

Pyridine-2,6-dicarboxylic acid–pyridine-4-carboxamide–water (1/1/1)

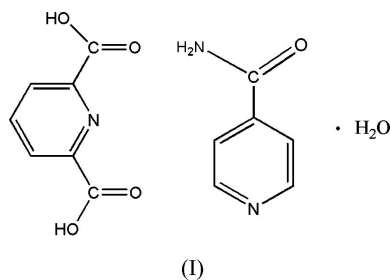
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The combination of pyridine-2,6-dicarboxylic acid (pydcH₂) and pyridine-4-carboxamide (pyca) in a 1:1 molar ratio, followed by recrystallization from water, leads to the formation of the molecular cocrystal pydcH₂·pyca·H₂O. In the crystal structure, the water molecules bridge the organic components, forming infinite zigzag chains, which are further linked together to form a hydrogen-bonded three-dimensional network.

Comment

The creation of new functional materials through the control of intermolecular bonding is a key aim of crystal engineering (Desiraju, 1989; Schmidt, 1971). The synthesis of crystalline supramolecular structures mediated by hydrogen bonds is of considerable importance. Among all the non-bonded interactions, hydrogen bonding has proved to be the most useful and reliable, because of its strength and directional properties (Aakeroy & Seddon, 1993).

In the case of cocrystals, these are generally formed by dissolution and recrystallization from a suitable solvent, although sublimation and growth from the melt are also used. Cocrystals are used to reveal specific recognition motifs, such as those proposed for rational drug design (Baures, 1999; Houk *et al.*, 1999) and crystal engineering applications.



The asymmetric unit of the title cocrystal, (I), is shown in Fig. 1 and selected geometrical parameters are given in Table 1. The C–O distances support the existence of the unionized acid molecules, indicating cocrystal formation. In (I), the O atoms of carboxylic groups make different types of hydrogen bonds (Table 2).

A remarkable feature in the crystal structure of (I) is the presence of a large number of O–H···O, O–H···N, N–H···O and C–H···O hydrogen bonds (Table 2). C–H···O hydrogen bonding is widely accepted (Desiraju & Steiner, 1999; Biradha *et al.*, 1993), and weak hydrogen bonding can be exploited in supramolecular chemistry and crystal structure design (Derewenda *et al.*, 1995; Bond, 2003). The CH groups in pyridine rings or heterocyclic compounds related to pyridine

Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.062
 wR factor = 0.153
Data-to-parameter ratio = 14.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

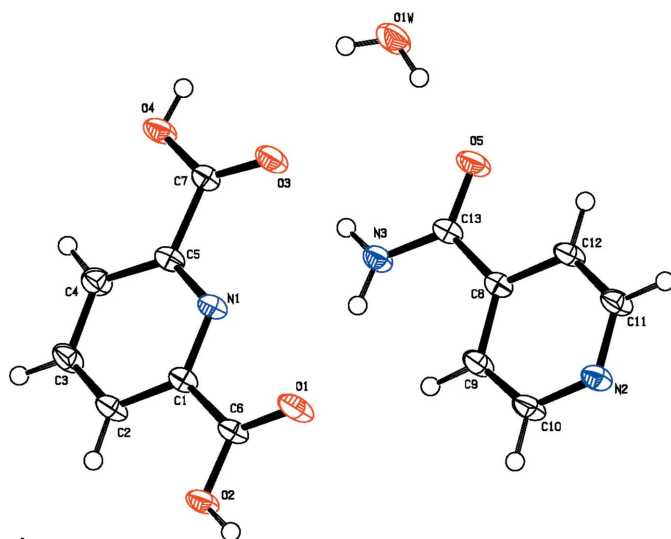


Figure 1
The asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

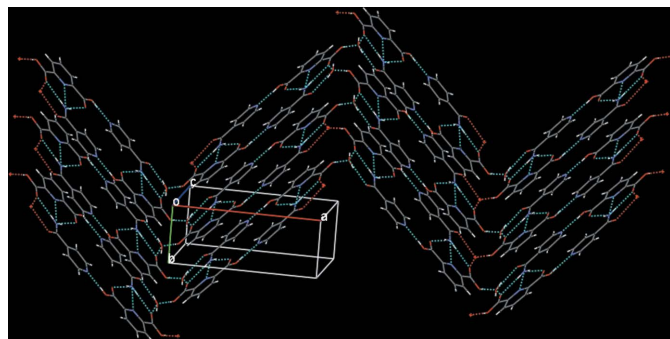


Figure 2
The packing of hydrogen-bonded chains in the crystal structure of (I), forming a layer parallel to (001). Hydrogen bonds are shown as dashed lines.

