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1,5-Diaminotetrazolium chloride

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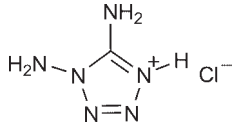
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(N–N) = 0.003 Å; R factor = 0.025; wR factor = 0.061; data-to-parameter ratio = 6.9.

The title compound, $CH_5N_6^+\cdot Cl^-$, crystallized with two indepedent 1,5-diaminotetrazolium cations and two independent chloride anions in the asymmetric unit. In the crystal, there are a number of N—H···Cl hydrogen-bonding interactions, which generate a three-dimensional network.

Related literature

For the preparation of the starting material, 1,5-diaminotetrazole, see: Galvez-Ruiz *et al.* (2005). For the preparation of 5-aminotetrazolium halogenide salts, see: Denffer *et al.* (2008) and of 1,5-diaminotetrazolium hydrochloride, see: He *et al.* (2009*a*). For the bond distances and angles in a related structure, see: He *et al.* (2009*b*). For van der Waals radii, see: http://biblo.chm.uri.edu/PeriodicTable/PeriodicTableoftheElements.htm.



Experimental

Crystal data

$CH_5N_6^+\cdot Cl^-$
M_r = 136.56
Orthorhombic, $Pna2_1$
a = 12.389 (3) Å
b = 6.4500 (12) Å
c = 13.305 (3) Å
V = 1063.1 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.61 mm^{-1}
T = 93 K
0.43 × 0.27 × 0.10 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.778, T_{max} = 0.942
7927 measured reflections
1268 independent reflections
1246 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.061
S = 1.07
1268 reflections
185 parameters
1 restraint
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···Cl2	0.93 (4)	2.16 (4)	3.017 (2)	154 (4)
N5—H5A···Cl1^{i}	0.79 (4)	2.77 (4)	3.555 (3)	179 (6)
N5—H5B···Cl2^{ii}	0.94 (4)	2.39 (4)	3.317 (2)	170 (3)
N6—H6A···Cl1^{iii}	0.86 (4)	2.65 (4)	3.376 (3)	142 (3)
N6—H6B···Cl2^{iv}	0.93 (4)	2.25 (4)	3.146 (2)	162 (3)
N10—H10···Cl1^{i}	0.79 (4)	2.30 (4)	3.021 (2)	152 (4)
N11—H11A···Cl2^{v}	0.96 (4)	2.65 (4)	3.567 (3)	161 (3)
N11—H11B···Cl1	0.85 (4)	2.47 (4)	3.306 (2)	170 (3)
N12—H12A···Cl2^{vi}	0.81 (4)	2.67 (4)	3.388 (3)	148 (3)
N12—H12B···Cl1^{vii}	0.80 (4)	2.39 (4)	3.173 (2)	171 (4)

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

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2159).

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Acta Cryst. (2010). E**66**, o984 [doi:10.1107/S1600536810009633]

1,5-Diaminotetrazolium chloride

Ling-Qiao Meng, Zhi-Ming Du, Chun-Lin He, Xiao-Min Cong, Shuai Yang and Lin-Shuang Zhao

S1. Comment

The synthesis and study of nitrogen-rich energetic salts and highly energetic materials for possible military as well as civil applications has attracted considerable interest in recent years, especially the salts with tetrazole-containing compounds (Galvez-Ruiz *et al.*, 2005; Denffer *et al.*, 2008). The nitrogen content of 5-amniotetrazole and 1,5-diamino-tetrazole, which are primary sources for preparing energetic salts, is 82.3% and 84%, respectively. Denffer *et al.* (2008) reported the synthesis of 5-aminotetrazolium hydrochloride and determinated its crystal structure. Our rearch group has recently reported on the synthesis of the title compound (He *et al.*., 2009a,b), and herein we report on its crystal structure.

The molecular structure of the title molecule is presented in Fig. 1. It crystallizes with two independent 1,5-Diamino-tetrazolium cations and two independent chloride anions per asymmetric unit. The bond distances and angles are as expected for a molecule of this kind, and are similar to the corresponding distances and angles reported by (He *et al.*, 2009a,b). The cations, excluding the N6 and N11 hydrogen atoms, are planar (maximum deviation 0.020 (2) Å).

