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Crystal structures of 4-(pyrimidin-2-yl)piperazin-1-ium chloride and 4-(pyrimidin-2-yl)piperazin-1-ium nitrate

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Keywords: crystal structure; pyrimidine–piperazine heterocyclic salts; chloride salt; nitrate salt; bifurcated hydrogen bonds

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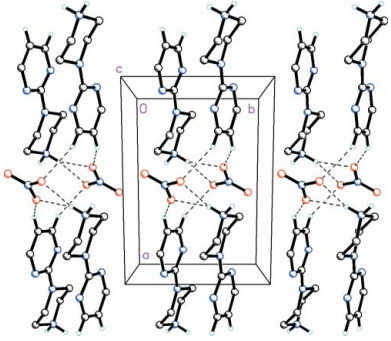
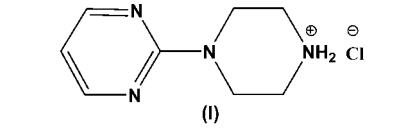
The title salts, $C_8H_{13}N_4^+\cdot Cl^-$, (I), and $C_8H_{13}N_4^+\cdot NO_3^-$, (II), contain linked pyridinium–piperazine heterocycles. In both salts, the piperazine ring adopts a chair conformation with protonation at the N atom not linked to the other ring. In the crystal of (I), weak N—H···Cl interactions are observed, leading to zigzag chains along [100]. In the crystal of (II), both H atoms on the NH_2^+ group form bifurcated N—H···(O,O) hydrogen bonds. Weak C—H···O interactions are also observed. These bonds collectively link the components into infinite chains along [100].

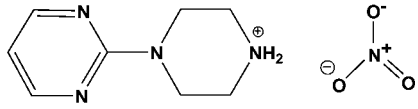
1. Chemical context

Pyrimidine-containing compounds exhibit various biological activities (Goldmann & Stoltefuss, 1991) and related fused heterocycles are unique classes of heterocyclic compounds that exhibit a broad spectrum of biological activities such as anticancer (Amin *et al.*, 2009; Pandey *et al.*, 2004), antiviral (Ibrahim & El-Metwally, 2010), antibacterial (Kuyper *et al.*, 1996) and anti-oxidant (Padmaja *et al.*, 2009), antidepressant (Kim *et al.*, 2010) and possess anti-inflammatory effects (Clark *et al.*, 2007). In addition, several piperazine derivatives have reached the stage of clinical application; among the known drugs that are used to treat anxiety is a pyrimidinylpiperazinyl compound, buspirone (trade name BuSpar®) (Tollefson *et al.*, 1991). Our research group has published a number of papers on incorporated heterocyclic ring structures, *viz.* imatinibium dipicrate (Jasinski *et al.*, 2010), 1-(2-hydroxyethyl)-4-[3-(2-trifluoromethyl-9*H*-thioxanthen-9-ylidene)propyl]piperazine-1,4-diium dichloride, which is the dihydrochloride salt of flupentixol (Siddegowda *et al.*, 2011*a*) and opipramolium fumarate (Siddegowda *et al.*, 2011*b*). Other related crystal structures are 4-(pyrimidin-2-yl)piperazin-1-ium (*E*)-3-carboxyprop-2-enoate (Yamuna *et al.*, 2014*a*), flupentixol tartarate and enrofloxacinium oxalate (Yamuna *et al.*, 2014*b*,*c*). As part of our ongoing studies in this area, we report herein the crystal structures of the title salts, (I) and (II).





(I)



(II)

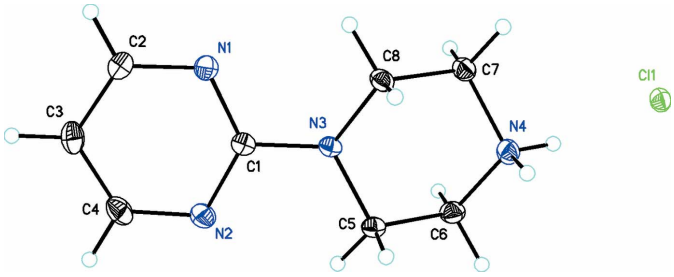


Figure 1
ORTEP drawing of $C_8H_{13}N_4^+\cdot Cl^-$, (I), showing 30% probability displacement ellipsoids.

