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1-Amino-3-ammonioguanidinium dichloride

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.004 Å
R factor = 0.052
wR factor = 0.090
Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $CH_9N_5^{2+}\cdot 2Cl^-$, has been determined. Strong N—H···Cl bonds are present, leading to a complex pattern of hydrogen-bonded rings.

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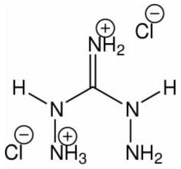
Comment

It has been shown recently that guanidinium ions and various sulfonates assemble into crystalline host frameworks with exceptionally reproducible lamellar architectures (Holman *et al.*, 2001). Interactions between ammonium cations and sulfonates lead to interesting crystalline inclusion architectures based upon second-sphere interactions (Reddy *et al.*, 2003). Diaminoguanidinium sulfonate compounds could combine these interactions and could be used as interesting tectons in porous crystalline networks. Published structures of diaminoguanidinium salts are rare; the Cambridge Structural Database (Version 5.24, update 2; Allen 2002) contains only three (Cromer *et al.*, 1988; Ritchie *et al.*, 1990; Savel'eva *et al.*, 1995). We attempted to synthesize diaminoguanidinium trifluoromethanesulfonate from diaminoguanidinium chloride and trifluoromethanesulfonic acid. The structure solution of the crystals present in the batch revealed a protonated diaminoguanidinium chloride salt, formally described as 1-amino-3-ammonioguanidinium dichloride, (I).



(I)

The molecular structure of (I) is presented in Fig. 1. The asymmetric unit contains one protonated 1,3-diaminoguanidinium ion and two chloride counter-ions. Table 1 gives selected geometric parameters of the molecular structure. Hydrogen bonds are abundant in this structure, as could be expected from the chemical formula and the liability of amino groups to act as donor: ten different N—H···Cl bonds are found, with H···Cl distances ranging from 2.14 to 2.75 Å. The two shortest, N8—H16···Cl2 (2.14 Å) and N7—H14···Cl1 (2.15 Å), have, in addition, nearly linear contact angles (167 and 165°, respectively). According to Brammer *et al.* (2001), the latter two bonds are among the strongest found for N—H···Cl contacts. Table 2 gives details of the hydrogen-bond geometry. Fig. 2 shows a projection of the structure on the *bc* plane; it gives an idea of the complex hydrogen-bond network formed. Among the more extended patterns formed are $R_3^5(16)$ and two different $R_2^2(8)$ rings (Bernstein *et al.*, 1995).

One ring involves two amino groups of symmetry-related guanidinium ions, whereas the second involves two ammonium groups.

Experimental

Single crystals of the title complex were obtained by slow evaporation of a methanol solution of diaminoguanidinium chloride (500 mg, 4 mmol) and trifluoromethanesulfonic acid (1800 mg, 12 mmol).

Crystal data

$CH_9N_5^{2+}\cdot 2Cl^-$
$M_r = 162.02$
Monoclinic, $P2_1/c$
$a = 4.503$ (2) Å
$b = 21.234$ (8) Å
$c = 6.936$ (2) Å
$\beta = 94.36$ (3)°
$V = 661.3$ (4) Å^3
$Z = 4$

$D_x = 1.627$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 reflections
$\theta = 10$–12°
$\mu = 0.89$ mm^{-1}
$T = 293$ K
Prism, colourless
0.40 × 0.10 × 0.10 mm

Data collection

Siemens *P*3 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*PLATON*; Spek, 2003)
$T_{\rm min} = 0.874$, $T_{\rm max} = 0.912$
3211 measured reflections
1840 independent reflections
1404 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.030$
$\theta_{\rm max} = 30.0°$
$h = -6 \rightarrow 6$
$k = -29 \rightarrow 25$
$l = 0 \rightarrow 9$
2 standard reflections frequency: 100 min intensity decay: 6.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.090$
$S = 1.00$
1404 reflections
73 parameters

