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1-Methylpiperazine-1,4-diium 4-nitrophthalate(2–) 4-nitrophthalic acid monohydrate

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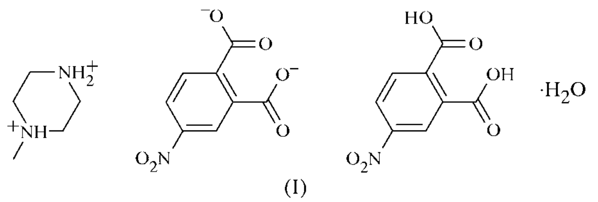
The title adduct, $C_5H_{14}N_2^{2+}\cdot C_8H_3NO_6^{2-}\cdot C_8H_5NO_6\cdot H_2O$, crystallizes in the monoclinic space group $P2_1$. All O atoms of the 4-nitrophthalate anions and neutral 4-nitrophthalic acid molecules are involved in hydrogen bonding with the piperazine dication and the water molecule of crystallization.

Comment

The design of new piperazine derivatives for application in medicinal chemistry and materials science has recently engrossed the author. Piperazine derivatives, which are efficient host–guest systems, have been studied extensively in the context of hydrogen-bond patterns and non-linear optical materials (Jin *et al.*, 2003; Loehlin *et al.*, 1994). The interest of the author in piperazine derivatives stems from their use in canalization of drug discovery and as host–guest systems. The author has recently reported the crystal structures of *N*-[4-(4-methylpiperazin-1-ylsulfonyl)phenyl]acetamide monohydrate (Guo, 2004*c*), 4-ammonio-1-methylpiperazin-1-ium oxalate dihydrate (Guo, 2004*b*), 2-(4-methylpiperazin-4-ium-1-ylcarbonyl)benzoate monohydrate (Guo, 2004*d*) and *N*-(4-methyl-1-piperazinyl)phthalimide (Guo, 2004*a*). The structure of the title adduct, (I), is reported here.



(I)

The hydrogen bonding of adduct (I) and the atom-numbering scheme are illustrated in Fig. 1. Interestingly, the crystal structure exhibits the unexpected result of co-crystallization of one neutral molecule of the anion in addition to an ionic pair.

The bond distances and angles in the cation, anion, neutral molecule and water molecule are normal, within experimental error. Selected geometric parameters are given in Table 1.

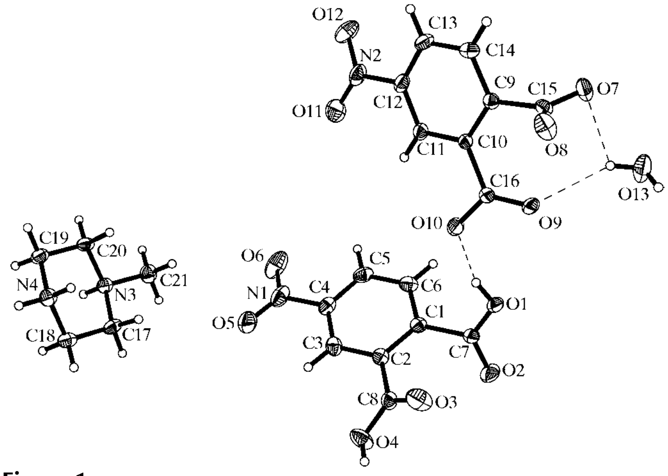


Figure 1
The structure of (I), with the atom-numbering scheme, showing 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and hydrogen bonds are indicated by dashed lines.

The crystal packing of (I) is illustrated in Fig. 2. The piperazine dication adopts a normal chair conformation, as reported previously (Kuppayee *et al.*, 1999), and participates in hydrogen bonds formed between the N3—H3 group and atom O7^{i} of a 4-nitrophthalate anion, the N4—H4*B* group and atom O9^{iii} of an anion, and the N4—H4*A* group and atom O13^{ii} of a water molecule (see Table 2 for symmetry codes). In addition, there also exist some weak C—H···acceptor interactions (Steiner, 1996), namely C19—H19*A*···O2^{viii}, C18—H18*A*···O8^{i}, C18—H18*B*···O12^{iv}, C21—H21*A*···O3^{ix}, C21—H21*B*···O1^{x} and C21—H21*C*···O8^{iii} (Table 2). The water molecules, which play an important role, link the 4-nitrophthalic acid moiety, the 4-nitrophthalate anion and the piperazine dication together *via* intermolecular O13—H13*A*···O9, O13—H13*A*···O7, O13—H13*B*···O1^{v} and

