

Piperazine-1,4-dium–2,4-dinitrophenolate–water (1/2/2)

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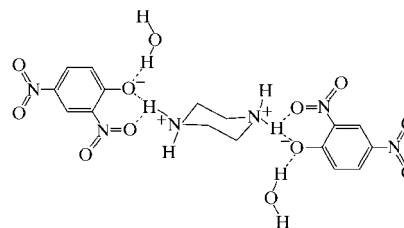
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In the title 1/2/2 adduct, $C_4H_{12}N_2^{2+} \cdot 2C_6H_3N_2O_5^- \cdot 2H_2O$, the dication lies on a crystallographic inversion centre and the asymmetric unit also has one anion and one water molecule in general positions. The 2,4-dinitrophenolate anions and the water molecules are linked by two $O-H \cdots O$ and two $C-H \cdots O$ hydrogen bonds to form molecular ribbons, which extend along the *b* direction. The piperazine dication acts as a donor for bifurcated $N-H \cdots O$ hydrogen bonds with the phenolate O atom and with the O atom of the *o*-nitro group. Six symmetry-related molecular ribbons are linked to a piperazine dication by $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds.

Comment

The crystal structures of the adducts of phenols or organic acids with diamines, such as piperazine, $C_4H_{10}N_2$, in various ratios have been investigated intensively (Coupar *et al.*, 1996*a,b*; Ferguson *et al.*, 1997, 1998; Charfi *et al.*, 1998; MacLean *et al.*, 1999; Burchell *et al.*, 2001). In these adducts, the two components are linked together by either $O-H \cdots N$ or $N-H \cdots O$ intermolecular hydrogen bonds, depending on the acidity of the phenols or organic acids. In the presence of weak acids, such as 4,4'-thiodiphenol (Coupar *et al.*, 1996*b*) or 1,1,1-tris(4-hydroxyphenyl)ethane (Ferguson *et al.*, 1997), piperazine acts solely as an acceptor of $O-H \cdots N$ hydrogen bonds, linking the two components into molecular chains. In contrast, with strong acids, such as phenol (Loehlin *et al.*, 1994), 4,4'-sulfonyldiphenol (Coupar *et al.*, 1996*a*), dihydrogenphosphate (Charfi *et al.*, 1998), 3,4-dihydro-3-butenedione (MacLean *et al.*, 1999) or 3,5-dinitrobenzoic acid (Burchell *et al.*, 2001), piperazine, which is a strongly basic amine, forms a dication and acts as an $N-H$ hydrogen-bond donor. In these cases, the strong acid transfers the H atom to a

piperazine molecule, making an ionic adduct. This observation prompted us to extend the study of hydrogen-bonding motifs to the crystal structures of adducts of piperazine. In this study, we have prepared and structurally characterized the title compound, (I), a dihydrate adduct of piperazine with 2,4-dinitrophenol (DNP), with the expectation of observing that an H atom has been transferred from DNP to the piperazine. DNP was selected since it has demonstrated the ability to transfer its H atom in its adducts with several amine bases, such as morpholine (Majerz *et al.*, 1996) and hexamethylenetetramine (Usman *et al.*, 2001).



(I)

The X-ray structural analysis of (I) shows unambiguously that DNP transfers an H atom from the hydroxy group to the unique N of the centrosymmetric piperazine moiety, to form a 2,4-dinitrophenolate (DNP^-) anion and a piperazine-1,4-dium dication.

