Pyridazine-3,6-dicarboxylic acid monohydrate

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The title compound, $C_4H_4N_2O_4 \cdot H_2O$, is a triclinic polymorphic form of pyridazine-3,6-dicarboxylic acid monohydrate. The dihedral angles between the planes of the carboxylic acid groups and the planar pyrazine ring are 2.0 (2) and 5.6 (2)°. The acid and water molecules form almost planar sheets connected by hydrogen bonds, with O···O distances ranging from 2.5143 (14) to 2.7330 (16) Å and an O···N distance of 2.8234 (18) Å. The shortest distance between two adjacent sheets is 3.2 (1) Å, indicating van der Waals-type interactions.

Comment

The structure of pyridazine-3,6-dicarboxylic acid monohydrate has been reported to be monoclinic (Sueur *et al.*, 1987), with the planes of the carboxylic acid groups forming dihedral angles of 10.7° with the planar pyridazine ring. The other feature of this structure was a three-dimensional network of hydrogen bonds linking the carboxyl groups and solvation water molecules. While attempting to obtain crystals of a calcium(II) complex with the pyridazine-3,6-dicarboxylate ligand, crystals of a new triclinic form of this acid, (I), have been found.

(I)
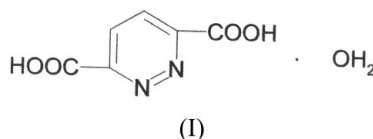
The molecules form sheets. The pyridazine ring is planar, with an r.m.s. deviation from the mean plane of 0.003 (1) Å. The dihedral angles between the plane of the pyridazine ring and the planes of of the carboxylic acid groups are 2.0 (2) (O1/C7/O2) and 5.6 (2)° (O3/C6/O4). The solvent water O atom (O10) is displaced by 0.366 (1) Å from the mean plane of the acid molecule. The observed bond distances and bond angles in the acid molecule agree well with those reported for the monoclinic phase. Fig. 1 shows the molecules of (I) with the atom-labelling scheme. Molecules related by inversion centres form dimeric units using a pair of hydrogen bonds between the carboxylic acid groups (O1—H1···O2). The solvent water molecules act as donors and acceptors in hydrogen bonds with the carboxylic acid O atoms belonging to two adjacent centrosymmetric dimers, thus forming molecular chains. In addition, each solvent water molecule is a donor in a hydrogen bond to a hetero-ring N atom in an adjacent chain. Fig. 2 shows a fragment of a sheet with the hydrogen bonds indicated by dashed lines. Contacts of the van der Waals type operate between adjacent sheets, as the shortest distance between two atoms is 3.2 (1) Å.

Experimental

A hot solution containing calcium(II) nitrate tetrahydrate (1 mmol) in water (50 ml) and another containing pyridazine-3,6-dicarboxylic acid monohydrate (1.2 mmol) in water (50 ml) were mixed with stirring. The resulting white precipitate and the mother liquid above it were left aside at room temperature. After a month, while fortuitously examining the dry product, well formed rectangular colourless single crystals of (I) were found in the mass of polycrystalline material.

Crystal data

$C_6H_4N_2O_4 \cdot H_2O$	$Z = 2$
$M_r = 186.13$	$D_x = 1.655$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.9630$ (14) Å	Cell parameters from 25
$b = 7.2888$ (15) Å	reflections
$c = 8.0319$ (16) Å	$\theta = 6$–15°
$\alpha = 80.30$ (3)°	$\mu = 0.15$ mm^{-1}
$\beta = 77.48$ (3)°	$T = 293$ (2) K
$\gamma = 70.66$ (3)°	Rectangular block, colourless
$V = 373.41$ (15) Å^3	$0.20 \times 0.16 \times 0.10$ mm

Data collection

Kuma KM-4 four-circle diffractometer	$\theta_{max} = 30.1°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction: none	$k = -9 \rightarrow 10$
1854 measured reflections	$l = -10 \rightarrow 11$
1725 independent reflections	3 standard reflections
1533 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{int} = 0.021$	intensity decay: 0.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1105P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$+ 0.0069P]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1725 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
142 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
All H-atom parameters refined	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
O10—H11$\cdots$O4	0.80 (2)	1.95 (2)	2.7330 (16)	165 (2)
O3—H3$\cdots$O10^i	0.82 (3)	1.70 (3)	2.5143 (14)	177 (3)
O10—H12$\cdots$N1^{ii}	0.86 (2)	1.98 (2)	2.8234 (18)	166 (2)
O1—H1$\cdots$O2^{iii}	0.94 (4)	1.71 (4)	2.6363 (13)	170 (3)

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

All H atoms were refined independently with isotropic displacement parameters. Only 86% of the data available to 25° in θ were collected because the intensities of reflections observed in the θ range close to 25° were very low and the data collection process was interrupted by the data collection software. Therefore, using these limited data for the refinement may reduce the precision of the results.
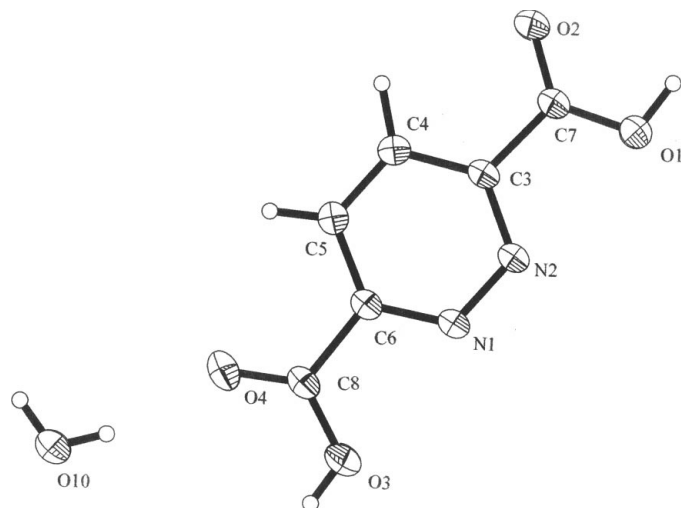

Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids of the non-H atoms are drawn at the 50% probability level.
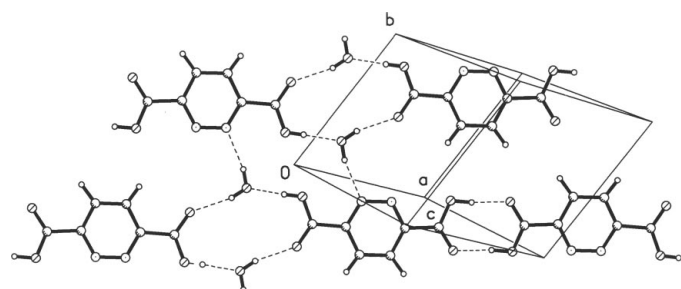

Figure 2
A fragment of a molecular sheet in the structure of (I). Hydrogen bonds are shown as dashed lines.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1992); software used to prepare material for publication: *SHELXL*97.

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