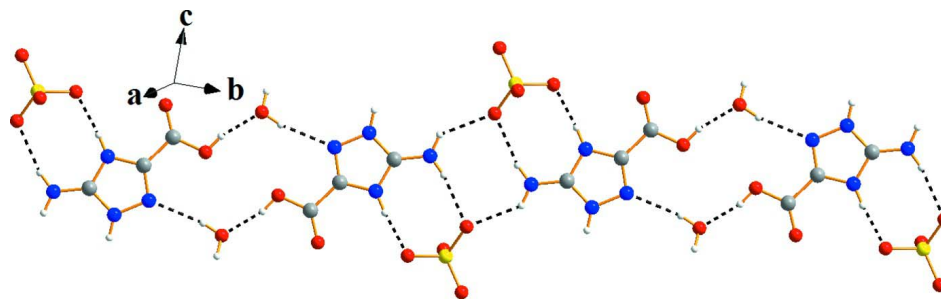
Figure 3

(Brandenburg & Berndt, 2001) A view of the mixed infinite chain. Hydrogen bonds are shown as dashed lines.

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Crystal data

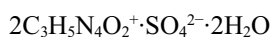|	
$2C_3H_5N_4O_2^+·SO_4^{2-}·2H_2O$	$F(000) = 808$
$M_r = 390.31$	$D_x = 1.821$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 19.4350$ (9) Å	Cell parameters from 1620 reflections
$b = 5.8467$ (2) Å	$\theta = 3.3–27.4°$
$c = 13.3343$ (6) Å	$\mu = 0.31$ mm^{-1}
$\beta = 109.981$ (2)°	$T = 150$ K
$V = 1423.98$ (10) Å^3	Needle, colourless
$Z = 4$	$0.48 \times 0.08 \times 0.06$ mm

Data collection

Bruker APEXII diffractometer	1470 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.032$
CCD rotation images, thin slices scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
11018 measured reflections	$h = -24 \rightarrow 25$
1620 independent reflections	$k = -7 \rightarrow 7$
	$l = -17 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.077$	
$S = 1.08$	H atoms treated by a mixture of independent and constrained refinement
1620 reflections	
121 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 1.9446P]$ where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.009$
	$\Delta\rho_{max} = 0.37$ e Å^{-3}
	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.32927 (7)	0.3566 (2)	0.60560 (11)	0.0136 (3)
C2	0.35578 (7)	0.2304 (2)	0.52873 (11)	0.0123 (3)
C3	0.40656 (7)	−0.0381 (2)	0.46589 (11)	0.0129 (3)
N1	0.38002 (6)	0.1265 (2)	0.39270 (9)	0.0138 (3)
H1	0.3827	0.125	0.3296	0.017*
N2	0.34797 (6)	0.2981 (2)	0.43222 (9)	0.0138 (3)
N3	0.39065 (6)	0.0245 (2)	0.55278 (9)	0.0123 (2)
H3	0.4005	−0.0502	0.6116	0.015*
N4	0.44239 (7)	−0.2252 (2)	0.45703 (10)	0.0169 (3)
H4A	0.451	−0.2519	0.399	0.02*
H4B	0.4571	−0.3201	0.5093	0.02*
O1	0.33947 (6)	0.28073 (19)	0.69430 (8)	0.0188 (2)
O2	0.29439 (6)	0.54386 (18)	0.56322 (8)	0.0186 (2)
H2	0.2817	0.612	0.6077	0.028*
O3	0.48758 (5)	0.50548 (17)	0.65377 (8)	0.0158 (2)
O4	0.56503 (6)	0.79464 (19)	0.76558 (8)	0.0190 (2)
S1	0.5	0.64445 (8)	0.75	0.01101 (13)
O1W	0.25419 (6)	0.69140 (19)	0.32536 (9)	0.0194 (2)
H1W	0.2751 (11)	0.724 (4)	0.2772 (17)	0.029*
H2W	0.2786 (11)	0.586 (4)	0.3624 (17)	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0118 (6)	0.0150 (7)	0.0148 (7)	−0.0021 (5)	0.0054 (5)	−0.0017 (5)
C2	0.0117 (6)	0.0128 (6)	0.0122 (7)	−0.0015 (5)	0.0037 (5)	−0.0008 (5)
C3	0.0119 (6)	0.0151 (7)	0.0117 (6)	−0.0026 (5)	0.0040 (5)	−0.0008 (5)
N1	0.0177 (6)	0.0155 (6)	0.0097 (6)	0.0011 (5)	0.0066 (5)	−0.0003 (4)
N2	0.0150 (6)	0.0143 (6)	0.0126 (6)	−0.0001 (4)	0.0053 (5)	−0.0008 (4)
N3	0.0145 (5)	0.0138 (6)	0.0093 (5)	0.0010 (4)	0.0052 (4)	0.0015 (4)
N4	0.0220 (6)	0.0162 (6)	0.0145 (6)	0.0034 (5)	0.0087 (5)	−0.0002 (5)
O1	0.0230 (5)	0.0213 (5)	0.0155 (5)	0.0024 (4)	0.0108 (4)	0.0015 (4)
O2	0.0227 (5)	0.0175 (5)	0.0170 (5)	0.0062 (4)	0.0086 (4)	−0.0006 (4)
O3	0.0182 (5)	0.0164 (5)	0.0125 (5)	−0.0004 (4)	0.0051 (4)	−0.0035 (4)
O4	0.0221 (5)	0.0243 (6)	0.0133 (5)	−0.0105 (4)	0.0094 (4)	−0.0049 (4)
S1	0.0129 (2)	0.0119 (2)	0.0090 (2)	0	0.00474 (17)	0
O1W	0.0228 (6)	0.0202 (5)	0.0187 (6)	0.0065 (4)	0.0117 (5)	0.0044 (4)

