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Bis(guanidinium) pyrazine-2,3-dicarboxylate trihydrate

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The title compound, $2CH_6N_3^+ \cdot C_6H_2N_2O_4^{2-} \cdot 3H_2O$, forms a three-dimensional hydrogen-bonded framework structure involving all six protons of the guanidinium cation as donors to the carboxylate O and hetero N atoms of the anions, as well as to the water molecules of solvation. The anions and one of the water molecules lie on crystallographic twofold rotational axes.

Comment

Guanidine (GU) is a strong base that is readily protonated by most organic acids with the resulting guanidinium species being particularly useful for molecular assembly purposes, forming hydrogen-bonding associations through its six donor protons. This is especially so with the compounds of guanidine with sulfonic and phosphonic acids where common two-dimensional cyclic $R_2^2(8)$ primary hydrogen-bonding associations may be extended into three-dimensional structures through the third acceptor O atom of the anion (Russell *et al.*, 1994*a*,*b*; Russell & Ward, 1996). This cyclic motif [the 'bidentate motif' (Haynes *et al.*, 2004)] has a *ca* 26% incidence among guanidinium sulfonates. With carboxylic acids, similar primary cyclic two-dimensional interactions might be expected but not the three-dimensional extension such as found with the sulfonates. However, unlike the sulfonates, crystal structures of the guanidinium carboxylates are not common, *e.g.* the 1:1 compounds with oxalic acid (Adams, 1978; Andrews *et al.*, 1979), acetylenedicarboxylic acid (Leban & Rupnik, 1992), tartaric acid (Zyss *et al.*, 1993) and 3,5-dinitrosalicylic acid (Smith *et al.*, 2001). In only one of these structures (with 3,5-dinitrosalicylic acid) is a cyclic hydrogen-bonding interaction found. The aromatic carboxylic acid used in the present work, pyrazine-2,3-dicarboxylic acid (PDCA), has been used successfully by our group for cocrystal formation and the structures of its compounds with the aromatic Lewis bases 3-hydroxypyridine (Lynch *et al.*, 1994), creatinine (Smith & White, 2001) and the isomeric monoaminobenzoic acids (Lynch *et al.*, 1994; Smith *et al.*, 1995) have been determined. The structure of (I), from the 1:1 stoichiometric reaction of PDCA with guanidine carbonate, is reported here.
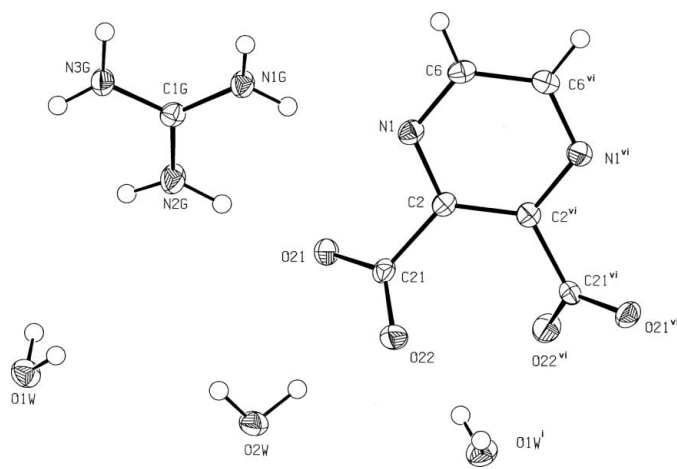

(I)
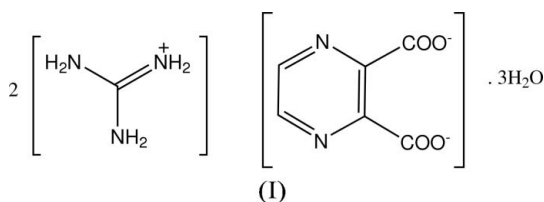
Figure 1
Molecular configuration and atom-naming scheme for the GU cation, the PDCA anion and the water molecules of solvation in (I). The symmetry code for the portion of the anion generated by twofold axis of rotation (vi) is $(-x + 2, y, -z + \frac{1}{2})$. For the other symmetry code, see Table 1. Displacement ellipsoids are drawn at the 50% probability level.
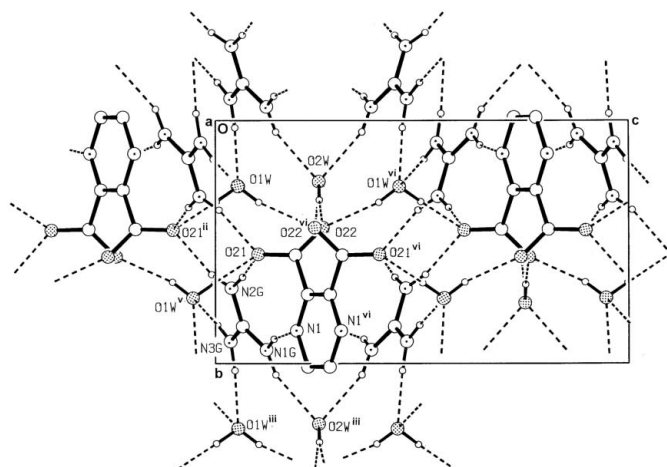

