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Piperazinium nitrate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.002 Å
R factor = 0.043
wR factor = 0.108
Data-to-parameter ratio = 19.7

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

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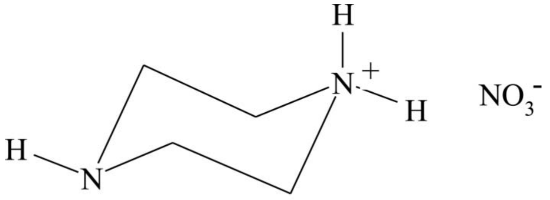
Crystals of the title compound, $C_4H_{11}N_2^+\cdot NO_3^-$, are built up from singly protonated piperazinium residues and nitrate anions. The components are linked by hydrogen bonds into a three-dimensional framework. The piperazinium residues are linked together *via* N—H···N hydrogen bonds into chains in the form of stacks along the [100] direction.

Comment

The present study is a continuation of the work on compounds that form non-covalent supramolecular framework structures in the solid-state *via* multiple hydrogen bonds (Perpétuo & Janczak, 2004), in order to expand our understanding of the physical–organic chemistry of systems containing multiple N—H···N and N—H···O hydrogen bonds in the solid state. We present here the solid-state structure of piperazinium nitrate, (I). Selected geometric parameters are given in Table 1.



(I)

The singly protonated piperazinium ring in the crystal structure of (I) adopts the chair conformation (Fig. 1) predicted by molecular orbital calculations for the isolated ion (Frisch *et al.*, 1998). As a result of protonation, the C—N bonds involving the protonated N atom are slightly longer than the C—N bonds containing the non-protonated N atom (Table 1). The correlation between the C—N bonds is similar to that found in the gas-phase structure obtained by DFT using the B3LYP method; the optimized C—N bond lengths involving the protonated N atom are 1.510 Å, while the C—N

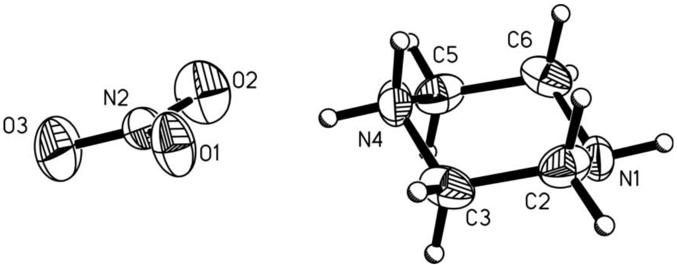


Figure 1
A view of the molecular structure of (I), showing displacement ellipsoids at the 50% probability level and H atoms as spheres of arbitrary radii.

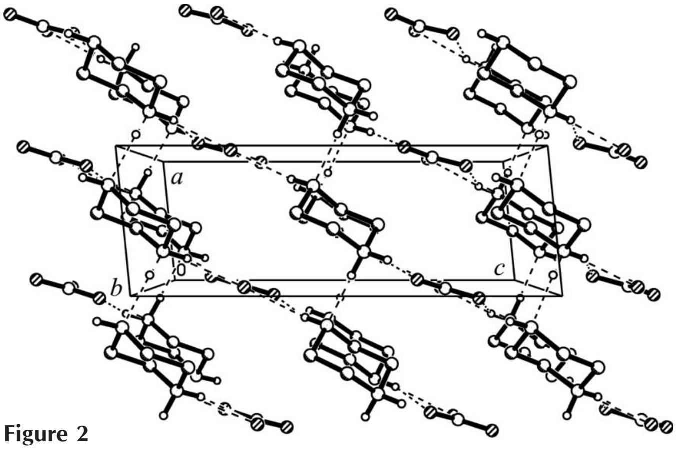


Figure 2
A view of the crystal packing, showing the hydrogen-bonded N—H···N chains (dashed lines) along the [100] direction.

bond lengths involving the non-protonated N atom are 1.445 Å.