The distance between the Cl1 anion and the plane formed by the cation ring 1, (= N1,N2,N3,N4,C1), is 0.445 (1) Å, and the perpendicular distances of this cation centroid, Cg1, to the parallel cation 2 ring planes (= N7,N8,N9,N10,C2), are 2.868 (1) Å (symmetry code: 1-x, -y, 0.5+z) and 2.922 (1) Å (symmetry code: 1-x, 1-y, 0.5+z). The distances of N2—C2 (2.864 (4) Å) and N8—C1^{i} (2.883 (4) Å) [symmetry code (i) = 0.5+x, 0.5-y, z] are smaller than the sum of the associated van der Waals Radii ($r_N + r_C$ = 3.25 Å), because of edge-to-face π-π interactions between the two cations. Both of the amino groups, in position 4 (N4) and position 5 (N6), form a long contact to the $Cl2^-$ anion (N4—Cl2 = 3.017 (2) Å and N6—Cl2^{ii} = 3.146 (2) Å [symmetry code (ii) = x, 1+y, z]), which is within the sum of the van der Waals radii ($r_N + r_{Cl}$ = 3.30 Å).

In the crystal there are a number of N-H···Cl hydrogen bonds which result in the foamation of a three-dimensional network (Table 1).

S2. Experimental

The starting material, 1,5-diaminotetrazole, was prepared according to the literature method (Galvez-Ruiz *et al.*, 2005). 1,5-diaminotetrazole (2.0043 g, 20.04 mmol) suspended in 40 mL of methanol, was reacted with 10 mL concentrated HCl. The reaction mixture was refluxed for 2 h and then the solvent was evaporated until precipitation occured. The concentrated solution was then placed in the refrigerator, and the white 1,5-diaminotetrazolium hydrochloride was obtained. The precipitate was filtered off and washed with water. The crude product was recrystallized from methanol (Yield: 2.4189 g, 88.6%). Crystals suitable for X-ray structure determination were obtained by slow evaporation of a solution in methanol at rt.

S3. Refinement

In the final cycles of refinement, in the absence of significant anomalous scattering effects, Friedel pairs were merged and Δf '' set to zero. All the H-atoms were located in difference Fourier maps and were freely refined: N-H = 0.79 (4) - 0.96 (4) Å.