2. Structural commentary

The structure of (I) and its atom numbering are shown in Fig. 1. It consists of a pyrimidylpiperazine cation joined by the C1/N3 atoms of each unit and a chloride anion. The C1—N3 bond is 1.373 (3) Å long, which compares favorably with similar ionic structures containing this cation [1.369 (3) (Yamuna *et al.*, 2014*a*), and 1.36 (6) and 1.37 (1) Å (Ding *et al.*, 2014)]. The N3/C5/C6/N4/C7/C8 piperazine unit adopts a slightly distorted chair conformation with protonation at the N4 nitrogen atom. The structure of (II) and its atom numbering are shown in Fig. 2. Similarly, it consists of a pyrimidylpiperazine cation joined by the C1/N3 atoms of each unit and a nitrate anion. The C1—N3 bond is 1.369 (3) Å, also in the range of the related structures described above. The N3/C5/C6/N4/C7/C8 piperazine unit also adopts a slightly distorted chair conformation with protonation at the N4 atom.

3. Supramolecular features

In the crystal of (I), N4—H4*A*···Cl1 and N4—H4*B*···Cl1 interactions are observed between pyrimidylpiperazine cations and chloride anions, forming zigzag chains along [100] (Fig. 3 and Table 1). In the crystal of (II), both of the H atoms on the N4 atom of the pyrimidylpiperazine cation are bifurcated, forming N—H···(O,O) hydrogen bonds (Fig. 4 and Table 2). Additional C—H···O interactions between the pyrimidyl unit and the nitrate anion are present which, in concert with the N—H···O hydrogen bonds between the piperazine group and nitrate anions, form infinite chains along [100].

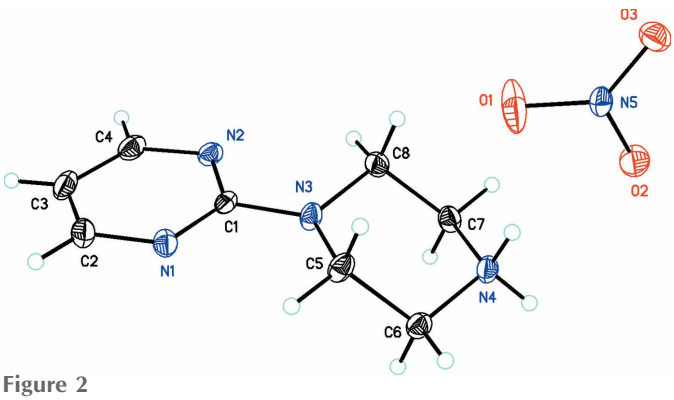


Figure 2
ORTEP drawing of $C_8H_{13}N_4^+\cdot NO_3^-$, (II), showing 30% probability displacement ellipsoids.

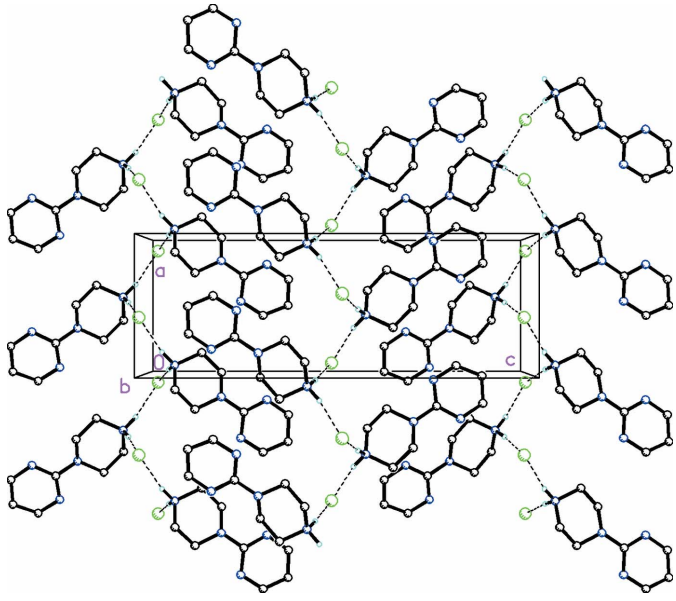


Figure 3
Molecular packing for $C_8H_{13}N_4^+\cdot Cl^-$, (I), viewed along the *b* axis. Dashed lines indicate N—H···Cl interactions forming zigzag chains along the *a* axis (see Table 1 for details). H atoms not involved in hydrogen bonding have been omitted for clarity.