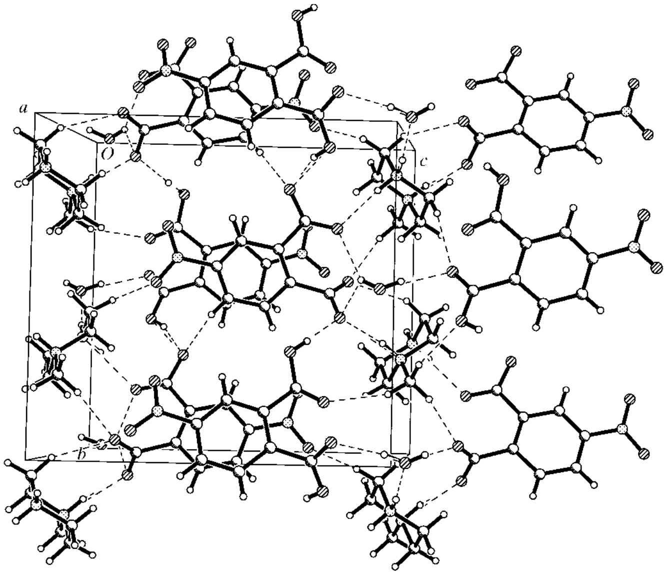


Figure 2
A packing diagram of (I), viewed down the *a* axis, showing the hydrogen-bonding interactions (dashed lines) for the piperazine dication and the water molecule.

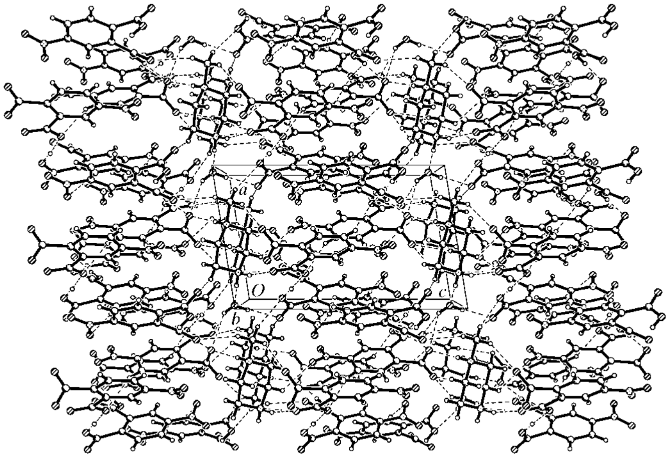


Figure 3
A packing diagram of (I), viewed down the *b* axis, showing the hydrogen-bonding interactions (dashed lines).

O13—H13*B*···O2^{v} hydrogen bonds. In addition, the 4-nitrophthalic acid moiety and the 4-nitrophthalate anion are linked together *via* O1—H1···O10 and O4—H4···O7^{iv} hydrogen bonds and weak C—H···acceptor interactions (C13—H13···O10^{vii} and C6—H6···O5^{vi}). In the crystal structure, these hydrogen bonds form rings of different sizes and build up a three-dimensional molecular network (Fig. 3 and Table 2).

This study was initiated as an exploration of the salt 1-methylpiperazinediium 4-nitrophthalate. However, the crystalline product obtained from a 1:1 molar ratio aqueous solution of 1-methylpiperazine and 4-nitrophthalic acid is the title adduct rather than 1-methylpiperazinediium 4-nitrophthalate. The title adduct thus appears to be more stable and more easily obtained in the crystalline form. This adduct crystallizes in the monoclinic space group $P2_1$. It is expected that (I) can be used in the canalization of optical material.

Experimental

Crystals of the title adduct were obtained from a 1:1 aqueous solution of 1-methylpiperazine and 4-nitrophthalic acid by slow concentration over a period of 2 d.