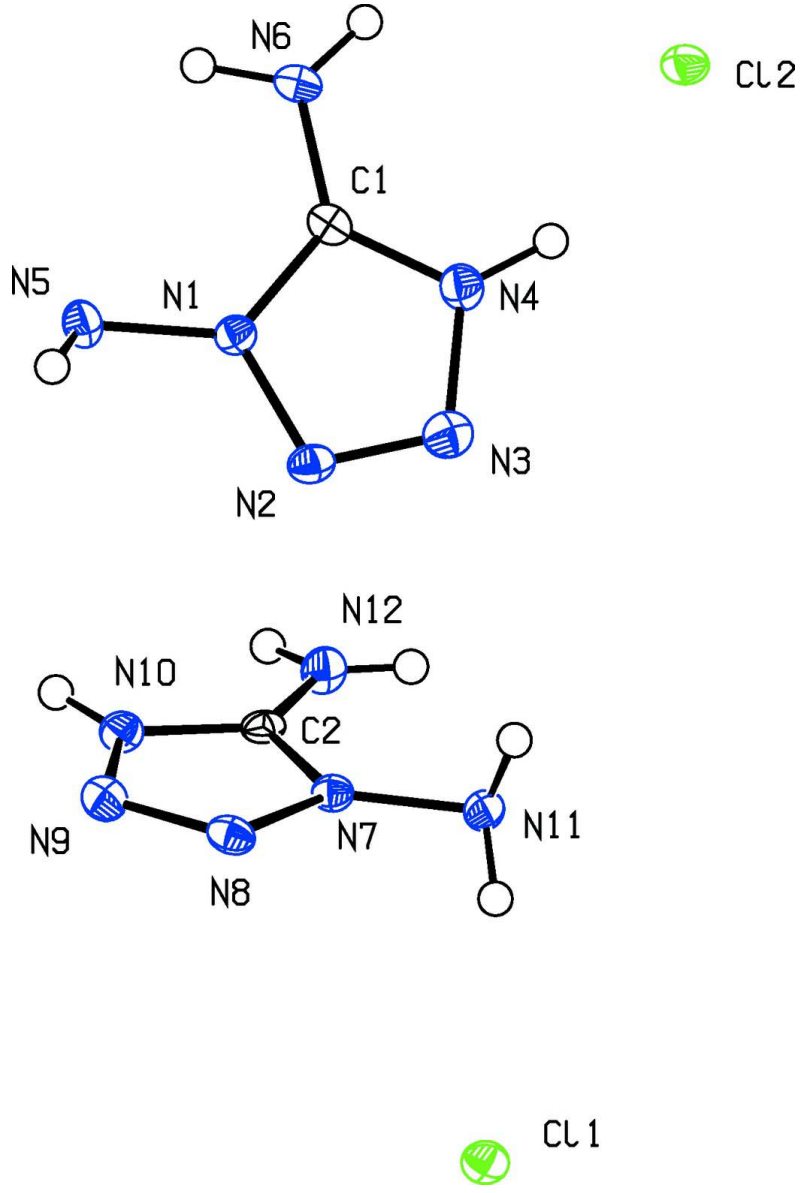

Figure 1

The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

1,5-Diaminotetrazolium chloride

Crystal data

$CH_5N_6^+ \cdot Cl^-$
M_r = 136.56

Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n

a = 12.389 (3) Å
b = 6.4500 (12) Å
c = 13.305 (3) Å
V = 1063.1 (4) Å^3
Z = 8
F(000) = 560
D_x = 1.706 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3581 reflections
θ = 3.1–27.5°
μ = 0.61 mm^{-1}
T = 93 K
Prism, colourless
0.43 × 0.27 × 0.10 mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
Radiation source: Rotating Anode
Graphite monochromator
Detector resolution: 28.5714 pixels mm^{-1}
Multi–scan
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2008)
T_{min} = 0.778, T_{max} = 0.942

7927 measured reflections
1268 independent reflections
1246 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −16→14
k = −8→8
l = −16→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.061
S = 1.07
1268 reflections
185 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.2133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2$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}
N1	0.44089 (16)	0.1470 (3)	0.39856 (16)	0.0134 (6)
N2	0.51729 (18)	0.2805 (3)	0.36265 (19)	0.0157 (6)
N3	0.48306 (18)	0.4641 (3)	0.37753 (18)	0.0191 (7)
N4	0.38470 (18)	0.4512 (3)	0.42323 (16)	0.0170 (6)
N5	0.44793 (18)	−0.0680 (3)	0.39178 (19)	0.0174 (6)
N6	0.26869 (18)	0.1788 (3)	0.4778 (2)	0.0173 (6)
C1	0.3577 (2)	0.2537 (4)	0.4364 (2)	0.0129 (7)
N7	0.68577 (16)	0.3860 (3)	0.20486 (15)	0.0128 (6)
N8	0.76391 (17)	0.2503 (3)	0.23810 (19)	0.0154 (6)
N9	0.73281 (18)	0.0683 (3)	0.21667 (17)	0.0170 (6)

N10	0.63448 (17)	0.0824 (3)	0.17032 (17)	0.0153 (6)
N11	0.68953 (18)	0.5995 (3)	0.21790 (18)	0.0154 (6)
N12	0.51472 (17)	0.3555 (3)	0.1248 (2)	0.0167 (6)
C2	0.6038 (2)	0.2794 (4)	0.1630 (2)	0.0131 (7)
Cl1	0.93591 (4)	0.67650 (9)	0.13004 (5)	0.0168 (2)
Cl2	0.19017 (4)	0.71516 (9)	0.47049 (5)	0.0174 (2)
H4	0.342 (3)	0.565 (7)	0.438 (3)	0.048 (12)*
H5A	0.446 (3)	−0.093 (7)	0.334 (3)	0.037 (11)*
H5B	0.514 (3)	−0.104 (5)	0.422 (3)	0.031 (9)*
H6A	0.215 (3)	0.259 (6)	0.492 (3)	0.037 (10)*
H6B	0.260 (3)	0.037 (6)	0.469 (3)	0.040 (10)*
H10	0.599 (3)	−0.016 (6)	0.158 (3)	0.028 (9)*
H11A	0.677 (3)	0.623 (5)	0.288 (3)	0.024 (8)*
H11B	0.753 (3)	0.634 (5)	0.200 (2)	0.016 (7)*
H12A	0.477 (3)	0.275 (5)	0.094 (3)	0.021 (9)*
H12B	0.502 (3)	0.476 (6)	0.129 (3)	0.028 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0118 (10)	0.0145 (10)	0.0140 (10)	−0.0003 (8)	−0.0009 (8)	0.0006 (8)
N2	0.0157 (11)	0.0187 (10)	0.0126 (12)	−0.0025 (8)	0.0014 (9)	0.0005 (8)
N3	0.0194 (11)	0.0213 (12)	0.0166 (12)	−0.0018 (8)	−0.0005 (10)	−0.0002 (10)
N4	0.0165 (11)	0.0161 (10)	0.0184 (11)	0.0005 (8)	−0.0008 (9)	−0.0015 (9)
N5	0.0182 (11)	0.0141 (10)	0.0198 (12)	0.0029 (8)	0.0002 (9)	−0.0009 (9)
N6	0.0132 (9)	0.0197 (11)	0.0189 (11)	0.0007 (8)	0.0042 (10)	−0.0004 (10)
C1	0.0118 (12)	0.0175 (11)	0.0093 (12)	0.0023 (9)	−0.0028 (9)	−0.0006 (9)
N7	0.0112 (9)	0.0146 (10)	0.0125 (10)	0.0000 (8)	−0.0001 (8)	0.0008 (8)
N8	0.0115 (11)	0.0202 (10)	0.0144 (12)	0.0026 (8)	0.0003 (9)	0.0007 (8)
N9	0.0170 (11)	0.0184 (11)	0.0156 (11)	0.0014 (8)	−0.0002 (9)	−0.0001 (9)
N10	0.0124 (10)	0.0164 (10)	0.0171 (10)	−0.0023 (8)	−0.0004 (8)	−0.0027 (9)
N11	0.0126 (10)	0.0137 (10)	0.0199 (12)	−0.0020 (8)	0.0008 (9)	−0.0013 (9)
N12	0.0134 (9)	0.0170 (11)	0.0196 (11)	−0.0020 (8)	−0.0037 (10)	−0.0016 (11)
C2	0.0134 (12)	0.0165 (12)	0.0094 (12)	−0.0031 (9)	0.0028 (10)	−0.0010 (9)
Cl1	0.0114 (3)	0.0194 (3)	0.0197 (3)	−0.0004 (2)	−0.0017 (3)	0.0002 (3)
Cl2	0.0126 (3)	0.0196 (3)	0.0199 (3)	−0.0011 (2)	0.0019 (3)	−0.0003 (3)

