

2,6-Bis[(2-hydroxy-3-methoxybenzylidene)hydrazinocarbonyl]pyridine monohydrate

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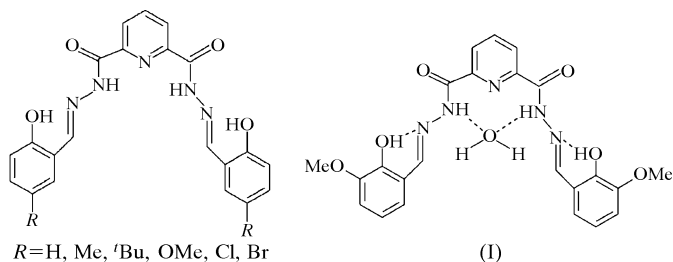
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In the title compound, $C_{23}H_{19}N_5O_6 \cdot H_2O$, the two components are linked into complex chains by a combination of two independent $O-H \cdots O$ and two independent $N-H \cdots O$ hydrogen bonds. The complex chains are linked into a two-dimensional sheet network *via* $\pi-\pi$ stacking interactions and $C-H \cdots O$ hydrogen bonds.

Comment

As part of our synthetic study of Schiff base systems, we are now focusing on the synthesis of propeller-shaped amido-containing organic compounds, which are important multi-dentate ligands for the construction of coordination complexes with metal centres (Wang *et al.*, 2005). In 1985, 5-*H*-substituted 2,6-bis(salicylidenehydrazinocarbonyl)pyridine as a potential mono-, di- and tri-nucleating ligand towards uranyl ions (Paolucci *et al.*, 1985) was reported. More recently, a series of 5-substituted 2,6-bis(salicylidenehydrazinocarbonyl)pyridine ligands (see scheme) and their copper(II) complexes have been reported (Chen *et al.*, 1996, 1997). However, the researchers only paid attention to the synthesis of their coordination complexes, and did not report the crystal structures of the organic ligands. In this report, we have synthesized



the title 3-methoxy derivative with a propeller shape, (I), and describe its crystal structure. For convenience, we denote the benzene ring containing atom C8 as *B*, the benzene ring containing atom C17 as *C* and the pyridine ring as *A*.

In compound (I), the two hydrazine components (N2–N3 and N4–N5) have essentially planar coordinations, and the N–N bond distances (Table 1) have values typical for hydrazine, with both N atoms having a planar coordination [mean value = 1.401 (3) Å; Allen *et al.*, 1987]. The fragments C5–C6(=O1)–N2–N3, C1–C15(=O4)–N4–N5, C8–C7–N3–N2 and C17–C16–N5–N4 are essentially planar, as shown by the key torsion angles. The dihedral angles between pyridine ring *A* and the two benzene rings, *B* and *C*, are 17.6 (1) and 17.72 (9)°, respectively. The dihedral angle between the two benzene rings is 33.48 (9)°.

Within the selected asymmetric unit (Fig. 1), two hydroxyl O atoms (O2 and O5) act as hydrogen-bond donors, *via* atoms H2 and H5, respectively, to atoms N3 and N5, thereby generating intramolecular hydrogen bonds of $R_1^1(6)$ motif (Bernstein *et al.*, 1995). Hydrazine atoms N2 and N4 act as hydrogen-bond acceptors, forming intermolecular hydrogen bonds of $R_1^1(10)$ motifs to water atom O7. The solvent water molecule O7 also donates two H atoms to carboxyl atoms O1 and O4 of two different molecules to form relatively strong $O-H \cdots O$ hydrogen bonds.

Through the two intermolecular $O-H \cdots O$ hydrogen bonds and two $N-H \cdots O$ hydrogen bonds to water molecules, compound (I) is linked into a one-dimensional chain along the [010] direction (Fig. 2). It is noteworthy that $\pi-\pi$ stacking interactions play an important role in building the one-

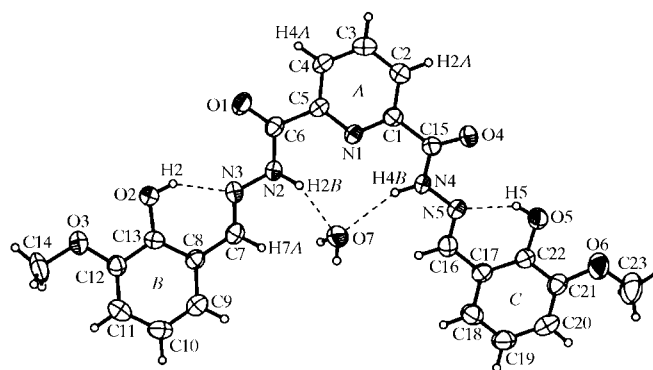


Figure 1
A view of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

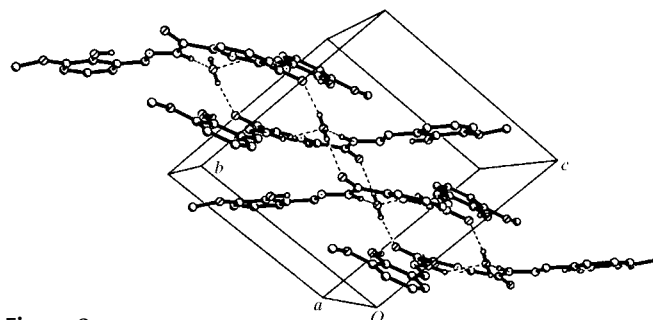


Figure 2
The one-dimensional chain structure of (I). Dashed lines indicate hydrogen bonds.

