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1-(4-Fluorophenyl)biguanid-1-ium chloride

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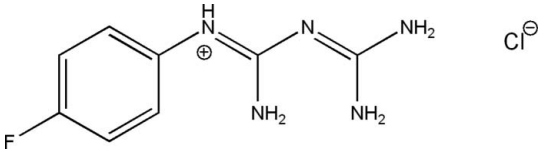
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.095; data-to-parameter ratio = 11.9.

The title compound, $C_8H_{11}FN_5^+\cdot Cl^-$, crystallized with a monoprotonated 1-(4-fluorophenyl)biguanidinium cation and a chloride anion in the asymmetric unit. The biguanidium group is not planar [dihedral angle between the two CN_3 groups = 52.0 (1)°] and is rotated with respect to the phenyl group [τ = 54.3 (3)°]. In the crystal, N—H···N hydrogen-bonded centrosymmetric dimers are connected into ribbons, which are further stabilized by N—H···Cl interactions, forming a three-dimensional hydrogen-bonded network.

Related literature

For related structures, see: Dalpiaz *et al.* (1996); Portalone *et al.* (2004); LeBel *et al.* (2005). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_8H_{11}FN_5^+\cdot Cl^-$
M_r = 231.67
Monoclinic, $P2_1/n$
a = 6.9954 (5) Å
b = 9.2187 (4) Å
c = 16.3149 (11) Å
β = 91.111 (5)°
V = 1051.93 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 173 K
0.40 × 0.40 × 0.20 mm

Data collection

STOE IPDS II two-circle-diffractometer
13661 measured reflections
1966 independent reflections
1605 reflections with $I > 2\sigma(I)$
R_{int} = 0.135

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.095
S = 1.03
1966 reflections
165 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected bond lengths (Å).

N8—C5	1.429 (2)	N10—C11	1.339 (2)
N8—C9	1.356 (2)	N12—C11	1.338 (3)
N9—C9	1.326 (2)	N13—C11	1.325 (3)
N10—C9	1.332 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N8—H8···Cl^{i}	0.83 (2)	2.50 (2)	3.2758 (17)	156 (2)
N9—H91···Cl^{ii}	0.88 (3)	2.47 (3)	3.3283 (18)	163 (2)
N9—H92···Cl^{i}	0.83 (3)	2.46 (3)	3.2358 (19)	155 (3)
N12—H121···Cl	0.87 (3)	2.50 (3)	3.3212 (19)	157 (2)
N12—H122···Cl^{iii}	0.88 (3)	2.80 (3)	3.5463 (19)	143 (2)
N13—H131···Cl	0.87 (3)	2.58 (3)	3.384 (2)	154 (2)
N13—H132···N10^{iv}	0.87 (3)	2.35 (3)	3.177 (3)	160 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008)and *XP* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank Professor Dr E. Egert (Goethe-Universität Frankfurt, Germany) for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2308).

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supplementary materials

Acta Cryst. (2010). E**66**, o2648 [**doi:10.1107/S1600536810037785**]

1-(4-Fluorophenyl)biguanid-1-ium chloride

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Comment

1-(4-Fluorophenyl)biguanid hydrochloride crystallized with a monoprotonated 1-(4-fluorophenyl)biguanidinium cation and a chloride anion in the asymmetric unit. The protonation occurs at the N atom (N8) attached to the phenyl ring (Fig. 1). The biguanidium group is rotated with respect to the phenyl group by the rotation angle τ = 54.3 (3)° [the angle τ is defined as: $\tau = |\omega 1 + \omega 2 \pm \pi|/2$, the torsion angles ω1 and ω2 being respectively C4—C5—N8—C9 and C6—C5—N8—C9 (Dalpiaz *et al.*, 1996)]. The planes defined by N8, C9, N9, N10 atoms and by N10, C11, N12, N13 atoms enclose a dihedral angle of 52.0 (1)°. Similar C—N bond lengths lead to the conclusion that the π- electron density is delocalized over the biguanidium group (Tab. 1). Two N—H···N hydrogen bonds stabilize a centrosymmetric dimer, which is further connected to a ribbon by $R^1_2(3)$ N—H···Cl^- interactions (Bernstein *et al.*, 1995; Fig. 2). The sixfold coordinated Cl^- anion forms another two N—H···Cl^- interactions leading to a three-dimensional hydrogen-bonded network.