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update May 2014: Allen 2002) revealed only three struc-

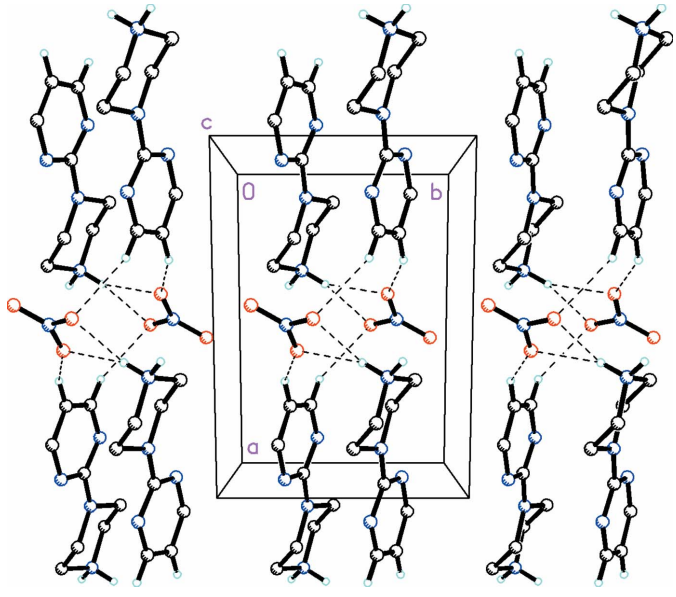


Figure 4
Molecular packing for $C_8H_{13}N_4^+\cdot NO_3^-$, (II), viewed along the *c* axis. Dashed lines indicate N—H···O hydrogen bonds and additional C—H···O interactions forming infinite chains along [100] (see Table 2 for details). H atoms not involved in hydrogen bonding have been omitted for clarity.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···Cl1	0.91	2.21	3.102 (2)	167
N4—H4B···Cl1^{i}	0.91	2.21	3.114 (2)	175

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O2^{i}	0.91	1.92	2.829 (3)	177
N4—H4A···O3^{i}	0.91	2.52	3.138 (3)	126
N4—H4B···O1	0.91	2.35	3.197 (3)	155
N4—H4B···O2	0.91	2.10	2.900 (3)	146
C3—H3···O1^{ii}	0.95	2.46	3.240 (3)	140
C4—H4···O2^{iii}	0.95	2.51	3.291 (3)	139

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

tures containing the 4-(pyrimidin-2-yl)piperazin-1-ium cation similar to the structures reported here. These include the salts of 4-(pyrimidin-2-yl)piperazin-1-ium 3-carboxyprop-2-enoate (Yamuna *et al.* 2014*a*), 4-(pyrimidin-2-yl)piperazin-1-ium hydrogen D-tartrate monohydrate (Ding *et al.*, 2014) and 4-(pyrimidin-2-yl)piperazin-1-ium hydrogen L-tartrate monohydrate (Ding *et al.* 2014). The 3-carboxyprop-2-enoate complex crystallizes in space group $P2_1/c$ while the two hydrogen (*D* and *L*)-tartrate monohydrate salts both crystallize in $P2_12_12_1$. In comparison, title salt (I) crystallizes in $P2_12_12_1$ while (II) crystallizes in space group $P2_1/c$. In addition, as a related observation, 109 structures containing the pyrimidine–piperazine unit were also identified in this search. Some of these include, uniquely, the 4-(pyrimidin-2-yl)piperazin-1-yl unit itself. These include 1-[4-(pyrimidin-2-yl)piperazin-1-yl]ethanone, (1-methyl-1*H*-pyrrol-2-yl)[4-(pyrimidin-2-yl)piperazin-1-yl]methanone, [4-(pyrimidin-2-yl)piperazin-1-yl](2-thienyl)methanone, (4-fluorophenyl)[4-(pyrimidin-2-yl)-piperazin-1-yl]methanone (Spencer *et al.*, 2011), (*E*)-1-phenyl-3-[4-(pyrimidin-2-yl)piperazin-1-yl]propan-1-one oxime (Kolasa *et al.*, 2006), *N*-(4-chlorophenyl)-4-(pyrimidin-2-yl)piperazine-1-carboxamide (Li, 2011) and 6-{3-[4-(pyrimidin-2-yl)-piperazin-1-yl]propyl}-2,3-dihydro-5*H*-[1,4]dithiino[2,3-*c*]pyrrole-5,7(6*H*)-dione (Bielenica *et al.*, 2011).

