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Synthesis and crystal structures of 3,6-dihydroxypicolinic acid and its labile intermediate dipotassium 3-hydroxy-6-(sulfonatoxy)pyridine-2-carboxylate monohydrate

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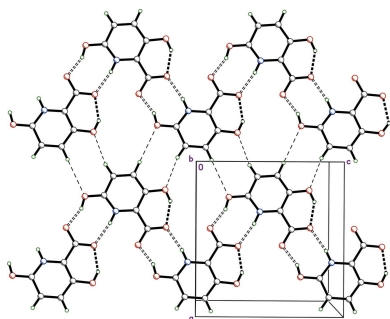
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A simplified two-step synthesis of 3,6-dihydroxypicolinic acid (3-hydroxy-6-oxo-1,6-dihydropyridine-2-carboxylic acid), $C_6H_5NO_4$ (**II**), an intermediate in the metabolism of picolinic acid, is described. The crystal structure of **II**, along with that of a labile intermediate, dipotassium 3-hydroxy-6-(sulfonatoxy)pyridine-2-carboxylate monohydrate, $2K^+ \cdot C_6H_3NO_7S^{2-} \cdot H_2O$ (**I**), is also described. Compound **I** comprises a pyridine ring with carboxylate, hydroxyl (connected by an intramolecular $O-H \cdots O$ hydrogen bond), and sulfate groups at the 2-, 3-, and 6-positions, respectively, along with two potassium cations for charge balance and one water molecule of crystallization. These components are connected into a three-dimensional network by $O-H \cdots O$ hydrogen bonds arising from the water molecule, $C-H \cdots O$ interactions and $\pi-\pi$ stacking of pyridine rings. In **II**, the ring nitrogen atom is protonated, with charge balance provided by the carboxylate group (*i.e.*, a zwitterion). The intramolecular $O-H \cdots O$ hydrogen bond observed in **I** is preserved in **II**. Crystals of **II** have unusual space-group symmetry of type *Abm2* in which extended planar networks of $O-H \cdots O$ and $N-H \cdots O$ hydrogen-bonded molecules form sheets lying parallel to the *ac* plane, constrained to $b = 0.25$ (and 0.75). The structure was refined as a 50:50 inversion twin. A minor disorder component was modeled by reflection of the major component across a mirror plane perpendicular to *c*.

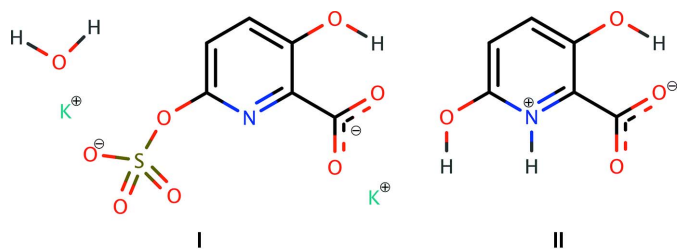
1. Chemical context

3,6-Dihydroxypicolinic acid (3-hydroxy-6-pyridone-2-carboxylic acid), $C_6H_5NO_4$, is an intermediate in the metabolism of picolinic acid by several microorganisms (Shukla & Kaul, 1973; Shukla *et al.*, 1977; Qiu *et al.*, 2019). It was isolated from culture media and partially characterized by Shukla & Kaul (1973; Shukla *et al.*, 1977) whose work is misrepresented by Qiu *et al.* (2019) by stating that their work was only theoretical. It was synthesized by a six-step procedure from 3-hydroxypicolinic acid and characterized by mass spectrometry and NMR data (Qiu *et al.*, 2019, with C. Shen).

We report here a two-step synthesis also starting with 3-hydroxypicolinic acid by an Elbs oxidation (Behrman, 1988; 2021) and crystal structures of both the intermediate sulfate ester (**I**) and of 3,6-dihydroxypicolinic acid (**II**). We considered two routes, as shown in Fig. 1. Both give the desired product but we chose the pathway from 3-hydroxypicolinic acid because in the first step, the dipotassium salt of the 6-sulfate ester precipitates from the mixture in an almost pure state.



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This sulfate ester is extraordinarily sensitive to acid-catalyzed hydrolysis; acidification at room temperature (RT) gives complete hydrolysis in a few minutes. The isomeric 6-oxo-picolinic acid-3-sulfate is much more stable although subject to anchimeric assistance (Benkovic, 1966); it is not completely hydrolyzed after 22 h, RT, pH 2. Nantka-Namirski & Rykowski (1972*a,b*) used boiling 20% sulfuric acid for four hours to effect the hydrolyses of the 5-sulfate esters of two dihydroxynicotinic acids. For the rapid hydrolysis of pyridyl-4-sulfate see Jerfy & Roy (1970) and Goren & Kochansky (1973) for the effects of impurities. A reasonable representation of the mechanism of the hydrolysis for the 4-sulfate is shown in Fig. 2*a*. The 2-sulfate should behave similarly (Fig. 2*b*). Jerfy & Roy (1970) also showed that sulfation of 2-pyridone gives the sulfamate, so that it has not yet been possible to prepare the pyridyl-2-sulfate for comparative purposes. However, a route to 5-hydroxypyridine-2-sulfate together with the isomeric 4- and 6-sulfate esters is known (Behrman & Pitt, 1958). Examination of these mixed esters by electrophoresis shows