Figure 2
A view of the packing in the unit cell viewed down the a cell direction showing hydrogen-bonding associations as dashed lines. For symmetry codes, see Fig. 1 and Table 1.

In (I), the PDCA^{2-} dianions lie on crystallographic twofold rotational axes which relate the hetero N atoms (N1, N1^{vi}) and the two *ortho*-related carboxylate substituent groups [symmetry code: (vi) $-x + 2, y, -z + \frac{1}{2}$] (Fig. 1). The carboxylate torsion angle N1—C2—C21—O21 is 45.86 (16)°. All six GU protons form hydrogen-bonding interactions with guanidine carboxylate-O and hetero-N acceptors as well as with the water molecules of hydration, one of which (O2W) also lies on the twofold axis (Table 1). However, there is no occurrence of any cyclic $R_2^2(8)$ guanidinium–carboxylato interactions such as is found in anhydrous guanidinium 3,5-dinitrosalicylate (Smith *et al.*, 2001) but there is a cyclic centrosymmetric $R_2^4(8)$ cation–anion association through both N2G proton donors and O21 acceptors (Fig. 2). The water molecules also act as donors to carboxylate O atoms, giving a three-dimensional framework structure.

Experimental

The title compound was synthesized by heating together 1 mmol quantities of pyrazine-2,3-dicarboxylic acid (PDCA) and guanidine carbonate (GU$_2$CO$_3$) in 50 ml of 50% isopropyl alcohol–water under reflux for 10 min. After concentration to *ca* 30 ml, partial room-temperature evaporation of the hot-filtered solution gave colourless crystal blocks (m.p. 565 K).

Crystal data

2CH$_6$N$_3^+$·C$_6$H$_2$N$_2$O$_4^{2-}$·3H$_2$O	$Z = 2$
$M_r = 340.32$	$D_x = 1.458$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation
$a = 7.7141 (8)$ Å	$\mu = 0.13$ mm^{-1}
$b = 7.7252 (8)$ Å	$T = 130 (2)$ K
$c = 13.0299 (13)$ Å	Block, colourless
$\beta = 93.403 (2)°$	$0.35 \times 0.30 \times 0.25$ mm
$V = 775.12 (14)$ Å^3	

Data collection

Bruker CCD area-detector diffractometer	1360 independent reflections
	1202 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.039$
Absorption correction: none	$\theta_{max} = 25.0°$
3904 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.0086P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
1360 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
141 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H11$W\cdots$O22^i	0.83 (2)	2.00 (2)	2.8160 (15)	167 (2)
O1W—H12$W\cdots$O21^{ii}	0.94 (2)	1.83 (2)	2.7700 (14)	178 (2)
O2W—H21$W\cdots$O22^i	0.930 (19)	1.865 (18)	2.7845 (12)	170 (2)
N1G—H11$G\cdots$O2W^{iii}	0.871 (16)	2.100 (16)	2.8836 (17)	149.3 (14)
N1G—H11$G\cdots$O2W^{iv}	0.871 (16)	2.100 (16)	2.8836 (17)	149.3 (14)
N1G—H12$G\cdots$N1	0.872 (15)	2.124 (15)	2.9743 (17)	164.6 (13)
N2G—H21$G\cdots$O21	0.928 (16)	2.009 (16)	2.9310 (17)	172.3 (16)
N2G—H22$G\cdots$O21^{ii}	0.890 (17)	1.986 (17)	2.8458 (16)	162.0 (14)
N3G—H31$G\cdots$O1W^{iii}	0.947 (15)	1.966 (15)	2.9021 (17)	169.6 (13)
N3G—H32$G\cdots$O1W^v	0.857 (15)	2.112 (16)	2.9434 (16)	163.3 (14)

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

H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. The single ring H atom was included in the refinement in a calculated position (C—H = 0.95 Å) using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C). Friedel pairs were merged for the data used in the refinement.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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