5. Synthesis and crystallization

For the preparation of title salt (I), a mixture of 1-(pyrimidin-2-yl)piperazine (0.2 g) and concentrated hydrochloric acid (5 ml) was stirred well over a magnetic stirrer at room temperature for 10 min and then warmed at 313 K for another 10 min. A white precipitate was obtained, which was dried in

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_8H_{13}N_4^+\cdot Cl^-$	$C_8H_{13}N_4^+\cdot NO_3^-$
M_r	200.67	227.23
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
Temperature (K)	173	173
a, b, c (Å)	6.84764 (17), 7.27667 (18), 19.1751 (5)	10.5272 (6), 7.2230 (3), 14.1575 (7)
α, β, γ (°)	90, 90, 90	90, 107.341 (6), 90
V (Å^3)	955.46 (4)	1027.58 (9)
Z	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	3.21	0.98
Crystal size (mm)	0.26 × 0.14 × 0.08	0.22 × 0.16 × 0.06
Data collection		
Diffractometer	Agilent Agilent Eos Gemini	Agilent Agilent Eos Gemini
Absorption correction	Multi-scan (*CrysAlis RED*; Agilent, 2012)	Multi-scan (*CrysAlis RED*; Agilent, 2012)
T_{min}, T_{max}	0.417, 1.000	0.727, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5514, 1841, 1761	6218, 1960, 1752
R_{int}	0.045	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615	0.613
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.091, 1.08	0.058, 0.163, 1.10
No. of reflections	1841	1960
No. of parameters	119	146
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.20	0.42, −0.25
Absolute structure	Flack x determined using 687 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)	–
Absolute structure parameter	0.056 (15)	–

Computer programs: *CrysAlis PRO* and *CrysAlis RED* (Agilent, 2012), *SUPERFLIP* (Palatinus & Chapuis, 2007), *SHELXL2012* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

the open air overnight and then dissolved in hot dimethyl sulfoxide solvent. After few days, colourless blocks were obtained on slow evaporation (m.p. above 563 K).

For the preparation of title salt (II), a mixture of 1-(pyrimidin-2-yl)piperazine, from Sigma–Aldrich (0.2 g), and concentrated nitric acid (5 ml) was stirred well over a magnetic stirrer at room temperature for 10 min. A white precipitate was obtained immediately, which was dried in the open air overnight and then dissolved in water. After a few days, colourless blocks were obtained on slow evaporation (m.p. 463–470 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In both (I) and (II), all of the H atoms were placed in their calculated positions and then refined using a riding model with C—H bond lengths of 0.93 (CH) or 0.97 Å (CH_2) and N—H bond lengths of 0.97 Å. Isotropic displacement parameters for these atoms were set at $1.2U_{eq}$(CH,CH_2,NH).

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supporting information

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Crystal structures of 4-(pyrimidin-2-yl)piperazin-1-ium chloride and 4-(pyrimidin-2-yl)piperazin-1-ium nitrate

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Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

(I) 4-(Pyrimidin-2-yl)piperazin-1-ium chloride

Crystal data

$C_8H_{13}N_4^+\cdot Cl^-$
M_r = 200.67
Orthorhombic, $P2_12_12_1$
a = 6.84764 (17) Å
b = 7.27667 (18) Å
c = 19.1751 (5) Å
V = 955.46 (4) Å^3
Z = 4
$F(000)$ = 424
D_x = 1.395 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 2676 reflections
θ = 4.6–71.5°
μ = 3.21 mm^{-1}
T = 173 K
Irregular, colourless
0.26 × 0.14 × 0.08 mm

Data collection

Agilent Agilent Eos Gemini diffractometer
Radiation source: Enhance (Cu) X-ray Source
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Agilent, 2012)
T_{min} = 0.417, T_{max} = 1.000
5514 measured reflections
1841 independent reflections
1761 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 71.4°, θ_{min} = 4.6°
h = −8→8
k = −8→4
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 1.08
1841 reflections
119 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.1163P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL2012* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0073 (13)