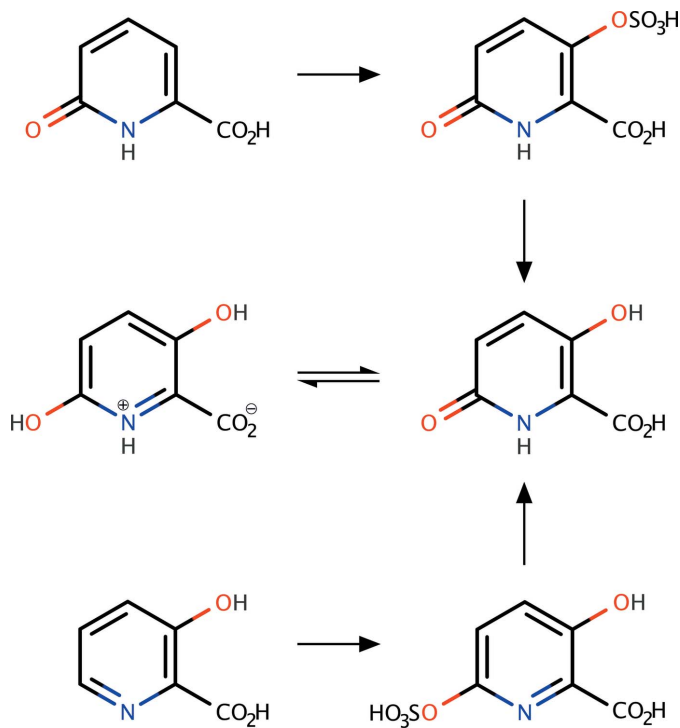


Figure 1
Two synthetic routes to 3,6-dihydroxypicolinic acid (**II**), showing tautomerism of the product.

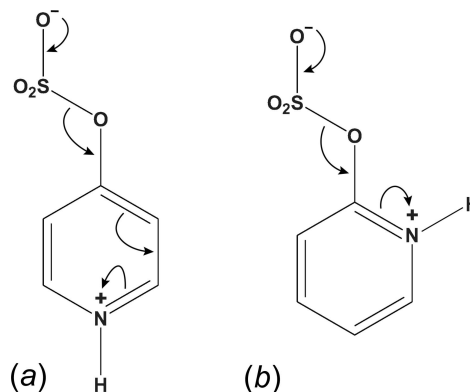


Figure 2
(*a*) A reasonable representation for the mechanism of hydrolysis for the 4-sulfate. (*b*) The *o*-sulfate analog ought to behave similarly.

that all three are rapidly hydrolyzed under acid catalysis, as predicted by the model. The reaction between potassium peroxydisulfate and 3-hydroxypicolinic acid was carried out as usual in KOH solution except that if there is excess peroxydisulfate, the sulfate ester and the peroxide precipitate from the reaction mixture together: to avoid this the persulfate was used as the limiting reagent. The ester was crystallized from water and 3,6-dihydroxypicolinic acid obtained by hydrolysis.

2. Structural commentary

The asymmetric unit in **I** (Fig. 3) contains a single pyridine ring with a carboxylate group at the 2-position, a hydroxyl group at the 3-position, and a sulfate group attached to the 6-position. Charge balance is provided by a pair of K^+ cations. There is also a single water molecule of crystallization present. The carboxylate C—O distances are 1.2510 (16) and 1.2758 (16) Å for C7—O3 and C7—O4, respectively. The longer of these is part of an *S*(6) intramolecular hydrogen-bonded ring with the hydroxyl group. In the sulfate group, the oxygen atom bound at the 6-position [C6—O2 = 1.3968 (14) Å] is longer [S1—O2 = 1.6343 (9) Å] than the other three S=O bonds [range

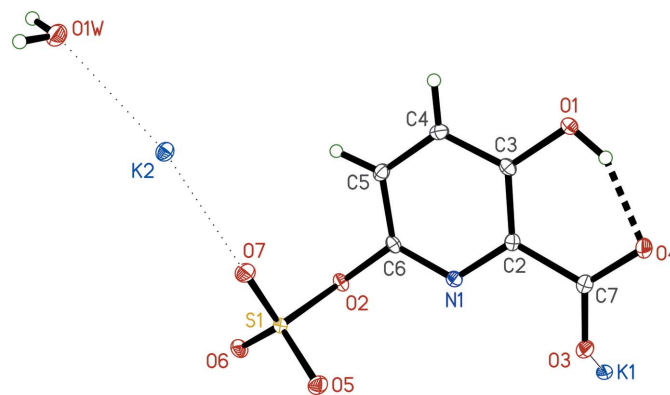


Figure 3
An ellipsoid (50% probability) plot of the asymmetric unit of **I**. The intramolecular hydrogen bond is shown by the thick dashed line. Dotted lines indicate close contacts of the K^+ cations.

