

# Crystal structure of *N*-hydroxypicolinamide mono-hydrate

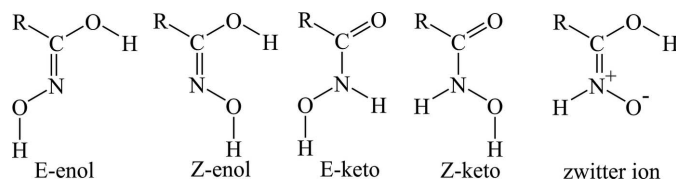
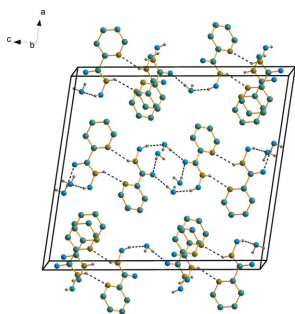
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The crystal structure of the title compound,  $C_6H_6N_2O_2 \cdot H_2O$ , consists of *N*-hydroxypicolinamide and water molecules connected through O—H...O and N—H...N hydrogen bonds. The O—H...O interactions and  $\pi$ - $\pi$  stacking interactions between the pyridine rings [centroid-centroid distance = 3.427 (1) Å] organize the components into columns extending along the *b* axis and the N—H...N hydrogen bonds link these columns into a two-dimensional framework parallel to (100). The *N*-hydroxypicolinamide molecule adopts a strongly flattened conformation and only the O—H group H atom deviates significantly from the molecule best plane. The dihedral angle between the hydroxamic group and the pyridine ring is 5.6 (2)°. The conformation about the hydroxamic group C—N bond is *Z* and that about the C—C bond between the pyridine and hydroxamic groups is *E*.

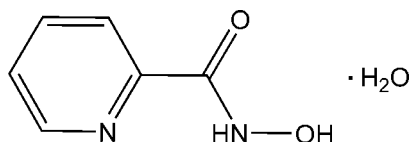
## 1. Chemical context

Hydroxamic acids (HA) are weak organic acids with the general formula  $R-C(=O)-NH-OH$ . HA can exist as keto and imino(enol) tautomers with two isomers, *E* and *Z*, for each form, and in the zwitterionic form (see Scheme below). They have found broad application in coordination chemistry due to their diversity and comparatively facile synthesis (Świątek-Kozłowska *et al.*, 2000; Dobosz *et al.*, 1999). In addition, they exhibit biological activities related to their enzyme-inhibitory properties (Marmion *et al.*, 2013). HAs are widely used in coordination and supramolecular chemistry as scaffolds in the preparation of metallacrowns (Seda *et al.*, 2007; Jankolovits *et al.*, 2013; Safyanova *et al.*, 2015) and as building blocks of coordination polymers (Gumienna-Kontecka *et al.*, 2007; Golenya *et al.*, 2014; Pavlishchuk *et al.*, 2010, 2011).



*N*-Hydroxypicolinamide, known also as picoline-2-hydroxamic acid (*o*-PicHA), has been used extensively for the synthesis of polynuclear complexes, especially in the synthesis of diverse metallacrowns (Stemmler *et al.*, 1999; Seda *et al.*, 2007; Jankolovits *et al.*, 2013; Golenya *et al.*, 2012; Gumienna-Kontecka *et al.*, 2013). Presently, the Cambridge Structural Database (Groom & Allen, 2014) contains more than 20 entries of coordination compounds based on *N*-hydroxypicolinamide.

Our interest in *N*-hydroxypicolinamide stems also from the fact that in the course of synthesis of the title and related compounds from 2-picolinic acid esters (Hynes, 1970), the products are frequently contaminated with impurities that result from hydrolysis of the ester or hydroxamic groups to the carboxylic group. Structural information about the title compound will be helpful in controlling the purity of the synthesised ligand by powder diffraction.

