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A three-dimensional hydrogen-bonded framework in piperazine–3,4-dihydroxy-3-cyclobutene-1,2-dione–water (1/1/2)

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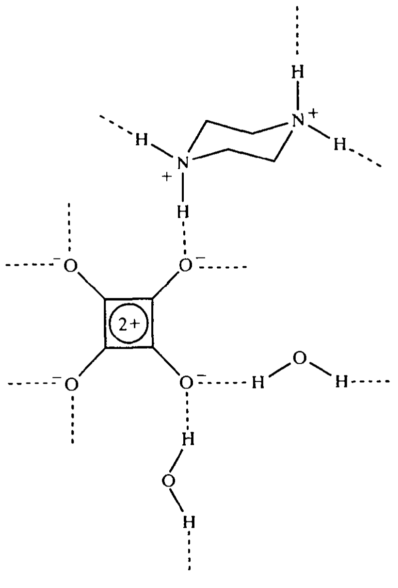
Abstract

The title compound, piperazine-1,4-diium 3,4-dihydroxy-3-cyclobutene-1,2-dionate(2−) dihydrate, is a hydrated salt, $C_4H_{12}N_2^{2+}\cdot C_4O_4^{2-}\cdot 2H_2O$. The water molecules and the centrosymmetric anions are linked by O—H···O hydrogen bonds into two-dimensional nets built from a single type of $R_8^6(24)$ ring. Adjacent nets are linked by the centrosymmetric cations, each of which forms four N—H···O hydrogen bonds, with four different anions as acceptors.

Comment

The dianion $(C_4O_4)^{2-}$ is readily formed from squaric acid (3,4-dihydroxy-3-butenedione, $C_4H_2O_4$) in the presence or organic bases such as amines and in such circumstances it can act as a powerful acceptor of hydrogen bonds, imparting a strong bias towards the formation of planar two-dimensional supramolecular structures (Karle *et al.*, 1996). Piperazine, $HN(CH_2CH_2)_2NH$, is a strongly basic amine which readily forms the $[H_2N(CH_2CH_2)_2NH_2]^{2+}$ dication, where all four N—H bonds, which lie in a common plane, are generally active in hydrogen-bond formation (Coupar *et al.*, 1996; Ferguson *et al.*, 1998). The combination of these two ions might therefore be reasonably expected to give rise to a planar supramolecular system.

Cocrystallization of piperazine and squaric acid from organic solvents such as light alcohols, acetone or tetrahydrofuran gave extremely rapid precipitation of very tiny crystals wholly unsuitable for single-crystal X-ray diffraction, presumably because of the rather low solubility of the ionic product in these solvents. Cocrystallization from water, however, provided excellent crystals of the dihydrate, $(C_4H_{12}N_4)^{2+}\cdot(C_4O_4)^{2-}\cdot 2H_2O$, (1), whose structure is reported here.



(1)

The molecular structure of the asymmetric unit of (1) is shown in Fig. 1. Compound (1) has a three-dimensional framework structure but, as in previously reported examples of three-dimensional organic salts (Glidewell *et al.*, 1999; Gregson *et al.*, 1999), it is possible to identify a substructure of lower dimensionality built from a subset of the molecular building blocks. In compound (1), it is possible to identify two-dimensional nets (Fig. 2) built from just the anions and the water molecules, and the overall structure of (1) is most conveniently described in terms of firstly these nets and secondly the linking of these nets by the cations (Fig. 3), so forming the three-dimensional framework. The two-dimensional net can itself be most simply analysed in terms of a one-dimensional chain motif (Fig. 2).

The $(C_4H_{12}N_2)^{2+}$ cation and the $(C_4O_4)^{2-}$ anion both lie across centres of inversion, and the asymmetric unit (Fig. 1) consists of one half of each of these ions, together with a water molecule lying in a general position. The anion was placed across the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and hence, with the asymmetric unit selected, the cation is centred at $(0,1,\frac{1}{2})$. The cation

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and anion act as donor and acceptor, respectively, of four hydrogen bonds. The water molecule acts as a double donor of hydrogen bonds, but not as an acceptor (Table 2). In the anion, O1 is the acceptor in an N—H···O hydrogen bond and O2 is the acceptor in an O—H···O hydrogen bond.