Table 1
 Hydrogen-bond geometry (Å, °) for **I**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O4	0.843 (19)	1.760 (19)	2.5429 (13)	153.6 (17)
C4—H4 \cdots O5 ⁱ	0.95	2.64	3.3682 (16)	133
C5—H5 \cdots O6 ⁱⁱ	0.95	2.35	3.2943 (15)	175
O1W—H1W \cdots O3 ⁱⁱⁱ	0.83 (2)	1.97 (2)	2.7852 (13)	165 (2)
O1W—H2W \cdots O4 ^{iv}	0.83 (2)	2.09 (2)	2.8910 (14)	161 (2)

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

1.4361 (9) to 1.4486 (9) Å], as would be expected for this bonding arrangement.

In **II** (Fig. 4), the nitrogen atom of the ring is protonated. Charge balance is provided by the deprotonated 2-carboxylate group [C7—O3 = 1.262 (3), C7—O4 = 1.259 (3) Å], leading to a zwitterionic molecule. The intramolecular $S(6)$ hydrogen-bonded ring from **I** is preserved in **II**. The 6-position of the ring is occupied by a second hydroxyl group. As discussed in more detail in section 6 (*Refinement*), there is a small minor disorder component [refined occupancy 4.7 (3)%] and probable inversion twinning.

3. Supramolecular features

In the packing of **I**, strong $O_w-H\cdots O$ (w = water) hydrogen bonds exist in which the water molecule acts as a linker between c -glide-related anions. The water oxygen is also coordinated to the K^+ cations, both of which are seven coordinate. Around K1, coordination distances range from 2.7376 (9)–2.9102 (10) Å (for $K\cdots O$) and 2.7869 (11) Å ($K1\cdots N$). For K2, coordination distances range from 2.6769 (9) to 2.9525 (10) Å (all $K\cdots O$). The coordination geometry about each K^+ cation is very roughly pentagonal bipyramidal, with K1 much more distorted than K2. As each K^+ cation is coordinated to the water molecule, the KO_6N and KO_7 polyhedra augment the extended chains that propagate parallel to c (Fig. 5, Table 1). In addition, there are weaker C—

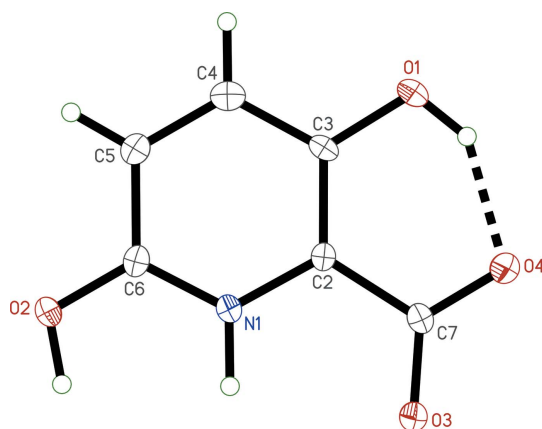


Figure 4
 An ellipsoid (50% probability) plot of the asymmetric unit of **II** with the intramolecular hydrogen bond shown as a thick dashed line.

Table 2
 Hydrogen-bond geometry (Å, °) for **II**.

The $D\cdots A$ distance for C4—H4 \cdots O2ⁱⁱⁱ is rather long, but within the bounds noted by Desiraju & Steiner (1999).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots O4 ⁱ	0.99	1.77	2.755 (3)	169
O1—H1O \cdots O4	0.89	1.76	2.535 (3)	145
C5—H5 \cdots O1 ⁱⁱ	0.95	2.34	3.269 (3)	166
C4—H4 \cdots O2 ⁱⁱⁱ	0.95	2.76	3.712 (4)	180
O2—H2O \cdots O3 ⁱ	0.94	1.57	2.459 (3)	156
O2—H2O \cdots O4 ⁱ	0.94	2.56	3.372 (3)	144

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

$H\cdots O$ contacts: pairs of C5—H5 \cdots O6ⁱⁱ interactions form $R_2^2(12)$ inversion-related dimers and C4—H4 \cdots O5ⁱ contacts link molecules *via c*-glide symmetry (symmetry codes as per Table 1). This in turn joins *c*-glide-related pyridine rings into an extended π - π stack along the c -axis direction. Adjacent rings within the stacks are almost parallel; the dihedral angle being 0.38 (4)° with a centroid–centroid distance of 3.698 (1) Å. These columns of hydrogen-bonded and π -stacked molecules are interlinked by the aforementioned chains of K^+ cations and water molecules into a three-dimensional network (Fig. 5).