The geometry of the nitrate anion in (I) shows a slight distortion from D_{3h} symmetry obtained by molecular orbital calculations [the three N—O bonds in the isolated NO_3^- ion are equivalent, with a length of 1.226 Å (Frisch *et al.*, 1998)] due to the interaction with the piperazinium cation and the formation of hydrogen bonds. The N—O bond lengths in the nitrate anion are indicative of a bond order between 1 and 2, reflecting delocalization of two π bonds over three N$\overset{\cdots}{—}$O bonds. The O atom with the shortest N—O bond length (O3) does not form a hydrogen bond and the other two O atoms are involved in hydrogen bonds as acceptors, one in two hydrogen bonds (O1) and the other in one hydrogen bond (O2) (Table 2).

In the crystal structure, the piperazinium $C_4H_{11}N_2^+$ cations are linked *via* N—H···N hydrogen bonds into chains, in the form of stacks parallel to the [100] direction (Fig. 2). These chains are interconnected *via* N—H···O hydrogen bonds with the nitrate anions into a three-dimensional framework superstructure.

A survey of the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002) for systems containing piperazinium cations yields over 300 structures with the doubly protonated piperazinium(2+) cation and a few structures with a singly protonated piperazinium(+) cation. The singly protonated piperazinium(+) cation mainly forms complexes with metals in which the non-protonated N atom of the piperazinium ring coordinates to the metal, as found in several open-framework structures (Neeraj *et al.*, 2001, 2002; Francis & Jacobson, 2001), or forms salts with large organic acids, as found in the structure of piperazinium 5,7-dihydroxy-3-(4-hydroxyphenyl)-4*H*-1-benzopyran-4-one hydrate (Kozerski *et al.*, 2003). In all structures containing the singly protonated piperazinium(+) cation, the ring, as observed for (I), adopts a chair conformation. The structures of piperazinium salts of basic organic or inorganic acids contain doubly protonated piperazinium(2+) cations. Thus, (I) represents the first structurally characterized simple inorganic salt containing a singly protonated piperazinium cation.

Experimental

Piperazine (99%) purchased from Aldrich was dissolved in 10% nitric acid. After several days, colourless single crystals appeared.

Crystal data

$C_4H_{11}N_2^+ \cdot NO_3^-$
$M_r = 149.16$
Monoclinic, $P2_1/c$
$a = 4.4420$ (9) Å
$b = 12.953$ (3) Å
$c = 12.677$ (3) Å
$\beta = 95.62$ (3)°
$V = 725.9$ (3) Å^3
$Z = 4$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 937 reflections
$\theta = 3.2$–29.5°
$\mu = 0.12$ mm^{-1}
$T = 295$ (2) K
Parallelepiped, colourless
0.42 × 0.35 × 0.22 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{min} = 0.948$, $T_{max} = 0.970$
8599 measured reflections
1874 independent reflections
939 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 29.5°$
$h = -5 \rightarrow 5$
$k = -17 \rightarrow 16$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.108$
$S = 1.05$
1874 reflections
95 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.14$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.012 (3)

Table 1
Selected geometric parameters (Å, °).

N2—O3	1.2114 (15)	N1—C6	1.4592 (19)
N2—O2	1.2340 (14)	C3—N4	1.4841 (18)
N2—O1	1.2388 (15)	N4—C5	1.4669 (18)
N1—C2	1.4445 (18)		
O3—N2—O2	124.63 (14)	O2—N2—O1	116.22 (12)
O3—N2—O1	119.14 (14)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H41···O1	0.90	2.07	2.9222 (14)	158
N4—H41···O2	0.90	2.32	3.0849 (15)	142
N4—H42···N1^{i}	0.90	1.92	2.8219 (16)	178
N1—H1···O1^{ii}	0.85 (2)	2.27 (2)	3.0486 (15)	153 (1)

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

The H atoms bonded to C atoms and N4 were placed in idealized positions and refined as riding atoms, with C—H and N—H distances constrained to 0.97 and 0.90 Å, respectively, and $U_{iso}(H) = 1.5U_{eq}$(parent atom). The H atom bonded to N1 was located in a difference Fourier map and restrained with N—H = 0.85 (1) Å and $U_{iso}(H) = 1.5U_{eq}(N1)$.

Data collection: *KM-4 CCD Software* (Kuma, 2001); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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