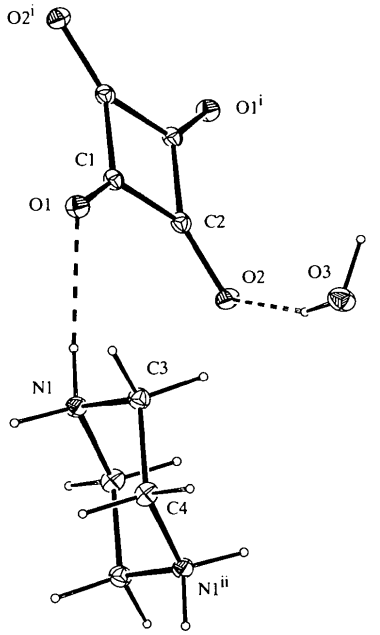

Fig. 1. The molecular aggregate in (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 2 - y, 1 - z$].

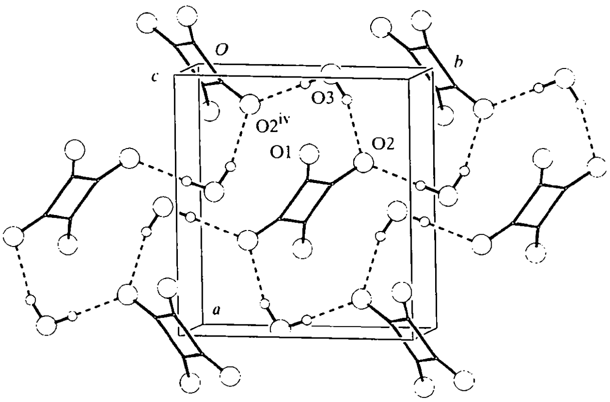

Fig. 2. Part of the crystal structure of (1), showing one of the $(10\bar{1})$ nets built from $R_8^6(24)$ rings [symmetry code: (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$].

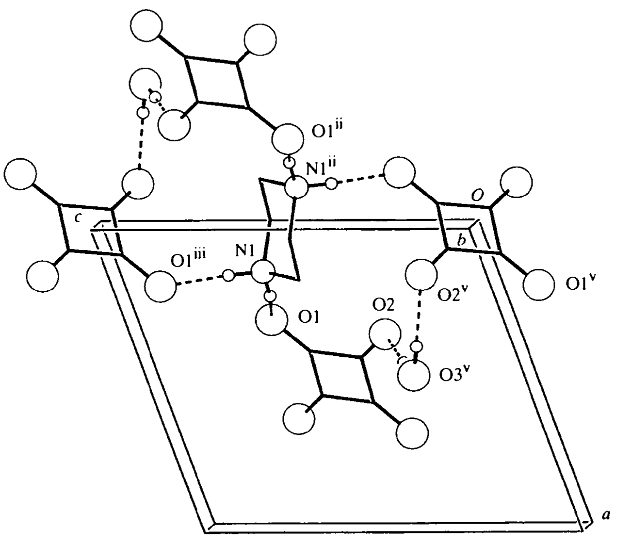

Fig. 3. Part of the crystal structure of (1), showing the linking of adjacent $(10\bar{1})$ nets by the cations [symmetry codes: (ii) $-x, 2 - y, 1 - z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$].

Within the asymmetric unit, the water acts as a hydrogen-bond donor *via* H31 to O2 in the anion, and the water molecule at (x, y, z) acts as a hydrogen-bond donor *via* H32 to O2 in the anion at ($\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$), and propagation of these two interactions produces a $C_2^2(4)$ chain running parallel to the [010] direction and generated by the 2_1 axis along $(\frac{1}{4},y,\frac{1}{4})$ (Fig. 2). The action upon these chains of the centres of inversion in the anions generates a continuous two-dimensional net parallel to $(10\bar{1})$ and built from a single type of centrosymmetric $R_8^6(24)$ ring. These rings are centred at $(\frac{1}{2},n,\frac{1}{2})$, $(1,n+\frac{1}{2},1)$ and so on, for $n = 0$ or integer (Fig. 2). The formation of one such two-dimensional net utilizes all the anions and water molecules within the unit cell, so that just one net is sufficient to describe the two-dimensional substructure.