The most remarkable feature of the packing in **II** are extended di-periodic hydrogen-bonded networks lying parallel to the ac plane (Fig. 6, Table 2) that are constrained to $b = 0.25$ (and 0.75) as a consequence of the unusual space-group symmetry of type $Abm2$. Strong O2—H2O \cdots O3ⁱ and N1—H1N \cdots O4ⁱ hydrogen bonds link pairs of 2_1 screw-related molecules into $R_2^2(8)$ motifs that extend to form ribbons parallel to c . Weaker C4—H4 \cdots O2ⁱⁱⁱ and C5—H5 \cdots O1ⁱⁱ (symmetry codes as per Table 2) interactions join 2_1 screw-related ribbons to form the aforementioned networks. Contacts between these planar networks are limited to weak van der Waals interactions.

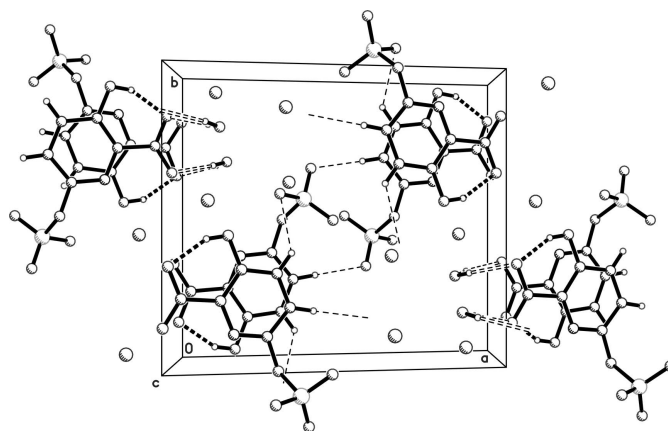


Figure 5
 A view of the packing in **I**, viewed down the c axis. Intramolecular hydrogen bonds are shown as thick dashed lines, open dashed lines indicate strong intermolecular hydrogen bonds, and thin dashed lines denote weaker C—H \cdots O interactions. Dangling hydrogen bonds extend beyond the depth of the view.

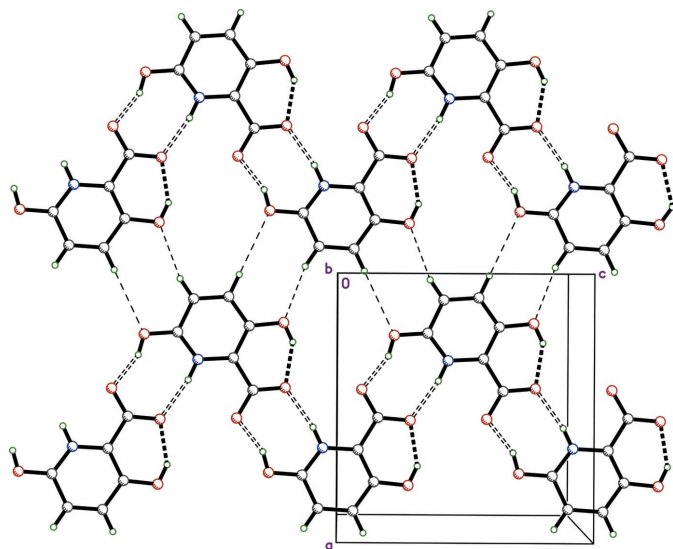


Figure 6

A view of the planar diperiodic network in crystalline **II**, viewed normal to the *ac* plane. Intramolecular hydrogen bonds are drawn as thick dashed lines, strong intermolecular hydrogen bonds (O–H···O and N–H···O) are drawn as double dashed lines. Weaker hydrogen bonds (C–H···O) are drawn as thin dashed lines.

4. Database survey

A search of the Cambridge Structure Database (CSD v5.42, Nov. 2020; Groom *et al.*, 2016) on a fragment composed of 3-picolinic acid with ‘any non-H’ at the 6-position gave only seven hits. None of these have much in common with **I** or **II**, but the most similar were AGUMEV (ammonium 2,4,6-tricarboxypyridine-3-olate monohydrate; Li *et al.*, 2010) and MAFTEU (6-chloro-3-trifluoromethoxy pyridine-2-carboxylic acid; Manteau *et al.*, 2010) in that their main components consist of a single pyridine ring with a carboxylic acid group adjacent to the ring nitrogen and an oxygen (O[−] in AGUMEV; O–CF₃ in MAFTEU) at the 3-position.

Space group *Abm2* is not common, with only 62 entries listed in v5.42 of the CSD. Excluding polymers, entries flagged with known errors, and those without deposited coordinates left only 47 hits, *i.e.* <0.005% of known structures. Of these, only 29 have $R_1 \leq 5\%$ and none form planar networks in a manner similar to **II**. By any measure, the crystal structure of **II** is unusual.

