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## Key indicators

Single-crystal X-ray study  
 $T = 120$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.058  
 $wR$  factor = 0.186  
Data-to-parameter ratio = 13.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Piperazinium bis(6-carboxypyridine-2-  
carboxylate) trihydrate

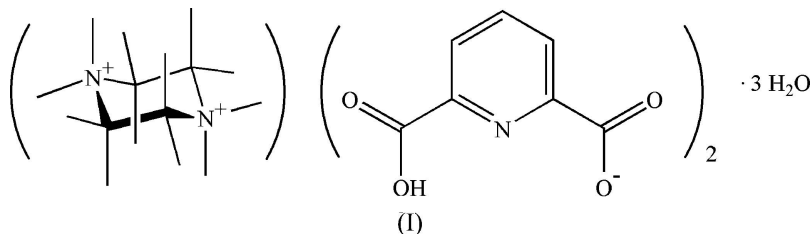
The title compound,  $\text{C}_{18}\text{H}_{26}\text{N}_4\text{O}_{11}$ , is a proton-transfer compound obtained from pyridine-2,6-dicarboxylic acid and piperazine. The asymmetric unit contains one half-cation, one anion and 1.5 water molecules. There is a centre of inversion at the centre of the cation ring and one water molecule lies on a twofold rotation axis. In the crystal structure, intermolecular  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds play an important role in the construction of the three-dimensional framework.

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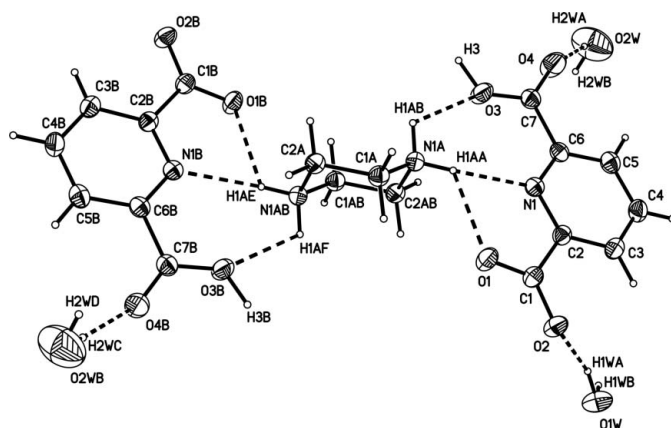
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## Comment

The hydrogen bond is one of the most effective and forces by which self-association and self-organization can be achieved to form discrete assemblies and extended structures both in the solid state and in solution. Several examples are known in which aromatic carboxylic acids associate through hydrogen-bonding interactions with 2,6-pyridinediamine (Smith *et al.*, 1999; 2000), creatinine (Smith & White, 2001), quinolin-8-ol (Smith, Wermuth & White, 2001) and 8-aminiquinoline (Smith, Wermuth, Bott *et al.*, 2001). Most of these adducts involve proton transfer from the carboxylic acid group to the adjacent heterocyclic N atom. In connection with such proton-transfer systems, we have previously reported some self-associated proton-transfer compounds, using pyridine-2,6-dicarboxylic acid (pydcH<sub>2</sub>), 4-hydroxy-pyridine-2,6-dicarboxylic acid (hypydcH<sub>2</sub>) and 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH<sub>2</sub>) as proton donors, and 2,6-pyridinediamine (pyda), creatinine (creat), 1,10-phenanthroline (phen) and guanidine (G) as proton acceptors, which formed the proton-transfer compounds (creatH)-(pydcH) (Moghimi, Sharif & Aghabozorg, 2004), (creatH)-(phendcH) (Soleimannejad *et al.*, 2005), (pydaH)-(pydcH) (Aghabozorg *et al.*, 2005), (pydaH<sub>2</sub>)(phendc) (Moghimi *et al.*, 2003), (phenH)<sub>2</sub>(pydc) (Moghimi, Sheshmani *et al.*, 2005), (GH)<sub>2</sub>(pydc) (Moghimi, Sheshmani *et al.*, 2004) and (GH)(hypydcH)·H<sub>2</sub>O (Moghimi, Aghabozorg *et al.*, 2005).



In the title compound, (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The



**Figure 1**

The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (B)  $\frac{1}{2} - x, -\frac{1}{2} - y, 2 - z$ ].

asymmetric unit contains one half-cation, one anion and 1.5 water molecules. There is a centre of inversion at the centre of the cation ring and one water molecule lies on a twofold rotation axis.