Crystal data

$C_5H_{14}N_2^{2+}\cdot C_8H_3NO_6^{2-}\cdot C_8H_5NO_6\cdot H_2O$
$M_r = 540.44$
Monoclinic, $P2_1$
$a = 7.882$ (2) Å
$b = 12.050$ (3) Å
$c = 12.602$ (4) Å
$\beta = 99.273$ (5)°
$V = 1181.3$ (6) Å^3
$Z = 2$
$D_x = 1.519$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 997 reflections
$\theta = 3.3$–25.6°
$\mu = 0.13$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.18 × 0.16 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.975$, $T_{max} = 0.990$
6800 measured reflections
2514 independent reflections
2127 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 26.4°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 15$
$l = -13 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.090$
$S = 1.05$
2514 reflections
346 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.3064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—O6	1.213 (5)	O3—C8	1.200 (4)
N1—O5	1.231 (5)	O4—C8	1.299 (4)
N2—O12	1.223 (4)	O7—C15	1.276 (4)
N2—O11	1.225 (4)	O8—C15	1.210 (4)
O1—C7	1.259 (4)	O9—C16	1.211 (3)
O2—C7	1.219 (4)	O10—C16	1.286 (4)
O6—N1—O5	124.1 (3)	O3—C8—O4	124.0 (3)
O12—N2—O11	124.2 (3)	O8—C15—O7	125.0 (3)
O2—C7—O1	122.7 (3)	O9—C16—O10	124.9 (3)
C7—C1—C2—C8	9.4 (4)	C15—C9—C10—C16	−1.8 (4)
C2—C1—C7—O2	59.7 (4)	C10—C9—C15—O8	−79.1 (4)
C2—C1—C7—O1	−122.7 (3)	C10—C9—C15—O7	104.7 (3)
C1—C2—C8—O3	33.1 (5)	C9—C10—C16—O9	−9.2 (4)
C1—C2—C8—O4	−149.2 (3)	C9—C10—C16—O10	171.8 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O7^{i}	0.91	1.87	2.766 (3)	170
N4—H4*A*···O13^{ii}	0.90	1.84	2.715 (4)	163
N4—H4*B*···O9^{iii}	0.90	2.00	2.877 (3)	163
O1—H1···O10	0.82	1.65	2.430 (3)	160
O4—H4···O7^{iv}	0.82	1.75	2.569 (3)	177
O13—H13*A*···O9	0.85	2.51	3.253 (4)	147
O13—H13*A*···O7	0.85	2.54	3.017 (4)	117
O13—H13*B*···O2^{v}	0.85	1.97	2.810 (4)	171
O13—H13*B*···O1^{v}	0.85	2.59	3.058 (4)	116
C6—H6···O5^{vi}	0.93	2.55	3.476 (5)	172
C11—H11···O10	0.93	2.35	2.677 (4)	100
C13—H13···O10^{vii}	0.93	2.55	3.436 (4)	159
C17—H17*B*···O12^{iv}	0.97	2.58	3.022 (4)	108
C18—H18*A*···O8^{i}	0.97	2.37	3.262 (4)	153
C18—H18*B*···O12^{iv}	0.97	2.46	3.121 (4)	125
C19—H19*A*···O2^{viii}	0.97	2.27	3.140 (4)	148
C21—H21*A*···O3^{ix}	0.96	2.33	3.198 (5)	150
C21—H21*B*···O1^{x}	0.96	2.57	3.499 (5)	164
C21—H21*C*···O8^{iii}	0.96	2.57	3.445 (4)	153

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

The value of the absolute structure parameter (Flack, 1983) of the title adduct is meaningless because Mo radiation was used and no atoms heavier than oxygen are present. Therefore, in the absence of anomalous dispersion effects, 1574 Friedel pairs were merged before the final refinement. The H atoms of the water molecule were found in difference Fourier maps. However, during refinement, their positions were fixed at O—H distances of 0.85 Å and their U_{iso}(H) values were set at $1.2U_{eq}$(O). The O—H distances of the carboxy group were fixed at 0.82 Å and their U_{iso}(H) values were set at $1.2U_{eq}$(O). H atoms attached to N and C atoms were treated as riding, with N—H distances in the range 0.90–0.91 Å and C—H distances in the range 0.93–0.97 Å. For H atoms attached to atom C21, the $U_{\rm iso}$(H) value was set at 1.5$U_{\rm eq}$(C21); otherwise, $U_{\rm iso}$(H) values were set at 1.2$U_{\rm eq}$(N,C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1248). Services for accessing these data are described at the back of the journal.

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