5. Synthesis and crystallization

3-Hydroxypyridine-2-carboxylic acid-6-sulfate dipotassium salt monohydrate (I): Potassium hydroxide (85%, 1 g, 15 mmol) was dissolved in 10 ml of water and cooled. 3-Hydroxypicolinic acid (0.82 g, 6 mmol) followed by potassium peroxydisulfate (0.9 g, 3.3 mmol) were added. The reaction mixture was stirred at RT for 24 h. The precipitate was filtered and dried by washing with acetone, yielding 0.46–0.49 g (~44%) of the dipotassium salt of 3-hydroxypyridine-2-carboxylic acid-6-sulfate monohydrate (**I**). Compound **I** migrates on paper electrophoresis at pH 7.5 with $R_p = 2$ as a fluorescent

spot. R_p is the migration distance relative to picric acid at $R_p = 1$ (the starting material has $R_p = 1.1$). Crystals of **I** grow from aqueous solution when treated as follows: 0.16 g were suspended in 2.0 ml of water, dissolved by heating carefully to about 313 K, and then cooled slowly to RT. Further cooling to 278 K overnight gave 0.12 g of needles. Analysis (%) calculated for C₆H₅NO₈K₂S: C, 21.88; H, 1.53; N, 4.25. Found: C, 21.97; H, 1.44; N, 4.25. IR(Nujol): 3485, 3310, 3096, 1701, 1684, 1624, 1574, 1250, 1059, 957, 860, 833, 768, 716, 638 cm^{−1}. NMR(D₂O, 600 MHz) δ 7.27 (*d*, $J = 8.82$ Hz), 7.45 (*d*, $J = 8.82$ Hz). UV (in water): λ_{\max} , (nm), ϵ (l mol^{−1} cm^{−1}): 307, 1120; 230, 1200; 205, 4180. Heating behavior: **I** begins to discolor at about 448 K and then gets darker without melting up to 523 K.

3,6-Dihydroxypicolinic acid (II): The crude sulfate (**I**, 150 mg), was suspended in 2 ml of water and then heated to about 313 K to dissolve it. HCl was then added to about pH 2. A heavy precipitate formed immediately. After cooling, the colorless solid was filtered and washed with cold water to yield 50–60 mg of the product (yield 67–80%), $R_p = 1$. The proton NMR spectrum of **II** agreed with that reported by Qiu *et al.* (2019) except that our spectrum was taken in D₂O, 600 MHz, δ 6.69 (*d*, $J = 9.65$ Hz) and 7.45 (*d*, $J = 9.65$ Hz). These are shifted because of the solvent difference from Qiu *et al.* (2019), but the couplings are the same, as is the difference between the two resonances (δ 0.76). 50 mg of **II** was crystallized from 11 ml of hot water under argon to form 35 mg of crystals. Analytical results show that the precipitate is very nearly as clean as the crystals. Analysis (%): calculated for C₆H₅NO₄: C, 46.46; H, 3.25; N, 9.03. Found (crystals), C, 46.22; H, 3.20; N, 9.07. (precipitate), C, 45.65; H, 3.16; N, 9.10. IR: Nujol, 3120, 1614, 1540, 1360, 1269, 1100, 845, 810, 760, 621 cm^{−1}. Later, larger crystals were obtained using 88% formic acid as solvent. Upon heating, **II** carbonizes above 473 K without melting. UV (in water): λ_{\max} , (nm), ϵ (l mol^{−1} cm^{−1}) at pH 7: 346, 5970; 243, 4350; 221.5, 9450. Shukla & Kaul (1973) reported the pH-dependence of the spectrum. [See also Qiu *et al.* (2019), but on p. S2, line 3, read ‘240’ for ‘360’.]

6. Data collection, structure solution and refinement

The crystals were mounted using polyisobutene oil on the tip of fine glass fibers, which were fastened in copper mounting pins with electrical solder. Crystals of **I** were placed directly into the cold gas stream of a liquid-N₂ based cryostat, while crystals of **II** were handled using methods developed for macromolecular cryocrystallography (Parkin & Hope, 1998*b*). Diffraction data were collected with the crystals at 90 K. Crystal data, data collection and refinement details are summarized in Table 3. In **II**, a small minor disorder component was apparent in a difference map. It was modeled by reflection of the major component across a mirror plane perpendicular to its *c* axis, with coordinates related by the mirror plane and constrained by mapping its coordinates to the major component *via* SHELXL FVAR parameters. A test for twinning by inversion using the Flack parameter [$x = 0.5$ (3); Flack & Bernardinelli, 1999] was indeterminate.

Table 3
Experimental details.

	I	II
Crystal data		
Chemical formula	$2\text{K}^+\cdot\text{C}_6\text{H}_3\text{NO}_7\text{S}^{2-}\cdot\text{H}_2\text{O}$	$\text{C}_6\text{H}_3\text{NO}_4$
M_r	329.37	155.11
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Abm2$
Temperature (K)	90	90
a, b, c (Å)	13.3366 (4), 11.5467 (3), 7.3078 (2)	10.2045 (6), 6.1282 (4), 9.7293 (6)
α, β, γ (°)	90, 103.553 (1), 90	90, 90, 90
V (Å ³)	1094.02 (5)	608.42 (7)
Z	4	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm ⁻¹)	1.09	1.27
Crystal size (mm)	0.18 × 0.16 × 0.13	0.14 × 0.10 × 0.02
Data collection		
Diffractometer	Bruker D8 Venture dual source	Bruker D8 Venture dual source
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.793, 0.862	0.799, 0.971
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22347, 2505, 2423	4025, 700, 690
R_{int}	0.036	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.650	0.634
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.020, 0.056, 1.08	0.024, 0.068, 1.11
No. of reflections	2505	700
No. of parameters	174	74
No. of restraints	3	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.40, -0.44	0.20, -0.25
Absolute structure	–	Refined as a perfect inversion twin
Absolute structure parameter	–	0.5

Computer programs: *APEX3* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008) and *CIFFIX* (Parkin, 2013).