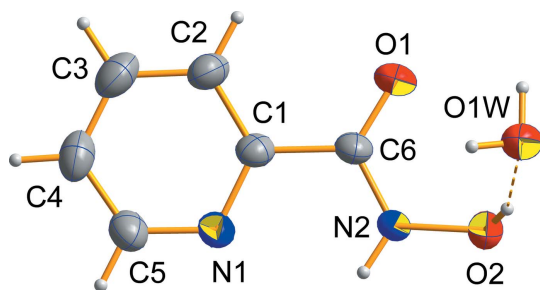


## 2. Structural commentary

The molecular structure of the title compound is presented in Fig. 1. The crystal structure of the title compound consists of an *N*-hydroxypicolinamide molecule in the *Z*-keto tautomeric form in agreement with the C=O and C–N bond lengths [1.234 (2) and 1.325 (2) Å, respectively] and a water molecule. The *N*-hydroxypicolinamide molecule adopts a strongly flattened conformation and only the O–H group H atom deviates significantly from the molecular best plane. The maximum deviation from this plane for non-hydrogen atom is 0.083 (1) Å for O1 and the hydroxyl group H2 atom is displaced from the mean plane by 0.80 (1) Å in the direction of the water molecule. The dihedral angle between the hydroxamic group and the pyridine ring is 5.6 (2)°. The configuration about the hydroxamic group C–N bond is *Z* and that about the C–C bond between the pyridine and hydroxamic groups is *E* [torsion angles O2–N2–C6–O1 –0.4 (3)°, N1–C1–C6–O1 175.6 (2)°].

## 3. Supramolecular features

The molecular components of the title compound are connected by O–H···O and N–H···N hydrogen bonds (Table 1) into a two-dimensional framework parallel to (100) (Fig. 2). The O–H···O interactions and  $\pi$ – $\pi$  stacking interactions between the pyridine rings [centroid–centroid distance



**Figure 1**  
The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius. The dashed line indicates a hydrogen bond.

**Table 1**  
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···O1W	0.82	1.86	2.656 (2)	163
N2–H2A···N1 <sup>i</sup>	0.86	2.31	3.010 (2)	139
O1W–H1WA···O1 <sup>ii</sup>	0.85	2.14	2.976 (2)	168
O1W–H1WB···O1 <sup>iii</sup>	0.85	1.94	2.788 (2)	173

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

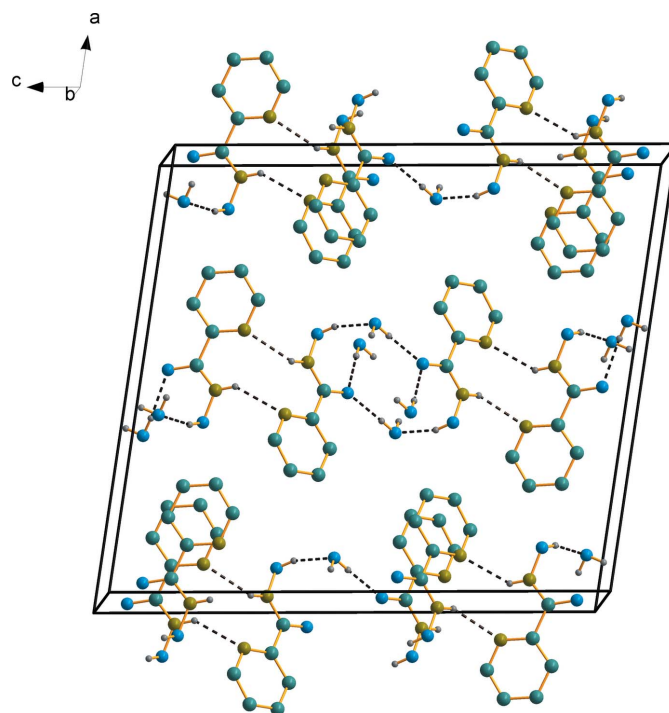
3.427 (1) Å] organize the crystal components into columns extending along the *b* axis while the N–H···N hydrogen bonds link these columns into a two-dimensional framework parallel to (100) (Fig. 2).

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.36, last update February 2015; Groom & Allen, 2014) revealed two crystal structures of isomeric pyridine hydroxamic acids and the crystal structure of 2,6-pyridinedihydroxamic acid (Golenya *et al.*, 2007; Makhmudova *et al.*, 2001; Griffith *et al.*, 2008).