Absolute structure: Flack x determined using 687 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.* (2013)
Absolute structure parameter: 0.056 (15)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.08383 (9)	0.49612 (9)	0.48653 (3)	0.0262 (2)
N1	0.6948 (4)	0.6820 (3)	0.81551 (12)	0.0251 (5)
N2	0.9664 (4)	0.5690 (3)	0.74930 (13)	0.0286 (6)
N3	0.6688 (3)	0.6293 (3)	0.69659 (12)	0.0224 (5)
N4	0.4359 (4)	0.6322 (3)	0.57422 (12)	0.0258 (5)
H4A	0.3467	0.5800	0.5451	0.031*
H4B	0.4718	0.7422	0.5556	0.031*
C1	0.7813 (4)	0.6281 (4)	0.75588 (14)	0.0208 (5)
C2	0.8040 (4)	0.6746 (4)	0.87274 (15)	0.0269 (6)
H2	0.7471	0.7097	0.9159	0.032*
C3	0.9968 (5)	0.6181 (4)	0.87217 (16)	0.0318 (7)
H3	1.0742	0.6147	0.9133	0.038*
C4	1.0692 (5)	0.5668 (4)	0.80773 (17)	0.0330 (7)
H4	1.2013	0.5274	0.8052	0.040*
C5	0.7582 (4)	0.5944 (4)	0.62855 (14)	0.0245 (6)
H5A	0.8701	0.5096	0.6341	0.029*
H5B	0.8076	0.7111	0.6088	0.029*
C6	0.6103 (4)	0.5108 (4)	0.57949 (14)	0.0278 (6)
H6A	0.6694	0.4948	0.5328	0.033*
H6B	0.5705	0.3883	0.5969	0.033*
C7	0.3448 (4)	0.6631 (4)	0.64394 (14)	0.0246 (6)
H7A	0.2964	0.5449	0.6628	0.030*
H7B	0.2323	0.7475	0.6392	0.030*
C8	0.4936 (4)	0.7449 (4)	0.69357 (14)	0.0233 (6)
H8A	0.5297	0.8698	0.6777	0.028*
H8B	0.4359	0.7553	0.7407	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0230 (3)	0.0300 (4)	0.0255 (3)	−0.0007 (3)	−0.0033 (2)	0.0015 (3)
N1	0.0252 (12)	0.0254 (11)	0.0246 (11)	−0.0008 (10)	−0.0007 (10)	−0.0015 (9)
N2	0.0240 (14)	0.0310 (12)	0.0309 (12)	0.0064 (10)	0.0001 (10)	0.0014 (10)
N3	0.0184 (11)	0.0255 (11)	0.0233 (11)	0.0044 (9)	0.0015 (9)	−0.0022 (10)
N4	0.0228 (12)	0.0290 (11)	0.0256 (11)	−0.0051 (10)	−0.0032 (10)	0.0005 (10)

C1	0.0217 (13)	0.0157 (11)	0.0251 (13)	0.0000 (10)	0.0013 (11)	0.0022 (10)
C2	0.0342 (16)	0.0238 (13)	0.0229 (13)	−0.0013 (12)	0.0000 (12)	−0.0001 (11)
C3	0.0353 (16)	0.0287 (14)	0.0314 (14)	−0.0017 (14)	−0.0114 (14)	0.0056 (12)
C4	0.0238 (14)	0.0339 (14)	0.0413 (17)	0.0072 (13)	−0.0056 (14)	0.0062 (13)
C5	0.0208 (13)	0.0292 (14)	0.0233 (13)	0.0030 (11)	0.0031 (11)	−0.0032 (11)
C6	0.0256 (14)	0.0316 (14)	0.0261 (13)	0.0000 (14)	0.0035 (10)	−0.0058 (12)
C7	0.0200 (13)	0.0272 (13)	0.0267 (14)	−0.0009 (11)	−0.0007 (11)	0.0007 (11)
C8	0.0186 (13)	0.0244 (12)	0.0268 (13)	0.0046 (12)	−0.0004 (12)	−0.0027 (11)

Geometric parameters (Å, º)