The Hooft (Hooft *et al.*, 2008) and Parsons (Parsons *et al.*, 2013) parameters [$y = 0.63$ (7); $z = 0.62$ (10), respectively], however, each gave a much stronger suggestion of twinning by inversion. Since the space group itself has a twofold parallel to its c axis, this results in a mirror operation (*i.e.* a twofold rotation combined with inversion). Thus, the twinning and disorder in **II** may effectively be treated by the same operation, not unlike that in uric acid dihydrate (Parkin & Hope, 1998a; Parkin, 2000). To ensure satisfactory refinement of disorder, constraints (*SHELXL* command EADP) were used to equalize displacement parameters of superimposed groups. Full occupancy (and major component for **II**) hydrogen atoms were found in difference-Fourier maps. Carbon-bound hydrogen atoms were included using riding models with constrained distances set to 0.95 Å (Csp^2H). In **I**, the water H atoms were refined but subject to distance and angle–distance restraints, while the hydroxyl H atom was refined freely. In **II**, for O–H and N–H groups, riding models that allowed the bond distance to refine were used. $U_{\text{iso}}(H)$ parameters were set to values of either $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ (OH only) of the attached atom. The structures were validated using *PLATON* and *checkCIF* (Spek, 2020).

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Synthesis and crystal structures of 3,6-dihydroxypicolinic acid and its labile intermediate dipotassium 3-hydroxy-6-(sulfonatoxy)pyridine-2-carboxylate monohydrate

Edward J. Behrman and Sean Parkin

Computing details

For both structures, data collection: *APEX3* (Bruker, 2016); cell refinement: *APEX3* (Bruker, 2016); data reduction: *APEX3* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELX* (Sheldrick, 2008) and *CIFFIX* (Parkin, 2013).

Dipotassium 3-hydroxy-6-(sulfonatoxy)pyridine-2-carboxylate monohydrate (I)

Crystal data

$2\text{K}^+\cdot\text{C}_6\text{H}_3\text{NO}_7\text{S}^{2-}\cdot\text{H}_2\text{O}$

$M_r = 329.37$

Monoclinic, $P2_1/c$

$a = 13.3366$ (4) Å

$b = 11.5467$ (3) Å

$c = 7.3078$ (2) Å

$\beta = 103.553$ (1)°

$V = 1094.02$ (5) Å³

$Z = 4$

$F(000) = 664$

$D_x = 2.000$ Mg m⁻³

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

Cell parameters from 9459 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 1.09$ mm⁻¹

$T = 90$ K

Block, colourless

$0.18 \times 0.16 \times 0.13$ mm

Data collection

Bruker D8 Venture dual source
diffractometer

Radiation source: microsource

Detector resolution: 7.41 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Krause *et al.*, 2015)

$T_{\min} = 0.793$, $T_{\max} = 0.862$

22347 measured reflections

2505 independent reflections

2423 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -17 \rightarrow 17$

$k = -14 \rightarrow 14$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.056$

$S = 1.08$

2505 reflections

174 parameters

3 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.7213P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0116 (12)

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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

Refinement. Refinement progress was checked using *Platon* (Spek, 2020) and by an *R*-tensor (Parkin, 2000). The final model was further checked with the IUCr utility *checkCIF*.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	−0.11303 (2)	0.44196 (2)	0.29817 (4)	0.01068 (9)
K2	0.65851 (2)	0.37254 (2)	0.80722 (4)	0.01048 (9)
S1	0.39446 (2)	0.56402 (3)	0.68497 (4)	0.00841 (9)
O1	0.18689 (8)	0.05598 (7)	0.56350 (13)	0.01168 (19)
H1O	0.1278 (15)	0.0662 (15)	0.584 (3)	0.018*
O2	0.32641 (7)	0.49448 (8)	0.50302 (12)	0.00997 (18)
O3	0.01000 (7)	0.34563 (8)	0.61547 (13)	0.01185 (19)
O4	0.02411 (7)	0.15242 (8)	0.61413 (13)	0.01227 (19)
O5	0.32663 (7)	0.58023 (8)	0.81136 (13)	0.01295 (19)
O6	0.41500 (7)	0.66929 (8)	0.59303 (13)	0.01295 (19)
O7	0.48251 (7)	0.49241 (8)	0.76027 (14)	0.0149 (2)
N1	0.20276 (8)	0.37108 (9)	0.55903 (14)	0.0088 (2)
C2	0.16613 (9)	0.26318 (11)	0.57169 (17)	0.0088 (2)
C3	0.22393 (10)	0.16468 (11)	0.55284 (17)	0.0093 (2)
C4	0.32289 (10)	0.17884 (11)	0.52150 (17)	0.0105 (2)
H4	0.363874	0.113328	0.509029	0.013*
C5	0.35984 (9)	0.28931 (11)	0.50905 (17)	0.0104 (2)
H5	0.426568	0.302283	0.487955	0.013*
C6	0.29543 (10)	0.38126 (10)	0.52862 (17)	0.0089 (2)
C7	0.05895 (9)	0.25453 (11)	0.60404 (17)	0.0096 (2)
O1W	0.85262 (7)	0.30218 (9)	0.79832 (14)	0.0151 (2)
H1W	0.8909 (13)	0.3167 (17)	0.726 (2)	0.023*
H2W	0.8914 (13)	0.3145 (17)	0.903 (2)	0.023*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.00957 (14)	0.00968 (14)	0.01288 (14)	0.00117 (9)	0.00285 (10)	−0.00086 (9)