The nets are linked together by means of the cations: each cation forms four N—H···O hydrogen bonds to four different anions, which lie in two adjacent nets. The axial N—H bond at one end of the centrosymmetric cation and the equatorial N—H bond at the other end bind to one net, and their symmetry-related analogues bind to the neighbouring net (Fig. 3). The anions centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and (0,1,0) lie in one $(10\bar{1})$ net (Fig. 2), while those centred at $(-\frac{1}{2},\frac{3}{2},\frac{1}{2})$ and (0,1,1) (Fig. 3) lie in the adjacent net. Within each net, neighbouring anions are linked by water molecules (Fig. 2), and the linking of the nets by the cation generates $R_4^4(17)$ rings (Fig. 3).

Two data sets were obtained for compound (1): one set was measured using Mo $K\alpha$ radiation at 100 K and the second was measured using synchrotron radiation at 150 K. Despite the somewhat higher temperature, the synchrotron data set was substantially more intense, as expected, with *ca* 20% more reflections in total and *ca* 40% more having $I > 2\sigma(I)$. The synchrotron data provide slightly greater precision but somewhat larger R indices.

The structure of the $(C_4O_4)^{2-}$ anion exhibits almost perfect D_{4h} ($4/mmm$) molecular symmetry, with bond lengths entirely typical of those recorded for this anion in the Cambridge Structural Database (Allen & Kennard, 1993). In the cation, the C—N distances are significantly larger than those found in the salt with the phenolate anion $HOC_6H_4SO_2C_6H_4O^-$ [1.477 (3) Å; Coupar *et al.*, 1996].

Examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Equimolar quantities of piperazine and squaric acid were dissolved separately in water. The solutions were mixed and the mixture set aside to crystallize, producing colourless crystals of (1). Analysis, found: C 41.6, H 6.9, N 12.0%; $C_8H_{16}N_2O_6$ requires: C 40.7, H 6.8, N 11.9%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Compound (1), Mo $K\alpha$ data

Crystal data

$C_4H_{12}N_2^{2+}\cdot C_4O_4^{2-}\cdot 2H_2O$
$M_r = 236.23$
Monoclinic
$P2_1/n$
$a = 8.3594\ (3)$ Å
$b = 6.9360\ (4)$ Å
$c = 9.5026\ (3)$ Å
$\beta = 109.462\ (2)^\circ$
$V = 519.49\ (4)$ Å^3
$Z = 2$
$D_x = 1.510$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1179 reflections
$\theta = 2.82–27.47^\circ$
$\mu = 0.129$ mm^{-1}
$T = 100.0\ (1)$ K
Block
0.25 × 0.17 × 0.13 mm
Colourless

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.968$, $T_{max} = 0.983$
4834 measured reflections
1179 independent reflections

955 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.47^\circ$
$h = -10 \rightarrow 10$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 11$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 1.088$
1179 reflections
82 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.1380P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.237$ e Å^{-3}
$\Delta\rho_{min} = -0.194$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.029 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1), synchrotron data

Crystal data

$C_4H_{12}N_2^{2+}\cdot C_4O_4^{2-}\cdot 2H_2O$
$M_r = 236.23$
Monoclinic
$P2_1/n$
$a = 8.3393\ (8)$ Å
$b = 6.9360\ (7)$ Å
$c = 9.5034\ (9)$ Å
$\beta = 109.294\ (2)^\circ$
$V = 518.82\ (9)$ Å^3
$Z = 2$
$D_x = 1.512$ Mg m^{-3}
D_m not measured

Synchrotron radiation
$\lambda = 0.68910$ Å
Cell parameters from 4549 reflections
$\theta = 3.60–29.47^\circ$
$\mu = 0.130$ mm^{-1}
$T = 150\ (2)$ K
Plate
0.15 × 0.10 × 0.08 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: none
4403 measured reflections
1438 independent reflections
1340 reflections with $I > 2\sigma(I)$

$R_{int} = 0.036$
$\theta_{max} = 29.51^\circ$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -13 \rightarrow 12$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.115$
$S = 1.069$
1438 reflections
81 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.1456P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.500$ e Å^{-3}
$\Delta\rho_{min} = -0.270$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