N1—C1	1.346 (4)	C3—H3	0.9500
N1—C2	1.329 (4)	C3—C4	1.383 (4)
N2—C1	1.344 (4)	C4—H4	0.9500
N2—C4	1.323 (4)	C5—H5A	0.9900
N3—C1	1.373 (3)	C5—H5B	0.9900
N3—C5	1.463 (3)	C5—C6	1.510 (4)
N3—C8	1.466 (3)	C6—H6A	0.9900
N4—H4A	0.9100	C6—H6B	0.9900
N4—H4B	0.9100	C7—H7A	0.9900
N4—C6	1.489 (4)	C7—H7B	0.9900
N4—C7	1.492 (3)	C7—C8	1.516 (4)
C2—H2	0.9500	C8—H8A	0.9900
C2—C3	1.383 (4)	C8—H8B	0.9900
C2—N1—C1	116.2 (2)	N3—C5—H5B	109.6
C4—N2—C1	115.2 (3)	N3—C5—C6	110.2 (2)
C1—N3—C5	120.2 (2)	H5A—C5—H5B	108.1
C1—N3—C8	119.7 (2)	C6—C5—H5A	109.6
C5—N3—C8	114.0 (2)	C6—C5—H5B	109.6
H4A—N4—H4B	108.0	N4—C6—C5	110.0 (2)
C6—N4—H4A	109.4	N4—C6—H6A	109.7
C6—N4—H4B	109.4	N4—C6—H6B	109.7
C6—N4—C7	111.3 (2)	C5—C6—H6A	109.7
C7—N4—H4A	109.4	C5—C6—H6B	109.7
C7—N4—H4B	109.4	H6A—C6—H6B	108.2
N1—C1—N3	117.0 (2)	N4—C7—H7A	109.7
N2—C1—N1	126.0 (2)	N4—C7—H7B	109.7
N2—C1—N3	116.9 (2)	N4—C7—C8	109.9 (2)
N1—C2—H2	118.6	H7A—C7—H7B	108.2
N1—C2—C3	122.9 (3)	C8—C7—H7A	109.7
C3—C2—H2	118.6	C8—C7—H7B	109.7
C2—C3—H3	122.3	N3—C8—C7	110.4 (2)
C2—C3—C4	115.5 (3)	N3—C8—H8A	109.6
C4—C3—H3	122.3	N3—C8—H8B	109.6
N2—C4—C3	124.2 (3)	C7—C8—H8A	109.6
N2—C4—H4	117.9	C7—C8—H8B	109.6
C3—C4—H4	117.9	H8A—C8—H8B	108.1

N3—C5—H5A	109.6		
N1—C2—C3—C4	−0.8 (4)	C4—N2—C1—N1	−0.6 (4)
N3—C5—C6—N4	55.8 (3)	C4—N2—C1—N3	−178.9 (3)
N4—C7—C8—N3	−54.5 (3)	C5—N3—C1—N1	172.5 (2)
C1—N1—C2—C3	1.0 (4)	C5—N3—C1—N2	−9.0 (4)
C1—N2—C4—C3	0.8 (4)	C5—N3—C8—C7	55.2 (3)
C1—N3—C5—C6	151.9 (2)	C6—N4—C7—C8	57.4 (3)
C1—N3—C8—C7	−152.4 (2)	C7—N4—C6—C5	−58.1 (3)
C2—N1—C1—N2	−0.3 (4)	C8—N3—C1—N1	21.8 (4)
C2—N1—C1—N3	178.0 (2)	C8—N3—C1—N2	−159.8 (2)
C2—C3—C4—N2	−0.2 (5)	C8—N3—C5—C6	−55.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···Cl1	0.91	2.21	3.102 (2)	167
N4—H4*B*···Cl1^{i}	0.91	2.21	3.114 (2)	175

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

(II) 4-(Pyrimidin-2-yl)piperazin-1-ium nitrate

Crystal data

$C_8H_{13}N_4^+·NO_3^-$
M_r = 227.23
Monoclinic, $P2_1/c$
a = 10.5272 (6) Å
b = 7.2230 (3) Å
c = 14.1575 (7) Å
β = 107.341 (6)°
V = 1027.58 (9) Å^3
Z = 4
$F(000)$ = 480
D_x = 1.469 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 2763 reflections
θ = 6.2–71.4°
μ = 0.98 mm^{-1}
T = 173 K
Irregular, colourless
0.22 × 0.16 × 0.06 mm