## 5. Synthesis and crystallization

The title compound was obtained by the reaction of methyl 2-picolinate and hydroxylamine in methanol solution according to a reported procedure (Hynes, 1970). Colorless crystals



**Figure 2**  
A packing diagram of the title compound. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

suitable for X-ray diffraction were obtained from a methanol solution by slow evaporation at room temperature (yield 79%).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal was modelled as a non-merohedral twin with the volume ratio of two twin domains refined at 89:19. The C–H, N–H and O–H hydrogen atoms of the organic molecule were found from the difference Fourier maps but for further calculations they were positioned geometrically and constrained to ride on their parent atoms with C–H = 0.93 Å, N–H = 0.86 Å and O–H = 0.82 Å, and with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C,N})$  or  $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$ . The H atoms of the water molecule were located in the difference Fourier maps, the O–H distances standardized to 0.85 Å and refined in riding-model approximation with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

## Acknowledgements

Financial support from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement PIRSES-GA-2013–611488 is gratefully acknowledged. KAO acknowledges for the DAAD fellowship (Leonhard-Euler-Programm).

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**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> ·H <sub>2</sub> O
$M_r$	156.14
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	298
$a, b, c$ (Å)	18.7471 (13), 3.8129 (4), 20.4813 (17)
$\beta$ (°)	100.570 (7)
$V$ (Å <sup>3</sup> )	1439.2 (2)
$Z$	8
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.12
Crystal size (mm)	0.4 × 0.4 × 0.1
Data collection	
Diffractometer	Agilent Xcalibur, Sapphire3
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2013)
$T_{\text{min}}, T_{\text{max}}$	0.476, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	2491, 1401, 1053
$R_{\text{int}}$	0.037
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.053, 0.143, 0.99
No. of reflections	1401
No. of parameters	102
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.19, -0.25

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *OLEX2* (Dolomanov et al., 2009).

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## supporting information

*Acta Cryst.* (2016). E72, 117-119 [doi:10.1107/S2056989015024706]

Crystal structure of *N*-hydroxypicolinamide monohydrate

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## Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

*N*-Hydroxypyridine-2-carboxamide monohydrate

## Crystal data

$C_6H_6N_2O_2 \cdot H_2O$

$M_r = 156.14$

Monoclinic, *C2/c*

$a = 18.7471$  (13) Å

$b = 3.8129$  (4) Å

$c = 20.4813$  (17) Å

$\beta = 100.570$  (7)°

$V = 1439.2$  (2) Å<sup>3</sup>

$Z = 8$

$F(000) = 656$

$D_x = 1.441$  Mg m<sup>-3</sup>

Melting point: 393 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 893 reflections

$\theta = 4.1$ – $29.0$ °

$\mu = 0.12$  mm<sup>-1</sup>

$T = 298$  K

Plate, clear colourless

$0.4 \times 0.4 \times 0.1$  mm

## Data collection

Agilent Xcalibur, Sapphire3  
diffractometer

Radiation source: Enhance (Mo) X-ray Source  
Graphite monochromator

Detector resolution: 16.1827 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Agilent, 2013)

$T_{\min} = 0.476$ ,  $T_{\max} = 1.000$

2491 measured reflections

1401 independent reflections

1053 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 26.0$ °,  $\theta_{\min} = 3.3$ °

