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Key indicators

Single-crystal X-ray study
 $T = 297\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
Disorder in main residue
 R factor = 0.058
 wR factor = 0.183
Data-to-parameter ratio = 13.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Ethylenediaminium pyridine-2,5-dicarboxylate
dihydrate

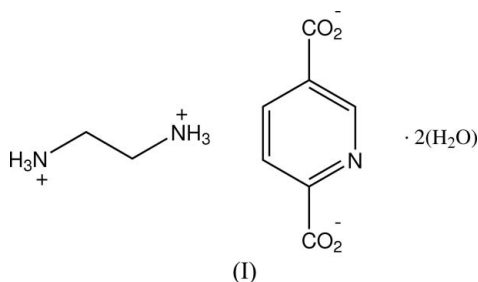
The title compound, $\text{C}_2\text{H}_{10}\text{N}_2^{2+} \cdot \text{C}_7\text{H}_3\text{NO}_4^{2-} \cdot 2\text{H}_2\text{O}$, forms a three-dimensional hydrogen-bonded framework structure in which both of the amine groups of ethylenediamine are protonated and participate in a total of six hydrogen-bonding interactions with carboxylate O-atom acceptors of the anions as well as the water molecules. The cations lie on crystallographic inversion centres and adopt extended conformations, while the anions have twofold rotational symmetry. This results in the pyridine N atom and its *ortho*-related CH group being disordered over two 50% occupancy sites.

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Comment

Ethylenediamine (1,2-ethanediamine, EN) has relatively close dissociation constants ($\text{p}K_{a1} = 7.3$ and $\text{p}K_{a2} = 10.1$), and in reaction with organic acids most commonly forms dication. Therefore with monoprotic acids, 1:2 salts are usual, *e.g.* with the aromatic acids 4-chlorobenzoic acid (Xia *et al.*, 2003), 4-nitrobenzoic acid (Lynch & Healy, 2003), 4-nitroanthranilic acid (Smith *et al.*, 2002), 5-nitrosalicylic acid (Smith *et al.*, 2005), 3,5-dinitrobenzoic acid (Nethaji *et al.*, 1992; Lynch *et al.*, 1994; Jones *et al.*, 2005) and 5-sulfosalicylic acid (Gao *et al.*, 2004). Even with diprotic acids, these 1:2 salts are commonly found, forming hydrogencarboxylates, *e.g.* with oxalic acid (Barnes *et al.*, 1998), malonic acid (Barnes & Weakley, 2000) and succinic acid (Schreuer & Muench, 1994). The six aminium protons on the EN^{2+} cations in these compounds may be involved in six or more intermolecular hydrogen-bonding interactions with suitable acceptor atoms, thus giving, in most cases, hydrogen-bonded framework structures which often incorporate water molecules of solvation (the 5-nitrosalicylate, the hydrogen malonate and the hydrogen oxalate are all monohydrates, the 4-nitrobenzoate and 4-nitroanthranilate are dihydrates, while the 5-sulfosalicylate is a tetrahydrate). However, the 1:1 stoichiometric reaction of ethylenediamine with diprotic pyridine-2,5-dicarboxylic acid (PYCA) gave a 1:1 dihydrate salt $\text{EN}^{2+} \cdot \text{PYCA}^{2-} \cdot 2\text{H}_2\text{O}$, (I), the structure of which is reported here.



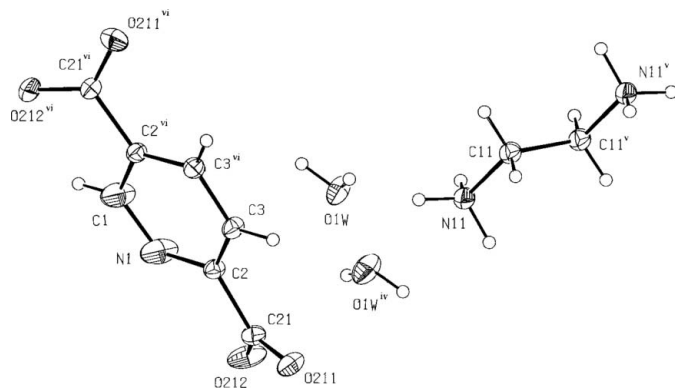


Figure 1

Molecular configuration and atom labelling scheme for the EN^{2+} cation, PYCA^{2-} anion and the water molecule in (I). The symmetry code for the inversion-related portion of the cation (v) is $(-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1)$, while the anion has twofold rotational symmetry [symmetry code: (vi) $-x + 2, y, -z + \frac{3}{2}$]. The inversion-related water molecule O1W^{v} (see Table 1 for symmetry code) is also shown. Displacement ellipsoids are drawn at the 30% probability level.