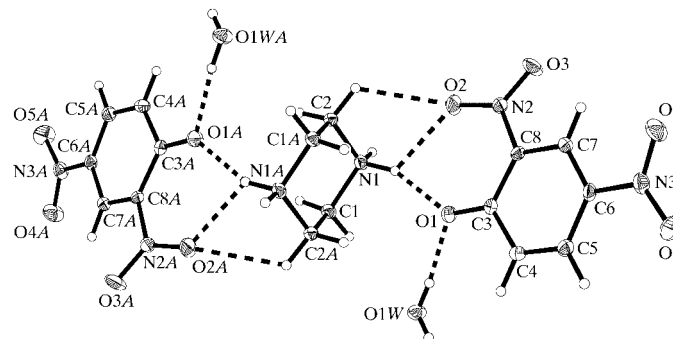


Figure 1

The structure of (I) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

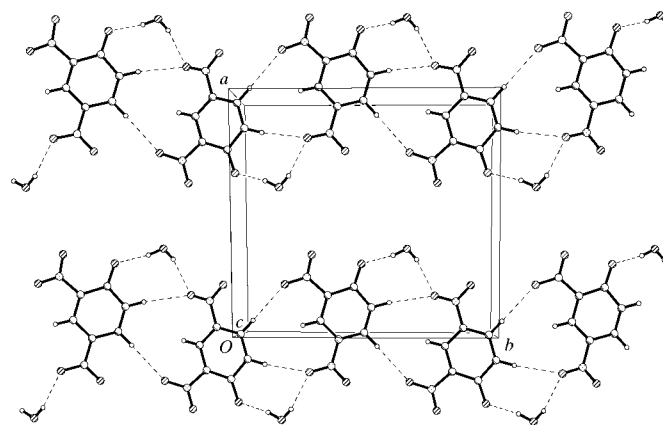


Figure 2

A packing diagram for (I) viewed down the *c* axis, showing only the molecular ribbons of 2,4-dinitrophenolate and water molecules.

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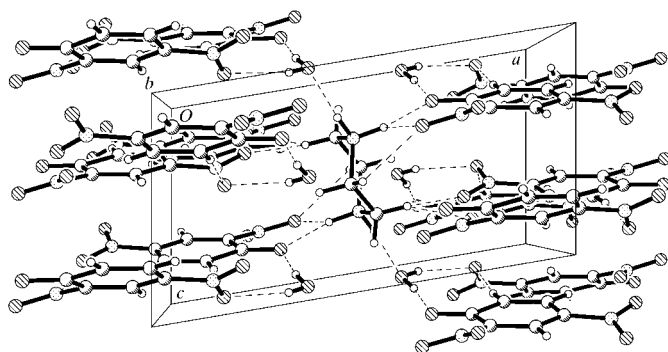


Figure 3
The linkage to the piperazine dication of the molecular 2,4-dinitrophenolate/water ribbons, viewed down the *b* axis.

The N1—C1 and N1—C2 bond distances [1.496 (2) and 1.494 (2) Å, respectively] of the piperazine dication are elongated compared with those in unprotonated piperazine [1.460 (3) and 1.462 (3) Å; Coupar *et al.*, 1996*b*]. The C—N and C—C bond distances of the piperazine dication are comparable with those reported for other piperazine dication adducts (Iwasaki & Mutai, 1984; Loehlin *et al.*, 1994; Coupar *et al.*, 1996*a*; MacLean *et al.*, 1999; Burchell *et al.*, 2001). Also similar is the chair conformation of the piperazine dication.

The H-atom transfer process also affects the delocalization of the π -electron in DNP[−], corresponding to an *o*-quinonic resonance structure, resulting in slight distortions in the N—O, C—N and C—O bond distances of the functional groups compared with the corresponding values in DNP (Iwasaki & Kawano, 1977). This is also shown by the distinct shortening of the C4—C5 and C6—C7 bonds and the lengthening of the C3—C4 and C3—C8 bonds (Table 1). In comparison, the bond lengths and angles in DNP[−] are in agreement with those in its adducts with morpholine and hexamethylenetetramine.

Within the asymmetric unit (Fig. 1), the piperazine dication and DNP[−] are linked by intermolecular N1—H1N \cdots O1 and N1—H1N \cdots O2 hydrogen bonds, with the piperazine dication acting as a hydrogen donor in this bifurcated system. These two components are also linked by an intermolecular C2—H2A \cdots O2 interaction. These intermolecular interactions form two closed-ring patterns, which are designated as $R_1^2(6)$ and $R_2^1(5)$ (Bernstein *et al.*, 1995).

The water molecule within the asymmetric unit of (I) acts as a hydrogen-bond donor *via* H1W to atom O1 of DNP[−], and this water molecule at (*x*, *y*, *z*) also acts as a hydrogen donor *via* H2W to atom O4 of the DNP[−] anion at $(2-x, y-\frac{1}{2}, \frac{1}{2}-z)$. These interactions involving the water molecule, along with the two linear C4—H4 \cdots O4($2-x, y-\frac{1}{2}, \frac{1}{2}-z$) and C5—H5 \cdots O3($2-x, y-\frac{1}{2}, \frac{1}{2}-z$) hydrogen bonds, interconnect the DNP[−] and water molecules into molecular ribbons, which extend along the *b* direction. The DNP[−]/water molecular ribbons (Fig. 2) contain two chains of rings, with the notation of these patterns being described as $C(8)[R_3^2(8)]$ and $C(7)[R_2^2(11)]$.