K2	0.00967 (14)	0.01126 (14)	0.01074 (14)	0.00044 (9)	0.00281 (10)	0.00146 (9)
S1	0.00738 (15)	0.00825 (15)	0.00966 (15)	-0.00042 (10)	0.00215 (11)	-0.00085 (10)
O1	0.0117 (5)	0.0075 (4)	0.0169 (5)	-0.0005 (3)	0.0054 (4)	0.0000 (3)
O2	0.0121 (4)	0.0089 (4)	0.0087 (4)	-0.0027 (3)	0.0019 (3)	-0.0002 (3)
O3	0.0096 (4)	0.0123 (4)	0.0142 (4)	0.0010 (3)	0.0038 (3)	0.0002 (3)
O4	0.0109 (4)	0.0112 (4)	0.0154 (4)	-0.0017 (3)	0.0044 (3)	0.0009 (3)
O5	0.0123 (4)	0.0164 (5)	0.0111 (4)	-0.0004 (4)	0.0048 (3)	-0.0019 (4)
O6	0.0147 (5)	0.0093 (4)	0.0160 (4)	-0.0028 (3)	0.0059 (4)	-0.0002 (3)
O7	0.0108 (4)	0.0139 (4)	0.0180 (5)	0.0033 (3)	-0.0005 (4)	-0.0017 (4)
N1	0.0096 (5)	0.0093 (5)	0.0072 (5)	-0.0002 (4)	0.0015 (4)	-0.0006 (4)
C2	0.0086 (5)	0.0101 (6)	0.0076 (5)	-0.0008 (4)	0.0018 (4)	0.0005 (4)
C3	0.0112 (6)	0.0082 (6)	0.0078 (5)	-0.0010 (4)	0.0008 (4)	0.0000 (4)
C4	0.0104 (6)	0.0109 (6)	0.0101 (6)	0.0021 (4)	0.0023 (4)	-0.0014 (4)
C5	0.0087 (5)	0.0132 (6)	0.0096 (5)	-0.0002 (5)	0.0026 (4)	-0.0014 (4)
C6	0.0108 (6)	0.0082 (5)	0.0070 (5)	-0.0021 (4)	0.0010 (4)	-0.0001 (4)
C7	0.0091 (6)	0.0129 (6)	0.0065 (5)	-0.0007 (4)	0.0011 (4)	0.0002 (4)
O1W	0.0113 (5)	0.0165 (5)	0.0181 (5)	0.0005 (4)	0.0044 (4)	0.0003 (4)

Geometric parameters (Å, °)