dimensional chains into two-dimensional layers parallel to (100) (Fig. 3). In the chains, the molecules are antiparallel to each other and the pyridine ring *A* at (*x*, *y*, *z*) is sandwiched by benzene rings *B* at (1 − *x*, −*y*, 1 − *z*) and *C* at (1 − *x*, 1 − *y*, 1 − *z*). The mean interplanar distances are 3.697 (3) and 3.749 (3) Å, respectively, indicating efficient π – π stacking interactions. Between adjacent chains, the benzene ring plane *C* at (*x*, *y*, *z*) is antiparallel to benzene ring *C* at (1 − *x*, 1 − *y*, −*z*), with an interplanar distance of 3.492 (3) Å. Additional C—H...O hydrogen bonds (Table 2) help to stabilize the layer structure.

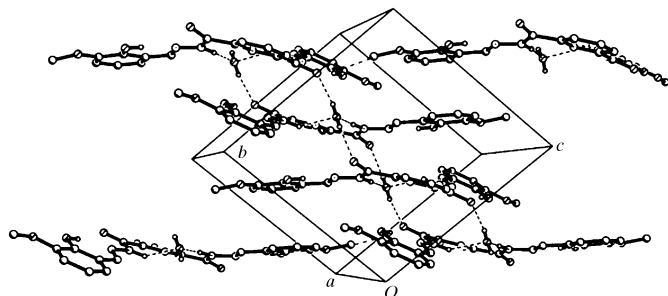


Figure 3
The two-dimensional layer structure of (I). Dashed lines indicate hydrogen bonds. H atoms attached to C atoms have been omitted for clarity.

Experimental

For the preparation of 2,6-bis(hydrazinocarbonyl)pyridine, diethyl pyridine-2,6-dicarboxylate (1.95 g, 10 mmol) and hydrazine hydrate (10 ml, 85%) were reacted in a 100 ml reaction flask in chloroform (60 ml). The product was recrystallized from a large amount of water as colourless needles (75% yield). For the preparation of 2,6-bis[(2-hydroxy-3-methoxybenzylidene)hydrazinocarbonyl]pyridine, 2,6-bis(hydrazinocarbonyl)pyridine (1.95 g, 10 mmol), 2-hydroxy-3-methoxybenzaldehyde (3.04 g, 20 mmol) and *p*-toluenesulfonic acid as catalyst were added to a 100 ml reaction flask with ethanol (60 ml). The mixture was stirred with a magnetic stirrer and refluxed for about 3 h. After filtration and removal of the ethanol by rotary evaporation, the crude product was obtained and this was recrystallized from methanol (85% yield).

Crystal data

$C_{23}H_{21}N_5O_6 \cdot H_2O$	$\gamma = 92.42 (3)^\circ$
$M_r = 481.46$	$V = 1122.6 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 10.184 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.842 (1) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$c = 11.034 (2) \text{ \AA}$	$T = 291 (2) \text{ K}$
$\alpha = 98.72 (3)^\circ$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 110.42 (2)^\circ$	

Data collection

Bruker SMART APEXII CCD	5277 measured reflections
area-detector diffractometer	5177 independent reflections
Absorption correction: multi-scan	4150 reflections with $I > 2\sigma(I)$
(SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.003$
$T_{\text{min}} = 0.968$, $T_{\text{max}} = 0.973$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	317 parameters
$wR(F^2) = 0.139$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
5177 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N2—N3	1.373 (2)	N4—N5	1.371 (3)
C5—C6—N2—N3	176.31 (17)	C1—C15—N4—N5	168.92 (16)
C8—C7—N3—N2	179.90 (18)	C17—C16—N5—N4	176.45 (16)

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>
O2—H2...N3	0.82	1.90	2.613 (2)	146
N2—H2B...O7	0.89	2.30	3.035 (2)	139
N4—H4B...O7	0.89	2.25	3.097 (2)	160
O5—H5...N5	0.82	1.87	2.593 (2)	146
O7—H7B...O1 ⁱ	0.82	2.04	2.848 (2)	170
O7—H7C...O4 ⁱⁱ	0.82	2.12	2.875 (2)	154
C14—H14B...O5 ⁱⁱⁱ	0.96	2.56	3.258 (3)	130

Symmetry codes: (i) −*x* + 1, −*y*, −*z* + 1; (ii) −*x* + 1, −*y* + 1, −*z* + 1; (iii) *x* + 1, *y* − 1, *z* + 1.

C-bound H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined as riding [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.2U_{\text{eq}}(\text{methyl C})$]. N-bound H atoms were found in difference maps, relocated in idealized positions (N—H = 0.89 Å) and refined as riding [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$]. Water and hydroxyl H atoms were found in difference maps, relocated in idealized positions (O—H = 0.82 Å) and refined as riding atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$].

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3088). Services for accessing these data are described at the back of the journal.

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