H-atom parameters constrained
Weighting scheme: see text
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.70$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N3—C6	1.313 (4)	C6—N7	1.351 (4)
N4—N5	1.414 (4)	N7—N8	1.412 (4)
N5—C6	1.299 (4)		
C6—N5—N4	118.1 (3)	N5—C6—N3	122.2 (3)
N7—C6—N5	117.3 (3)	N8—N7—C6	117.1 (3)
N7—C6—N3	120.5 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H9···Cl1$^{\rm i}$	0.88	2.51	3.318 (3)	152
N4—H10···Cl1$^{\rm ii}$	1.02	2.38	3.395 (3)	174
N5—H11···Cl1$^{\rm iii}$	0.91	2.43	3.223 (3)	146
N3—H12···Cl2$^{\rm iv}$	0.86	2.59	3.223 (3)	131
N3—H12···N4	0.86	2.21	2.655 (4)	112
N3—H13···Cl2$^{\rm v}$	0.86	2.36	3.196 (3)	164
N7—H14···Cl1$^{\rm vi}$	0.93	2.15	3.052 (3)	165
N8—H15···Cl1	0.82	2.39	3.101 (3)	146
N8—H15···Cl2$^{\rm vii}$	0.82	2.75	3.097 (3)	107
N8—H16···Cl2$^{\rm v}$	0.99	2.14	3.110 (3)	167
N8—H17···Cl2$^{\rm viii}$	0.86	2.28	3.096 (3)	160

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

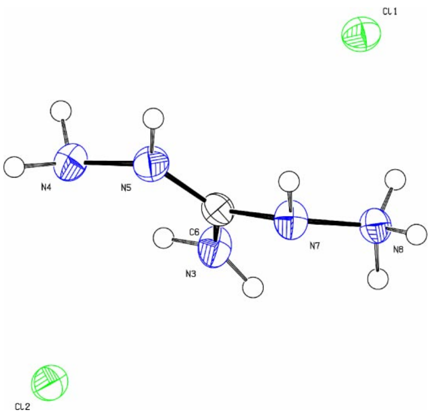


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level.

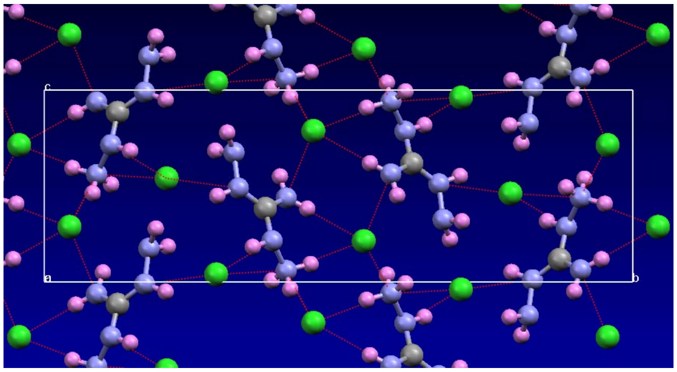


Figure 2
Projection of the crystal structure of (I) on the *bc* plane.

A Chebychev polynomial (Watkin, 1994; Prince, 1982) was used in the weighting scheme, [weight] = $1.0/[A_0T_0(x) + A_1T_1(x) \ldots + A_{n-1}T_{n-1}(x)]$, where A_i are the Chebychev coefficients listed below and $x = F_{\rm calc}/F_{\rm max}$. The robust weighting method (Prince, 1982) was used, with w = weight × $[1 - (\Delta F/6\sigma F)^2]^2$. A_{0-2} are 10.8, 13.7, and 4.14, respectively. H atoms were found in Fourier difference maps and were allowed to ride on their parent N atoms. H atoms were located in Fourier difference maps and allowed to ride on their parent N atoms, with $U_{\rm iso}$ values fixed at 0.05 Å^2.

Data collection: *P*3 (Siemens, 1993); cell refinement: *P*3; data reduction: *XDISK* in *P*3; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *Mercury* (CCDC, 2002) and *PLATON* (Spek, 2003); software used to prepare material for publication: *CRYSTALS*.

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