Data collection

Agilent Agilent Eos Gemini diffractometer
Radiation source: Cu Kα
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Agilent, 2012)
T_{min} = 0.727, T_{max} = 1.000
6218 measured reflections
1960 independent reflections
1752 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 71.0°, θ_{min} = 4.4°
h = −9→12
k = −8→8
l = −17→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.163
S = 1.10
1960 reflections
146 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.9595P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Extinction correction: *SHELXL2012* (Sheldrick, 2008), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0099 (14)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4119 (2)	0.6964 (4)	0.41222 (17)	0.0615 (7)
O2	0.50951 (18)	0.6257 (2)	0.30424 (14)	0.0381 (5)
O3	0.55020 (17)	0.8884 (2)	0.37996 (13)	0.0323 (5)
N5	0.49103 (17)	0.7390 (3)	0.36677 (13)	0.0238 (4)
N1	0.00592 (19)	0.2396 (3)	0.48106 (14)	0.0291 (5)
N2	−0.11846 (18)	0.3821 (3)	0.32856 (15)	0.0273 (5)
N3	0.10930 (18)	0.3372 (3)	0.36702 (14)	0.0268 (5)
N4	0.33344 (18)	0.3134 (3)	0.29632 (15)	0.0278 (5)
H4A	0.3814	0.2536	0.2617	0.033*
H4B	0.3777	0.4191	0.3216	0.033*
C1	−0.0049 (2)	0.3204 (3)	0.39365 (16)	0.0220 (5)
C2	−0.1085 (3)	0.2126 (3)	0.50188 (19)	0.0346 (6)
H2	−0.1054	0.1544	0.5627	0.042*
C3	−0.2307 (2)	0.2647 (4)	0.4398 (2)	0.0362 (6)
H3	−0.3111	0.2420	0.4553	0.043*
C4	−0.2290 (2)	0.3519 (3)	0.3537 (2)	0.0329 (6)
H4	−0.3113	0.3927	0.3097	0.039*
C5	0.2387 (2)	0.2876 (4)	0.43489 (16)	0.0282 (5)
H5A	0.2266	0.2035	0.4867	0.034*
H5B	0.2848	0.4005	0.4676	0.034*
C6	0.3222 (2)	0.1932 (3)	0.37877 (17)	0.0270 (5)
H6A	0.4121	0.1674	0.4242	0.032*
H6B	0.2808	0.0738	0.3519	0.032*
C7	0.1993 (2)	0.3620 (3)	0.22801 (17)	0.0277 (5)
H7A	0.1537	0.2483	0.1960	0.033*
H7B	0.2095	0.4461	0.1755	0.033*
C8	0.1166 (2)	0.4552 (3)	0.28517 (17)	0.0276 (5)
H8A	0.1571	0.5756	0.3112	0.033*
H8B	0.0258	0.4789	0.2407	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0614 (14)	0.0836 (17)	0.0562 (13)	−0.0362 (13)	0.0431 (11)	−0.0184 (12)
O2	0.0436 (10)	0.0314 (10)	0.0460 (11)	−0.0072 (8)	0.0238 (8)	−0.0153 (8)
O3	0.0379 (9)	0.0249 (9)	0.0353 (9)	−0.0045 (7)	0.0129 (7)	−0.0021 (7)

N5	0.0175 (9)	0.0301 (10)	0.0240 (9)	−0.0015 (7)	0.0064 (7)	0.0012 (8)
N1	0.0292 (10)	0.0327 (11)	0.0282 (10)	0.0020 (8)	0.0126 (8)	0.0038 (8)
N2	0.0210 (9)	0.0270 (10)	0.0331 (11)	0.0037 (7)	0.0071 (8)	0.0001 (8)
N3	0.0189 (9)	0.0380 (11)	0.0243 (9)	0.0068 (8)	0.0075 (7)	0.0087 (8)
N4	0.0231 (9)	0.0278 (10)	0.0368 (11)	−0.0042 (8)	0.0153 (8)	−0.0045 (8)
C1	0.0207 (10)	0.0220 (10)	0.0246 (11)	0.0023 (8)	0.0087 (8)	−0.0035 (8)
C2	0.0416 (14)	0.0328 (13)	0.0372 (13)	−0.0021 (11)	0.0235 (11)	−0.0014 (10)
C3	0.0300 (13)	0.0340 (13)	0.0525 (15)	−0.0049 (10)	0.0247 (11)	−0.0130 (12)
C4	0.0224 (11)	0.0304 (12)	0.0456 (15)	0.0020 (9)	0.0098 (10)	−0.0063 (11)
C5	0.0208 (11)	0.0395 (13)	0.0234 (11)	0.0087 (9)	0.0054 (9)	0.0023 (9)
C6	0.0219 (10)	0.0296 (12)	0.0293 (11)	0.0038 (9)	0.0074 (9)	0.0014 (9)
C7	0.0291 (11)	0.0305 (12)	0.0255 (11)	−0.0013 (9)	0.0111 (9)	0.0039 (9)
C8	0.0267 (11)	0.0290 (12)	0.0283 (11)	0.0033 (9)	0.0098 (9)	0.0080 (9)