Experimental

Single crystals of title compound were obtained by cocrystallization of the commercially available 1-(4-fluorophenyl)biguanid hydrochloride (2.6 mg) and propylthiouracil (1.1 mg) from methanol (50 µ*L*) at room temperature.

Refinement

All H atoms were initially located by a difference Fourier synthesis. Subsequently, H atoms bonded to aromatic C atoms were refined using a riding model, with C—H = 0.95 Å, and with U_{iso}(H) = 1.2 U_{eq}(C). H atoms bonded to N atoms were freely refined.

Figures

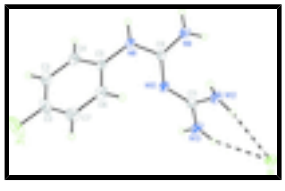

Fig. 1. A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates the N—H···Cl^- interactions.

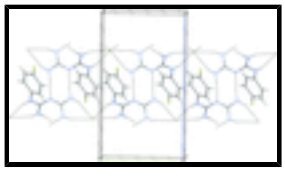

Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

1-(4-Fluorophenyl)biguanid-1-ium chloride

Crystal data

$C_8H_{11}FN_5^+ \cdot Cl^-$	$F(000) = 480$
$M_r = 231.67$	$D_x = 1.463$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 8763 reflections
$a = 6.9954$ (5) Å	$\theta = 3.3$–$26.0°$
$b = 9.2187$ (4) Å	$\mu = 0.35$ mm^{-1}
$c = 16.3149$ (11) Å	$T = 173$ K
$\beta = 91.111$ (5)°	Block, colourless
$V = 1051.93$ (11) Å^3	0.40 × 0.40 × 0.20 mm
$Z = 4$	

Data collection

STOE IPDS II two-circle-diffractometer	1605 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.135$
graphite	$\theta_{max} = 25.6°$, $\theta_{min} = 3.3°$
ω scans	$h = -8 \rightarrow 8$
13661 measured reflections	$k = -11 \rightarrow 11$
1966 independent reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
1966 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
165 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.008 (2)

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}
F1	1.1564 (2)	0.20564 (19)	0.36588 (9)	0.0508 (4)
C2	1.0273 (3)	0.1954 (3)	0.42677 (13)	0.0300 (5)
C3	0.8876 (3)	0.0914 (2)	0.41942 (13)	0.0269 (4)
H3	0.8799	0.0298	0.3728	0.032*
C4	0.7580 (3)	0.0793 (2)	0.48238 (12)	0.0217 (4)
H4	0.6598	0.0083	0.4791	0.026*
C5	0.7707 (3)	0.16967 (19)	0.54979 (11)	0.0186 (4)
C6	0.9161 (3)	0.2732 (2)	0.55575 (13)	0.0240 (4)
H6	0.9266	0.3338	0.6027	0.029*
C7	1.0446 (3)	0.2868 (2)	0.49308 (15)	0.0307 (5)
H7	1.1430	0.3578	0.4957	0.037*
N8	0.6343 (2)	0.15622 (17)	0.61347 (10)	0.0210 (4)
H8	0.611 (3)	0.075 (3)	0.6328 (15)	0.021 (6)*
C9	0.5280 (3)	0.26846 (19)	0.64102 (12)	0.0184 (4)
N9	0.4158 (3)	0.2418 (2)	0.70383 (11)	0.0259 (4)
H91	0.325 (4)	0.301 (3)	0.7203 (17)	0.035 (7)*
H92	0.411 (4)	0.159 (4)	0.7249 (19)	0.043 (8)*
N10	0.5351 (2)	0.39359 (16)	0.60039 (10)	0.0212 (4)
C11	0.5124 (2)	0.5212 (2)	0.63811 (12)	0.0197 (4)
N12	0.5563 (3)	0.5444 (2)	0.71722 (11)	0.0243 (4)
H121	0.562 (4)	0.634 (3)	0.7336 (16)	0.035 (7)*
H122	0.632 (4)	0.480 (3)	0.7417 (17)	0.037 (7)*
N13	0.4489 (3)	0.63199 (19)	0.59356 (12)	0.0259 (4)
H131	0.448 (4)	0.718 (3)	0.6155 (17)	0.035 (7)*
H132	0.423 (4)	0.618 (3)	0.5418 (19)	0.036 (7)*
Cl	0.48546 (6)	0.89909 (5)	0.73525 (3)	0.02180 (17)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0368 (8)	0.0794 (11)	0.0369 (8)	−0.0062 (7)	0.0206 (6)	−0.0049 (7)
C2	0.0218 (10)	0.0440 (12)	0.0245 (11)	0.0048 (9)	0.0080 (8)	0.0022 (9)
C3	0.0235 (9)	0.0357 (11)	0.0214 (10)	0.0108 (9)	−0.0021 (7)	−0.0060 (9)
C4	0.0184 (8)	0.0200 (9)	0.0265 (10)	0.0043 (7)	−0.0029 (7)	−0.0025 (8)
C5	0.0211 (9)	0.0160 (8)	0.0186 (9)	0.0053 (7)	0.0014 (7)	0.0024 (7)
C6	0.0251 (10)	0.0210 (9)	0.0259 (10)	0.0010 (8)	−0.0004 (8)	−0.0029 (8)
C7	0.0255 (10)	0.0304 (11)	0.0362 (12)	−0.0037 (9)	0.0028 (9)	0.0013 (9)