Geometric parameters (Å, º)

C1—O1	1.2144 (18)	N3—H3	0.86
C1—O2	1.3098 (17)	N4—H4A	0.86
C1—C2	1.4905 (19)	N4—H4B	0.86
C2—N2	1.3046 (18)	O2—H2	0.82
C2—N3	1.3648 (18)	O3—S1	1.4674 (10)
C3—N4	1.3236 (19)	O4—S1	1.4941 (10)
C3—N1	1.3420 (18)	S1—O3^i	1.4674 (10)
C3—N3	1.3480 (18)	S1—O4^i	1.4941 (10)
N1—N2	1.3774 (17)	O1W—H1W	0.89 (2)
N1—H1	0.86	O1W—H2W	0.83 (2)
O1—C1—O2	127.86 (13)	C3—N3—H3	126.9
O1—C1—C2	120.61 (13)	C2—N3—H3	126.9
O2—C1—C2	111.50 (12)	C3—N4—H4A	120
N2—C2—N3	112.37 (12)	C3—N4—H4B	120
N2—C2—C1	125.24 (13)	H4A—N4—H4B	120
N3—C2—C1	122.38 (12)	C1—O2—H2	109.5
N4—C3—N1	127.67 (13)	O3—S1—O3^i	112.76 (9)
N4—C3—N3	125.69 (13)	O3—S1—O4	109.00 (6)
N1—C3—N3	106.63 (12)	O3^i—S1—O4	108.98 (6)
C3—N1—N2	110.85 (11)	O3—S1—O4^i	108.98 (6)
C3—N1—H1	124.6	O3^i—S1—O4^i	109.00 (6)
N2—N1—H1	124.6	O4—S1—O4^i	108.01 (9)
C2—N2—N1	103.94 (11)	H1W—O1W—H2W	106.3 (19)
C3—N3—C2	106.20 (11)		
O1—C1—C2—N2	−179.54 (13)	C1—C2—N2—N1	−179.34 (12)
O2—C1—C2—N2	2.06 (19)	C3—N1—N2—C2	−0.42 (14)
O1—C1—C2—N3	1.6 (2)	N4—C3—N3—C2	177.99 (13)
O2—C1—C2—N3	−176.82 (12)	N1—C3—N3—C2	−1.19 (14)
N4—C3—N1—N2	−178.13 (13)	N2—C2—N3—C3	1.00 (16)
N3—C3—N1—N2	1.03 (15)	C1—C2—N3—C3	−179.99 (12)
N3—C2—N2—N1	−0.37 (15)		

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H2*W*···N2	0.83 (2)	2.16 (2)	2.9774 (16)	169 (2)
O1*W*—H1*W*···O1^{ii}	0.89 (2)	1.93 (2)	2.7941 (17)	163 (2)
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N3—H3···O4^v	0.86	1.79	2.6436 (15)	171

N4—H4*A*···O3^{vi}	0.86	2.17	2.8452 (17)	136
N4—H4*B*···O3^{vii}	0.86	2.08	2.9255 (16)	168

Symmetry codes: (ii) *x*, −*y*+1, *z*−1/2; (iii) −*x*+1/2, −*y*+3/2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+1, *y*−1, −*z*+3/2; (vi) −*x*+1, −*y*, −*z*+1; (vii) *x*, *y*−1, *z*.