The packing of the structure is built from alternating layers of DNP[−]/water molecular ribbons and piperazine dications, interconnected by C1—H1B \cdots O3($1-x, y-\frac{1}{2}, \frac{1}{2}-z$), N1—H2N \cdots O1W($1-x, 1-y, -z$), C1—H1B \cdots O5($x-1, y, z$)

and C2—H2B \cdots O5($x-1, y, z$) hydrogen bonds along the *a* direction, in which six symmetry-related DNP[−]/water molecular ribbons are linked to each piperazine dication (Fig. 3).

The hydrogen-bonded N \cdots O distances in (I) are in the range 2.772 (2)–2.840 (2) Å and are comparable with those observed in other piperazine-1,4-dium adducts (Coupar *et al.*, 1996*a*; MacLean *et al.*, 1999; Burchell *et al.*, 2001). Full details of the hydrogen bonding are given in Table 2.

Experimental

The title adduct, (I), was prepared by thoroughly mixing equimolar amounts of piperazine (5 mmol) and 2,4-dinitrophenol. The mixture was dissolved in ethanol (40 ml) with the addition of distilled water (3 ml), and was warmed until a clear solution was obtained. The solution was then filtered and the filtrate was left to evaporate slowly in air. Yellow single crystals of (I) suitable for X-ray diffraction studies were obtained from the solution after a few days [m.p. 515 K (decomposition)].

Crystal data

$C_4H_{12}N_2^{2+} \cdot 2C_6H_3N_2O_5^- \cdot 2H_2O$	$D_x = 1.598 \text{ Mg m}^{-3}$
$M_r = 490.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4041 reflections
$a = 12.1140$ (6) Å	$\theta = 3.1\text{--}28.3^\circ$
$b = 12.9702$ (6) Å	$\mu = 0.14 \text{ mm}^{-1}$
$c = 6.5813$ (3) Å	$T = 183$ (2) K
$\beta = 99.646$ (1) $^\circ$	Needle, yellow
$V = 1019.44$ (8) Å ³	$0.30 \times 0.14 \times 0.14 \text{ mm}$
$Z = 2$	

Data collection

Siemens SMART CCD area-detector diffractometer	2453 independent reflections
ω scans	1725 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.065$
$T_{\text{min}} = 0.960, T_{\text{max}} = 0.981$	$\theta_{\text{max}} = 28.3^\circ$
5886 measured reflections	$h = -13 \rightarrow 16$
	$k = -14 \rightarrow 17$
	$l = -8 \rightarrow 8$

Table 1

Selected interatomic distances (Å).

O1—C3	1.271 (2)	N3—C6	1.438 (2)
O2—N2	1.235 (2)	C3—C4	1.444 (3)
O3—N2	1.2330 (19)	C3—C8	1.442 (2)
O4—N3	1.246 (2)	C4—C5	1.365 (3)
O5—N3	1.230 (2)	C6—C7	1.380 (2)
N2—C8	1.446 (2)		

Table 2

Hydrogen-bonding geometry (Å, $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1N \cdots O1	0.99 (2)	1.83 (2)	2.772 (2)	156 (2)
N1—H1N \cdots O2	0.99 (2)	2.22 (2)	2.840 (2)	119 (2)
N1—H2N \cdots O1W ⁱ	0.95 (2)	1.85 (3)	2.776 (2)	165 (2)
O1W—H1W \cdots O1	0.89 (3)	1.84 (3)	2.721 (2)	171 (2)
O1W—H2W \cdots O4 ⁱⁱ	0.78 (4)	2.14 (4)	2.890 (2)	162 (4)
C1—H1B \cdots O5 ⁱⁱⁱ	0.97 (2)	2.49 (2)	3.316 (2)	142 (1)
C1—H1B \cdots O3 ^{iv}	0.97 (2)	2.53 (2)	3.234 (2)	129 (1)
C2—H2A \cdots O2	0.99 (2)	2.48 (2)	3.072 (2)	118 (2)
C2—H2B \cdots O5 ⁱⁱⁱ	0.99 (2)	2.58 (2)	3.380 (2)	137 (2)
C4—H4 \cdots O4 ⁱⁱ	0.99 (2)	2.53 (2)	3.513 (2)	173 (2)
C5—H5 \cdots O3 ⁱⁱ	1.02 (2)	2.59 (2)	3.604 (2)	178 (2)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.120$
 $S = 0.92$
 2453 reflections
 199 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXTL*
 (Sheldrick, 1997)
 Extinction coefficient: 0.067 (6)

All H atoms were located in difference maps and were refined isotropically, with C—H = 0.94 (2)–1.02 (2) Å. 31 reflections listed as inconsistent equivalents were removed before the final refinement.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1130). Services for accessing these data are described at the back of the journal.

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