N8	0.0296 (9)	0.0119 (7)	0.0218 (8)	0.0036 (6)	0.0079 (7)	0.0022 (7)
C9	0.0213 (9)	0.0155 (9)	0.0183 (9)	0.0025 (7)	−0.0002 (7)	−0.0011 (7)
N9	0.0322 (10)	0.0164 (8)	0.0295 (10)	0.0056 (7)	0.0122 (8)	0.0029 (7)
N10	0.0305 (8)	0.0148 (7)	0.0182 (8)	0.0048 (6)	0.0030 (6)	0.0008 (6)
C11	0.0180 (9)	0.0171 (9)	0.0243 (10)	0.0019 (7)	0.0045 (7)	0.0020 (7)
N12	0.0361 (10)	0.0155 (8)	0.0211 (9)	0.0034 (8)	−0.0017 (7)	−0.0006 (7)
N13	0.0392 (10)	0.0150 (8)	0.0234 (10)	0.0055 (7)	−0.0048 (7)	0.0006 (7)
Cl	0.0265 (3)	0.0155 (2)	0.0235 (3)	−0.00112 (17)	0.00391 (17)	0.00160 (17)

Geometric parameters (Å, °)

F1—C2	1.359 (2)	N8—H8	0.83 (2)
C2—C3	1.373 (3)	N9—C9	1.326 (2)
C2—C7	1.375 (3)	N10—C9	1.332 (2)
C3—C4	1.388 (3)	N9—H91	0.88 (3)
C3—H3	0.9500	N9—H92	0.83 (3)
C4—C5	1.381 (3)	N10—C11	1.339 (2)
C4—H4	0.9500	N12—C11	1.338 (3)
C5—C6	1.397 (3)	N13—C11	1.325 (3)
N8—C5	1.429 (2)	N12—H121	0.87 (3)
C6—C7	1.380 (3)	N12—H122	0.88 (3)
C6—H6	0.9500	N13—H131	0.87 (3)
C7—H7	0.9500	N13—H132	0.87 (3)
N8—C9	1.356 (2)		
F1—C2—C3	117.8 (2)	C9—N8—H8	116.9 (15)
F1—C2—C7	118.9 (2)	C5—N8—H8	119.4 (15)
C3—C2—C7	123.26 (19)	N9—C9—N10	125.00 (17)
C2—C3—C4	117.75 (19)	N9—C9—N8	116.83 (17)
C2—C3—H3	121.1	N10—C9—N8	118.04 (17)
C4—C3—H3	121.1	C9—N9—H91	124.2 (17)
C5—C4—C3	120.55 (18)	C9—N9—H92	121 (2)