Geometric parameters (Å, º)

O1—N5	1.233 (3)	C2—C3	1.376 (4)
O2—N5	1.263 (2)	C3—H3	0.9500
O3—N5	1.232 (2)	C3—C4	1.377 (4)
N1—C1	1.342 (3)	C4—H4	0.9500
N1—C2	1.337 (3)	C5—H5A	0.9900
N2—C1	1.349 (3)	C5—H5B	0.9900
N2—C4	1.333 (3)	C5—C6	1.512 (3)
N3—C1	1.369 (3)	C6—H6A	0.9900
N3—C5	1.459 (3)	C6—H6B	0.9900
N3—C8	1.459 (3)	C7—H7A	0.9900
N4—H4A	0.9100	C7—H7B	0.9900
N4—H4B	0.9100	C7—C8	1.512 (3)
N4—C6	1.487 (3)	C8—H8A	0.9900
N4—C7	1.496 (3)	C8—H8B	0.9900
C2—H2	0.9500		
O1—N5—O2	118.2 (2)	C3—C4—H4	118.2
O3—N5—O1	121.9 (2)	N3—C5—H5A	109.7
O3—N5—O2	119.82 (18)	N3—C5—H5B	109.7
C2—N1—C1	115.6 (2)	N3—C5—C6	109.86 (18)
C4—N2—C1	115.5 (2)	H5A—C5—H5B	108.2
C1—N3—C5	121.45 (19)	C6—C5—H5A	109.7
C1—N3—C8	121.92 (18)	C6—C5—H5B	109.7
C5—N3—C8	114.01 (18)	N4—C6—C5	110.12 (18)
H4A—N4—H4B	108.0	N4—C6—H6A	109.6
C6—N4—H4A	109.4	N4—C6—H6B	109.6
C6—N4—H4B	109.4	C5—C6—H6A	109.6
C6—N4—C7	111.33 (17)	C5—C6—H6B	109.6
C7—N4—H4A	109.4	H6A—C6—H6B	108.2
C7—N4—H4B	109.4	N4—C7—H7A	109.7
N1—C1—N2	126.0 (2)	N4—C7—H7B	109.7
N1—C1—N3	116.88 (19)	N4—C7—C8	109.99 (18)

N2—C1—N3	117.06 (19)	H7A—C7—H7B	108.2
N1—C2—H2	118.3	C8—C7—H7A	109.7
N1—C2—C3	123.4 (2)	C8—C7—H7B	109.7
C3—C2—H2	118.3	N3—C8—C7	109.85 (18)
C2—C3—H3	122.1	N3—C8—H8A	109.7
C2—C3—C4	115.8 (2)	N3—C8—H8B	109.7
C4—C3—H3	122.1	C7—C8—H8A	109.7
N2—C4—C3	123.6 (2)	C7—C8—H8B	109.7
N2—C4—H4	118.2	H8A—C8—H8B	108.2
N1—C2—C3—C4	−1.3 (4)	C4—N2—C1—N1	−2.7 (3)
N3—C5—C6—N4	55.5 (3)	C4—N2—C1—N3	175.4 (2)
N4—C7—C8—N3	−55.3 (2)	C5—N3—C1—N1	−6.3 (3)
C1—N1—C2—C3	−0.7 (4)	C5—N3—C1—N2	175.4 (2)
C1—N2—C4—C3	0.2 (3)	C5—N3—C8—C7	56.9 (3)
C1—N3—C5—C6	141.1 (2)	C6—N4—C7—C8	56.9 (2)
C1—N3—C8—C7	−141.2 (2)	C7—N4—C6—C5	−57.0 (2)
C2—N1—C1—N2	2.9 (3)	C8—N3—C1—N1	−166.9 (2)
C2—N1—C1—N3	−175.2 (2)	C8—N3—C1—N2	14.8 (3)
C2—C3—C4—N2	1.6 (4)	C8—N3—C5—C6	−57.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O2^{i}	0.91	1.92	2.829 (3)	177
N4—H4*A*···O3^{i}	0.91	2.52	3.138 (3)	126
N4—H4*B*···O1	0.91	2.35	3.197 (3)	155
N4—H4*B*···O2	0.91	2.10	2.900 (3)	146
C3—H3···O1^{ii}	0.95	2.46	3.240 (3)	140
C4—H4···O2^{iii}	0.95	2.51	3.291 (3)	139

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