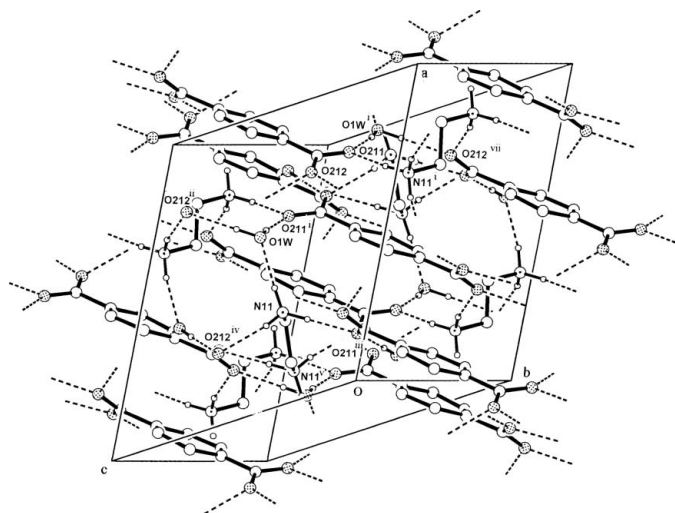


Figure 2

Perspective view of the packing in the unit cell, showing hydrogen-bonding associations as dashed lines. Symmetry code (vii) for O212^{vii} is $(-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$. Symmetry code (i) as in Fig. 1; the other symmetry codes are listed in Table 1.

Compound (I) comprises an EN^{2+} cation which lies across a crystallographic inversion centre [symmetry code: (v) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$], a PYCA^{2-} anion which lies across a twofold rotation axis [symmetry code: (vi) $-x + 2, y, -z + \frac{3}{2}$] and two water molecules (Fig. 1). The EN^{2+} cations adopt an extended conformation, with torsion angle $\text{N11}-\text{C11}-\text{C11}^{\text{v}}-\text{N11}^{\text{v}} = 180^\circ$. The occurrence of centrosymmetric EN^{2+} cations in the structures of EN salts is quite common, e.g. in ethylenediaminium terephthalate (Moritani & Kashino, 1991), which is structurally analogous to (I). The carboxylate groups in the PYCA^{2-} anions are related by twofold rotation symmetry, which means that the pyridine N (N1) and the *ortho*-related $\text{C1}^{\text{vi}}/\text{H1}^{\text{vi}}$ group are disordered over two 50% occupancy sites. The carboxylate groups of the anion are rotated slightly out of the plane of the benzene ring [$\text{C3}-\text{C2}-\text{C21}-\text{O212} =$

$-159.0(4)^\circ$]. All six aminium protons are involved in hydrogen-bonding interactions (Table 1), two to water molecules of solvation and the remainder to separate carboxylate-O-atom acceptors. The water molecules also act as donors to carboxylate O atoms, leading to a three-dimensional layered framework structure (Fig. 2).

Experimental

The title compound was synthesized by heating together 1 mmol quantities of PYCA and EN in 50 ml of 50% ethanol–water under reflux for 10 min. After concentration to ca 30 ml, total room-temperature evaporation of the hot-filtered solution gave colourless crystal plates (m.p. 527 K) of (I).

Crystal data

$\text{C}_2\text{H}_{10}\text{N}_2^{2+} \cdot \text{C}_7\text{H}_3\text{NO}_4^{2-} \cdot 2\text{H}_2\text{O}$
 $M_r = 263.26$
 Monoclinic, $C2/c$
 $a = 11.4733(16) \text{ \AA}$
 $b = 12.1572(13) \text{ \AA}$
 $c = 10.0129(13) \text{ \AA}$
 $\beta = 118.750(9)^\circ$
 $V = 1224.5(3) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.428 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.12 \text{ mm}^{-1}$
 $T = 297(2) \text{ K}$
 Plate, colourless
 $0.30 \times 0.30 \times 0.12 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: none
 1699 measured reflections
 1408 independent reflections
 1017 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\text{max}} = 27.5^\circ$
 3 standard reflections
 frequency: 150 min
 intensity decay: 2.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.183$
 $S = 0.89$
 1408 reflections
 102 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 9.335P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1W}-\text{H1W} \cdots \text{O211}^{\text{i}}$	0.91 (5)	1.86 (5)	2.769 (3)	179 (7)
$\text{O1W}-\text{H2W} \cdots \text{O212}^{\text{ii}}$	0.91 (5)	1.83 (5)	2.740 (4)	176 (5)
$\text{N11}-\text{H111} \cdots \text{O211}^{\text{iii}}$	0.98 (4)	1.85 (4)	2.811 (3)	168 (4)
$\text{N11}-\text{H112} \cdots \text{O212}^{\text{iv}}$	0.85 (5)	1.96 (5)	2.786 (4)	164 (4)
$\text{N11}-\text{H113} \cdots \text{O1W}$	0.92 (6)	1.90 (6)	2.796 (4)	166 (3)

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

H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement in calculated positions ($\text{C}-\text{H} = 0.93$ and 0.95 \AA) using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ with the exception of C1, which was set invariant with U_{iso} arbitrarily as ca. $U_{\text{eq}}(\text{C1})$. The pyridine N atom and its *ortho*-related CH group, which

are related by crystallographic twofold symmetry, were refined with 50% N,C—H site occupancy.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* for Windows (Molecular Structure Corporation, 1999); 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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