C5—C4—H4	119.7	H91—N9—H92	113 (3)
C3—C4—H4	119.7	C9—N10—C11	121.78 (16)
C4—C5—C6	120.18 (17)	N13—C11—N12	118.33 (18)
C4—C5—N8	119.54 (17)	N13—C11—N10	117.81 (19)
C6—C5—N8	120.28 (17)	N12—C11—N10	123.82 (17)
C7—C6—C5	119.64 (19)	C11—N12—H121	117.2 (18)
C7—C6—H6	120.2	C11—N12—H122	117.0 (17)
C5—C6—H6	120.2	H121—N12—H122	118 (3)
C2—C7—C6	118.6 (2)	C11—N13—H131	119.0 (19)
C2—C7—H7	120.7	C11—N13—H132	118.7 (17)
C6—C7—H7	120.7	H131—N13—H132	122 (3)
C9—N8—C5	123.55 (16)		
F1—C2—C3—C4	178.81 (18)	C5—C6—C7—C2	−1.1 (3)
C7—C2—C3—C4	0.2 (3)	C4—C5—N8—C9	−125.8 (2)
C2—C3—C4—C5	0.1 (3)	C6—C5—N8—C9	54.3 (3)
C3—C4—C5—C6	−0.9 (3)	C5—N8—C9—N9	−176.00 (18)
C3—C4—C5—N8	179.33 (16)	C5—N8—C9—N10	8.0 (3)
C4—C5—C6—C7	1.4 (3)	N9—C9—N10—C11	34.9 (3)

N8—C5—C6—C7	−178.78 (18)	N8—C9—N10—C11	−149.46 (18)
F1—C2—C7—C6	−178.25 (19)	C9—N10—C11—N13	−154.64 (18)
C3—C2—C7—C6	0.3 (3)	C9—N10—C11—N12	27.7 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8···Cl^{i}	0.83 (2)	2.50 (2)	3.2758 (17)	156 (2)
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N12—H122···Cl^{iii}	0.88 (3)	2.80 (3)	3.5463 (19)	143 (2)
N13—H131···Cl	0.87 (3)	2.58 (3)	3.384 (2)	154 (2)
N13—H132···N10^{iv}	0.87 (3)	2.35 (3)	3.177 (3)	160 (2)

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

Fig. 1

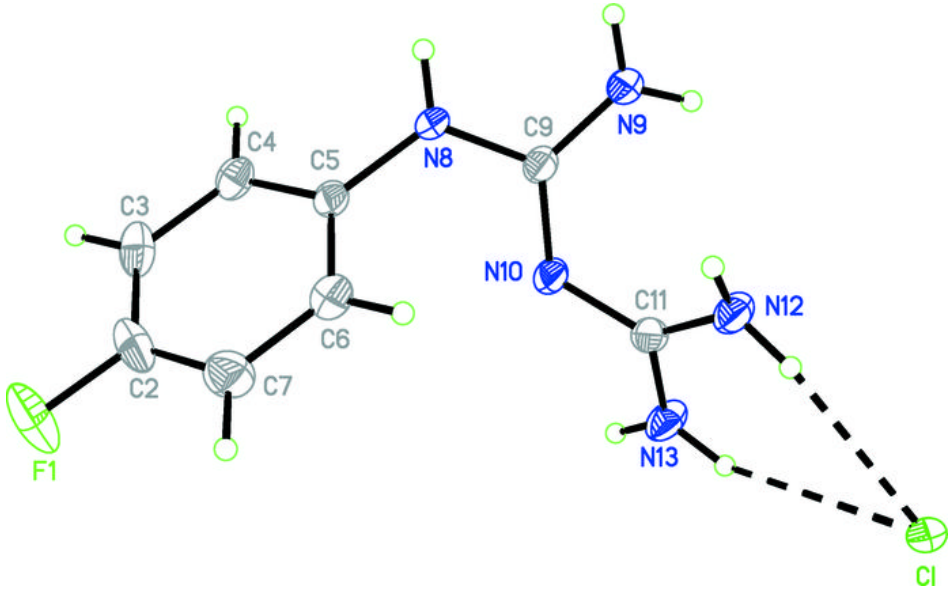

Fig. 2