	Mo $K\alpha$ data	Synchrotron data
O1—C1	1.2642 (16)	1.2594 (11)
O2—C2	1.2552 (17)	1.2502 (11)
C1—C2	1.4670 (18)	1.4660 (13)
C1—C2^{i}	1.4639 (19)	1.4653 (12)
N1—C3	1.4964 (18)	1.4930 (13)
N1—C4^{ii}	1.4951 (18)	1.4896 (13)
C3—C4	1.5133 (19)	1.5114 (14)
O1—C1—C2	134.16 (13)	134.15 (9)
O1—C1—C2^{i}	135.39 (13)	135.38 (9)
O2—C2—C1	134.96 (12)	135.06 (9)
O2—C2—C1^{i}	135.48 (12)	135.41 (9)
C1—C2—C1^{i}	89.55 (11)	89.53 (7)
C2—C1—C2^{i}	90.45 (11)	90.47 (7)
N1—C3—C4	110.17 (12)	110.00 (8)
N1—C4—C3^{ii}	110.32 (11)	110.46 (8)
C3—N1—C4^{ii}	111.12 (10)	111.13 (7)
O1—C1—C2—O2	−1.5 (3)	−1.0 (2)
O1—C1—C2—C1^{i}	179.4 (2)	179.84 (14)
O2—C2—C1—C2^{i}	179.1 (2)	179.19 (14)
N1—C3—C4—N1^{ii}	56.96 (15)	56.96 (11)
C4—C3—N1—C4^{ii}	−57.43 (15)	−57.36 (11)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, 2-y, 1-z$.

Table 2. *Hydrogen bonding parameters (Å, °)*

D—H$\cdots$*A*	*D*$\cdots$*A*	H$\cdots$*A*	*D*—H$\cdots$*A*
Mo *Kα* data			
N1—H1*A*$\cdots$O1	2.8243 (16)	1.98	152
N1—H1*B*$\cdots$O1^{iii}	2.7493 (14)	1.83	176
O3—H31—O2	2.8268 (15)	1.95 (2)	164 (2)
O3—H32—O2^{iv}	2.7669 (15)	1.87 (2)	178 (2)
Synchrotron data			
N1—H1*A*$\cdots$O1	2.8255 (12)	1.98	152
N1—H1*B*$\cdots$O1^{iii}	2.7450 (11)	1.82	176
O3—H31—O2	2.8233 (12)	1.98 (2)	163 (2)
O3—H32—O2^{iv}	2.7605 (12)	1.89 (2)	178 (2)

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

Compound (1) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. H atoms bonded to C and N were treated as riding, with C—H = 0.99 and N—H = 0.92 Å. The two water H atoms were located from a difference map and then allowed to refine, subject to the restraints that they should both have the same O—H distance refined as a free variable, and a common isotropic displacement parameter, also refined as a free variable.

Data collection: *KappaCCD Server Software* (Nonius, 1997) for the Mo *Kα* data; *SMART* (Siemens, 1996) for the synchrotron data. Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997) for the Mo *Kα* data; *SMART* for the synchrotron data. Data reduction: *DENZO-SMN* for the Mo *Kα* data; *SAINT* (Siemens, 1996) for the synchrotron data. For both compounds, program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

One data set was collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. The other data set was collected at the CLRC synchrotron radiation facility, Daresbury. We acknowledge the provision of time on DARTS, the UK national synchrotron radiation service at the CLRC Daresbury Laboratory, through funding by the EPSRC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1317). Services for accessing these data are described at the back of the journal.

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(+)-*trans*-Pinononic acid: hydrogen-bonding patterns in a non-racemic δ-keto acid

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Abstract

The title keto acid, (+)-*trans*-3-acetyl-2,2-dimethylcyclobutanecarboxylic acid, $C_9H_{14}O_3$, derived from (−)-verbenone, aggregates in the solid as helical acid-to-ketone hydrogen-bonding chains extending in the *b*-cell direction [O$\cdots$O = 2.711 (3) Å]. Each of the carboxyl-O atoms has a close C—H contact to a separate neighboring molecule. Comparisons are drawn with the corresponding (−)-*cis*-epimer, as well as with the homologous (+)- and (±)-*cis*-pinonic acids.

Comment

Carboxylic acids and ketones are similar in basicity and sufficiently competitive as hydrogen-bond acceptors that keto acids display several hydrogen-bonding modes beyond those characteristic of functionally unelaborated acids. Our continuing interest in the crystal structures of keto carboxylic acids lies in mapping the molecular characteristics that control their five known hydrogen-bonding modes. The commonest of these is