Geometric parameters (Å, º)

N1—N2	1.366 (3)	N7—N8	1.378 (3)
N1—N5	1.392 (3)	N7—N11	1.389 (3)
N1—C1	1.338 (3)	N7—C2	1.347 (3)
N2—N3	1.273 (3)	N8—N9	1.268 (3)
N3—N4	1.364 (3)	N9—N10	1.368 (3)
N4—C1	1.329 (3)	N10—C2	1.330 (3)
N6—C1	1.324 (3)	N12—C2	1.310 (3)
N4—H4	0.93 (4)	N10—H10	0.79 (4)
N5—H5A	0.79 (4)	N11—H11A	0.96 (4)

N5—H5B	0.94 (4)	N11—H11B	0.85 (4)
N6—H6A	0.86 (4)	N12—H12A	0.81 (4)
N6—H6B	0.93 (4)	N12—H12B	0.80 (4)
N2—N1—N5	124.2 (2)	N7—N8—N9	107.6 (2)
N2—N1—C1	109.95 (19)	N8—N9—N10	108.08 (19)
N5—N1—C1	125.8 (2)	N9—N10—C2	110.6 (2)
N1—N2—N3	107.5 (2)	C2—N10—H10	126 (3)
N2—N3—N4	108.06 (19)	N9—N10—H10	122 (3)
N3—N4—C1	110.0 (2)	N7—N11—H11B	105 (2)
N3—N4—H4	124 (2)	N7—N11—H11A	105.9 (19)
C1—N4—H4	126 (3)	H11A—N11—H11B	112 (3)
N1—N5—H5A	105 (3)	C2—N12—H12B	120 (3)
H5A—N5—H5B	113 (4)	C2—N12—H12A	116 (3)
N1—N5—H5B	106 (2)	H12A—N12—H12B	123 (4)
C1—N6—H6A	121 (3)	N4—C1—N6	127.9 (2)
C1—N6—H6B	114 (2)	N1—C1—N4	104.5 (2)
H6A—N6—H6B	122 (3)	N1—C1—N6	127.6 (2)
N8—N7—N11	124.48 (19)	N7—C2—N12	127.2 (2)
N8—N7—C2	109.76 (19)	N10—C2—N12	128.8 (2)
N11—N7—C2	125.7 (2)	N7—C2—N10	104.0 (2)
N5—N1—N2—N3	177.3 (2)	N11—N7—N8—N9	177.8 (2)
C1—N1—N2—N3	0.0 (3)	C2—N7—N8—N9	0.9 (3)
N2—N1—C1—N4	−0.2 (3)	N8—N7—C2—N10	−0.9 (3)
N2—N1—C1—N6	180.0 (3)	N8—N7—C2—N12	178.8 (3)
N5—N1—C1—N4	−177.4 (2)	N11—N7—C2—N10	−177.7 (2)
N5—N1—C1—N6	2.8 (4)	N11—N7—C2—N12	1.9 (4)
N1—N2—N3—N4	0.1 (3)	N7—N8—N9—N10	−0.5 (3)
N2—N3—N4—C1	−0.2 (3)	N8—N9—N10—C2	−0.1 (3)
N3—N4—C1—N1	0.2 (3)	N9—N10—C2—N7	0.6 (3)
N3—N4—C1—N6	−179.9 (3)	N9—N10—C2—N12	−179.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry codes: (i) $x-1/2, -y+1/2, z$; (ii) $x+1/2, -y+1/2, z$; (iii) $-x+1, -y+1, z+1/2$; (iv) $x, y-1, z$; (v) $x+1/2, -y+3/2, z$; (vi) $-x+1/2, y-1/2, z-1/2$; (vii) $x-1/2, -y+3/2, z$.