$h = -22$ → $22$

$k = -4$ → $4$

$l = -24$ → $24$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.053$

$wR(F^2) = 0.143$

$S = 0.99$

1401 reflections

102 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.19$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.25$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refined as a 2-component twin. Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.52649 (8)	0.3700 (4)	0.43254 (7)	0.0468 (5)
O2	0.40179 (7)	0.5190 (5)	0.35109 (7)	0.0506 (5)
H2	0.3916	0.6429	0.3808	0.076*
N1	0.59448 (9)	0.8106 (5)	0.30306 (8)	0.0366 (5)
N2	0.46909 (9)	0.6163 (5)	0.33806 (8)	0.0410 (5)
H2A	0.4722	0.7305	0.3025	0.049*
C1	0.59810 (10)	0.6575 (5)	0.36271 (9)	0.0323 (5)
C2	0.66231 (11)	0.6152 (6)	0.40743 (11)	0.0428 (6)
H2B	0.6628	0.5119	0.4487	0.051*
C3	0.72601 (11)	0.7308 (6)	0.38915 (13)	0.0519 (7)
H3	0.7703	0.7030	0.4178	0.062*
C4	0.72296 (11)	0.8863 (6)	0.32857 (13)	0.0482 (6)
H4	0.7650	0.9656	0.3154	0.058*
C5	0.65653 (12)	0.9234 (6)	0.28737 (11)	0.0434 (6)
H5	0.6549	1.0327	0.2465	0.052*
C6	0.52864 (10)	0.5321 (6)	0.38079 (9)	0.0332 (5)
O1W	0.39862 (8)	0.9488 (5)	0.45255 (8)	0.0501 (5)
H1WA	0.4308	1.0938	0.4455	0.075*
H1WB	0.4202	0.8351	0.4861	0.075*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0447 (8)	0.0657 (11)	0.0287 (8)	0.0009 (7)	0.0035 (6)	0.0147 (7)
O2	0.0332 (8)	0.0832 (13)	0.0350 (9)	-0.0121 (8)	0.0051 (6)	0.0062 (8)
N1	0.0370 (9)	0.0465 (11)	0.0267 (9)	-0.0051 (8)	0.0069 (7)	-0.0036 (8)
N2	0.0307 (9)	0.0670 (13)	0.0252 (9)	-0.0038 (8)	0.0048 (7)	0.0107 (9)
C1	0.0344 (10)	0.0371 (11)	0.0252 (10)	0.0012 (8)	0.0047 (8)	-0.0061 (8)
C2	0.0369 (11)	0.0543 (14)	0.0347 (12)	0.0052 (9)	0.0000 (9)	-0.0030 (11)
C3	0.0322 (11)	0.0640 (17)	0.0554 (16)	0.0028 (11)	-0.0027 (10)	-0.0116 (13)
C4	0.0351 (11)	0.0569 (15)	0.0552 (15)	-0.0091 (10)	0.0156 (10)	-0.0148 (12)
C5	0.0435 (12)	0.0538 (15)	0.0348 (12)	-0.0062 (11)	0.0121 (9)	-0.0047 (11)
C6	0.0359 (11)	0.0409 (12)	0.0224 (10)	-0.0012 (9)	0.0043 (8)	-0.0013 (9)
O1W	0.0408 (8)	0.0687 (11)	0.0404 (9)	0.0044 (8)	0.0068 (7)	0.0163 (8)

## Geometric parameters (Å, °)

O1—C6	1.234 (2)	C2—C3	1.387 (3)
O2—N2	1.387 (2)	C2—H2B	0.9300
O2—H2	0.8200	C3—C4	1.367 (3)
N1—C5	1.334 (3)	C3—H3	0.9300
N1—C1	1.344 (3)	C4—C5	1.378 (3)
N2—C6	1.325 (2)	C4—H4	0.9300
N2—H2A	0.8600	C5—H5	0.9300
C1—C2	1.382 (3)	O1W—H1WA	0.8503
C1—C6	1.496 (3)	O1W—H1WB	0.8499
N2—O2—H2	109.5	C4—C3—H3	120.4
C5—N1—C1	117.26 (17)	C2—C3—H3	120.4
C6—N2—O2	119.60 (16)	C3—C4—C5	118.9 (2)
C6—N2—H2A	120.2	C3—C4—H4	120.6
O2—N2—H2A	120.2	C5—C4—H4	120.6
N1—C1—C2	123.08 (19)	N1—C5—C4	123.4 (2)
N1—C1—C6	117.54 (16)	N1—C5—H5	118.3
C2—C1—C6	119.38 (18)	C4—C5—H5	118.3
C1—C2—C3	118.2 (2)	O1—C6—N2	122.15 (18)
C1—C2—H2B	120.9	O1—C6—C1	122.66 (17)
C3—C2—H2B	120.9	N2—C6—C1	115.17 (17)
C4—C3—C2	119.2 (2)	H1WA—O1W—H1WB	102.7
C5—N1—C1—C2	0.3 (3)	C3—C4—C5—N1	-1.0 (4)
C5—N1—C1—C6	179.67 (17)	O2—N2—C6—O1	-0.4 (3)
N1—C1—C2—C3	-1.2 (3)	O2—N2—C6—C1	-178.54 (17)
C6—C1—C2—C3	179.4 (2)	N1—C1—C6—O1	175.6 (2)
C1—C2—C3—C4	1.0 (3)	C2—C1—C6—O1	-5.0 (3)
C2—C3—C4—C5	0.0 (4)	N1—C1—C6—N2	-6.2 (3)
C1—N1—C5—C4	0.8 (3)	C2—C1—C6—N2	173.20 (18)

## 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...O1W	0.82	1.86	2.656 (2)	163
N2—H2A...N1 <sup>i</sup>	0.86	2.31	3.010 (2)	139
O1W—H1WA...O1 <sup>ii</sup>	0.85	2.14	2.976 (2)	168
O1W—H1WB...O1 <sup>iii</sup>	0.85	1.94	2.788 (2)	173

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