are often observed to act as donor groups in C—H...A interactions (Oswald *et al.*, 2004; Li *et al.*, 2005). In (I), the H9A...O1 distance (2.34 Å) as well as the C9—H9A...O1 angle (163°) are within the distance and angle criteria for a general C—H...O hydrogen bond (Desiraju, 1996; Srinivasan *et al.*, 2006; Ramezanipour *et al.*, 2004; Dalir Kheirollahi *et al.*, 2005).

In the crystal structure of (I), water molecules bridge the organic components, forming infinite zigzag chains (Fig. 2), which are further linked together to form a hydrogen-bonded three-dimensional network. Consequently, (I) can be considered to be a supramolecular structure formed by non-covalent interactions.

Experimental

An equimolar mixture of pyridine-2,6-dicarboxylic acid, (pydcH₂), (1.67 g, 10 mmol) and pyridine-4-carboxamide (1.52 g, 10 mmol) in tetrahydrofuran (30 ml) was refluxed for 10 h. After filtration and removal of the solvent, a white powder was obtained. Colourless crystals of (I) were obtained by recrystallization of the powder from water over a period of four weeks.

Crystal data

C₇H₅NO₄·C₆H₆N₂O·H₂O
M_r = 307.26
 Monoclinic, *P*2₁/*c*
a = 13.410 (3) Å
b = 5.0467 (10) Å
c = 19.937 (4) Å
 β = 100.85 (3)°
V = 1325.2 (5) Å³

Z = 4
D_x = 1.540 Mg m⁻³
 Mo *K*α radiation
 μ = 0.12 mm⁻¹
T = 173 (2) K
 Prism, colourless
 0.45 × 0.20 × 0.20 mm

Data collection

Rebuilt Syntex *P*2₁/Siemens *P*3
 four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 5684 measured reflections
 2895 independent reflections

2310 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.061
 θ_{\max} = 27.0°
 2 standard reflections
 every 98 reflections
 intensity decay: 2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.062
wR(*F*²) = 0.153
 S = 1.00
 2895 reflections
 205 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 2.9P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.010$
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

O1—C6	1.219 (3)	O4—C7	1.310 (3)
O2—C6	1.304 (3)	O5—C13	1.242 (3)
O3—C7	1.218 (3)		
O1—C6—O2	124.2 (2)	O4—C7—C5	113.6 (2)
O1—C6—C1	122.5 (2)	O5—C13—N3	123.5 (2)
O2—C6—C1	113.3 (2)	O5—C13—C8	118.6 (2)
O3—C7—O4	124.3 (2)	N3—C13—C8	117.9 (2)
O3—C7—C5	122.0 (2)		
N1—C5—C7—O3	4.4 (4)	N1—C1—C6—O2	−179.7 (2)
N1—C5—C7—O4	−176.2 (2)	C12—C8—C13—O5	4.2 (4)
N1—C1—C6—O1	0.9 (4)	C12—C8—C13—N3	−175.6 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4O...O1W ⁱ	0.82	1.75	2.559 (3)	167
O2—H2O...N2 ⁱⁱ	0.82	1.76	2.574 (3)	175
O1W—H1WB...O5	0.82	1.92	2.733 (3)	170
N3—H3NA...O3	0.87	2.04	2.905 (3)	177
O1W—H1WA...O3	0.82	2.30	2.920 (3)	132
N3—H3NB...O1	0.87	2.07	2.934 (3)	172
C9—H9A...O1	0.95	2.34	3.264 (3)	163

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

The H atoms of H₂O, OH and NH₂ groups were located in difference syntheses, idealized and refined as riding, with N—H = 0.87 Å and O—H = 0.82 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(N,O). The remaining H atoms were positioned geometrically, with C—H = 0.95 Å for aromatic H atoms, and constrained to ride on their parent atoms, with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(methyl C).

Data collection: *P3/PC* (Siemens, 1989); cell refinement: *P3/PC*; data reduction: *P3/PC*; 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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