The piperazine ring is not planar, having a total puckering amplitude  $Q_T$  of 1.431 (3) Å, and a chair conformation [ $\varphi = -49.57$  (5)° and  $\theta = 0.02$  (3)°] (Cremer & Pople, 1975). The pyridine ring is, of course, planar.

An important feature of the structure is the presence of the anionic, (pydcH)<sup>-</sup>, and the cationic, (pipzH<sub>2</sub>)<sup>2+</sup> fragments. In the crystal structure, two monoanionic units are joined together by hydrogen bonding, forming a supramolecular structure (Table 1 and Fig. 2). The protonated position in the cation is the N atom of the piperazine ring. The intermolecular forces, which exist between anions and cations in the proton-transfer compound, consist of hydrogen bonding and ion-pairing.

Intermolecular O—H...O, N—H...O and N—H...N hydrogen bonds (Table 1) seem to be effective in the stabilization of the crystal structure. Hydrogen bonds play an important role in the construction of the three-dimensional framework. It is of interest to note that the crystal-packing diagram indicates a layered structure. The space between two layers of (pydcH)<sup>-</sup> fragments is filled with a layer of (pipzH<sub>2</sub>)<sup>2+</sup> cations.

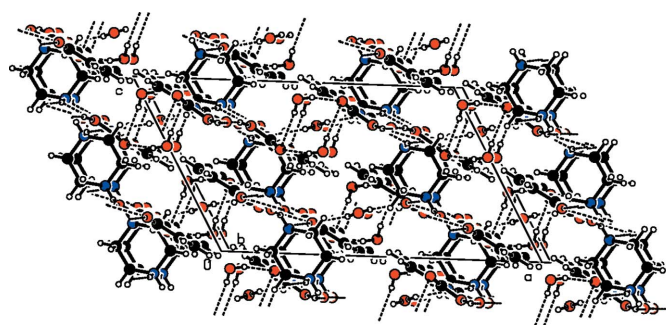
### Experimental

To an aqueous solution of pyridine-2,6-dicarboxylic acid (835 mg, 5 mmol) in tetrahydrofuran (THF, 80 ml) was added a solution of piperazine (430 mg, 5 mmol) in THF (10 ml). Colourless crystals of (I) were obtained by slow evaporation of the solvent at room temperature after four weeks (yield 95%, m.p. 546 K).

#### Crystal data

C<sub>4</sub>H<sub>12</sub>N<sub>2</sub><sup>2+</sup>·2C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub><sup>-</sup>·3H<sub>2</sub>O  
 $M_r = 474.43$   
 Monoclinic,  $C2/c$   
 $a = 16.966$  (3) Å  
 $b = 13.406$  (2) Å  
 $c = 10.3516$  (17) Å  
 $\beta = 118.795$  (3)°  
 $V = 2063.3$  (6) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.527$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 Cube, colourless  
 $0.50 \times 0.50 \times 0.50$  mm



**Figure 2**

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

#### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  
 $T_{\min} = 0.939, T_{\max} = 0.939$

9040 measured reflections  
 2034 independent reflections  
 1656 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 26.0^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.058$   
 $wR(F^2) = 0.187$   
 $S = 0.99$   
 2034 reflections  
 150 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1254P)^2 + 3.9531P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.76$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

| D—H...A                      | D—H  | H...A | D...A     | D—H...A |
|------------------------------|------|-------|-----------|---------|
| O3—H3...O1 <sup>ii</sup>     | 0.98 | 1.52  | 2.483 (3) | 167     |
| N1A—H1AA...N1                | 0.92 | 2.22  | 3.012 (3) | 144     |
| N1A—H1AA...O1                | 0.92 | 2.30  | 2.932 (2) | 125     |
| N1A—H1AB...O2 <sup>ii</sup>  | 0.92 | 1.98  | 2.859 (2) | 159     |
| O1W—H1WA...O2                | 0.85 | 2.01  | 2.789 (2) | 152     |
| O2W—H2WA...O4                | 0.85 | 1.90  | 2.728 (5) | 166     |
| O2W—H2WB...O4 <sup>iii</sup> | 0.85 | 2.34  | 3.180 (5) | 172     |

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

Oxygen-bound H atoms were located in difference syntheses and refined as riding atoms, with O—H = 0.98 Å (for OH) and O—H = 0.85 Å (for OH<sub>2</sub>), and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The remaining H atoms were positioned geometrically, with N—H = 0.92 Å (for NH<sub>2</sub>) and C—H = 0.95 and 0.99 Å for aromatic and methylene H atoms, respectively, and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1998); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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