K1—O4 ⁱ	2.7376 (9)	K2—K2 ^x	4.6216 (3)
K1—O3	2.7428 (10)	S1—O7	1.4361 (9)
K1—O5 ⁱⁱ	2.7843 (10)	S1—O6	1.4457 (9)
K1—N1 ⁱⁱ	2.7869 (11)	S1—O5	1.4486 (9)
K1—O3 ⁱⁱ	2.8099 (10)	S1—O2	1.6343 (9)
K1—O1W ⁱⁱⁱ	2.856 (1)	O1—C3	1.3577 (15)
K1—O1 ^{iv}	2.9102 (10)	O1—H1O	0.843 (19)
K1—S1 ⁱⁱ	3.7848 (4)	O2—C6	1.3968 (14)
K1—K1 ⁱⁱ	3.9268 (5)	O3—C7	1.2510 (16)
K1—K2 ^v	4.2041 (4)	O4—C7	1.2758 (16)
K1—K2 ⁱⁱⁱ	4.7508 (4)	N1—C6	1.3112 (16)
K2—O7	2.6769 (9)	N1—C2	1.3492 (16)
K2—O6 ^{vi}	2.7084 (10)	C2—C3	1.3988 (17)
K2—O1W	2.7286 (10)	C2—C7	1.5057 (17)
K2—O2 ^{vii}	2.7842 (9)	C3—C4	1.4010 (17)
K2—O5 ^{viii}	2.8012 (9)	C4—C5	1.3781 (18)
K2—O6 ^{vii}	2.8993 (10)	C4—H4	0.9500
K2—O1 ^{ix}	2.9525 (10)	C5—C6	1.3940 (17)
K2—S1 ^{vii}	3.5751 (4)	C5—H5	0.9500
K2—S1 ^{vi}	3.6348 (4)	O1W—H1W	0.832 (15)
K2—K2 ⁱ	4.6216 (3)	O1W—H2W	0.831 (15)
O4 ⁱ —K1—O3	85.28 (3)	O5 ^{viii} —K2—K1 ^{xi}	41.02 (2)
O4 ⁱ —K1—O5 ⁱⁱ	125.34 (3)	O6 ^{vii} —K2—K1 ^{xi}	154.00 (2)
O3—K1—O5 ⁱⁱ	125.08 (3)	O1 ^{ix} —K2—K1 ^{xi}	43.784 (19)
O4 ⁱ —K1—N1 ⁱⁱ	152.53 (3)	S1 ^{vii} —K2—K1 ^{xi}	138.793 (10)
O3—K1—N1 ⁱⁱ	102.82 (3)	S1 ^{vi} —K2—K1 ^{xi}	106.147 (8)
O5 ⁱⁱ —K1—N1 ⁱⁱ	71.26 (3)	O7—K2—K2 ⁱ	112.19 (2)

O4 ⁱ —K1—O3 ⁱⁱ	96.31 (3)	O6 ^{vi} —K2—K2 ⁱ	75.48 (2)
O3—K1—O3 ⁱⁱ	90.00 (3)	O1W—K2—K2 ⁱ	67.86 (2)
O5 ⁱⁱ —K1—O3 ⁱⁱ	123.94 (3)	O2 ^{vii} —K2—K2 ⁱ	71.370 (18)
N1 ⁱⁱ —K1—O3 ⁱⁱ	58.00 (3)	O5 ^{viii} —K2—K2 ⁱ	153.22 (2)
O4 ⁱ —K1—O1W ⁱⁱⁱ	74.51 (3)	O6 ^{vii} —K2—K2 ⁱ	33.178 (19)
O3—K1—O1W ⁱⁱⁱ	70.34 (3)	O1 ^{ix} —K2—K2 ⁱ	124.254 (19)
O5 ⁱⁱ —K1—O1W ⁱⁱⁱ	75.87 (3)	S1 ^{vii} —K2—K2 ⁱ	50.703 (5)
N1 ⁱⁱ —K1—O1W ⁱⁱⁱ	132.96 (3)	S1 ^{vi} —K2—K2 ⁱ	56.517 (8)
O3 ⁱⁱ —K1—O1W ⁱⁱⁱ	158.67 (3)	K1 ^{xi} —K2—K2 ⁱ	131.084 (6)
O4 ⁱ —K1—O1 ^{iv}	81.77 (3)	O7—K2—K2 ^x	104.80 (2)
O3—K1—O1 ^{iv}	163.61 (3)	O6 ^{vi} —K2—K2 ^x	35.86 (2)
O5 ⁱⁱ —K1—O1 ^{iv}	71.02 (3)	O1W—K2—K2 ^x	90.71 (2)
N1 ⁱⁱ —K1—O1 ^{iv}	84.60 (3)	O2 ^{vii} —K2—K2 ^x	174.19 (2)
O3 ⁱⁱ —K1—O1 ^{iv}	81.53 (3)	O5 ^{viii} —K2—K2 ^x	49.13 (2)
O1W ⁱⁱⁱ —K1—O1 ^{iv}	115.26 (3)	O6 ^{vii} —K2—K2 ^x	129.27 (2)
O4 ⁱ —K1—S1 ⁱⁱ	142.24 (2)	O1 ^{ix} —K2—K2 ^x	108.403 (19)
O3—K1—S1 ⁱⁱ	111.50 (2)	S1 ^{vii} —K2—K2 ^x	152.157 (10)
O5 ⁱⁱ —K1—S1 ⁱⁱ	18.571 (19)	S1 ^{vi} —K2—K2 ^x	49.568 (8)
N1 ⁱⁱ —K1—S1 ⁱⁱ	59.06 (2)	K1 ^{xi} —K2—K2 ^x	64.932 (5)
O3 ⁱⁱ —K1—S1 ⁱⁱ	116.43 (2)	K2 ⁱ —K2—K2 ^x	104.485 (11)
O1W ⁱⁱⁱ —K1—S1 ⁱⁱ	79.72 (2)	O7—S1—O6	115.80 (6)
O1 ^{iv} —K1—S1 ⁱⁱ	84.87 (2)	O7—S1—O5	114.01 (6)
O4 ⁱ —K1—K1 ⁱⁱ	91.22 (2)	O6—S1—O5	113.72 (6)
O3—K1—K1 ⁱⁱ	45.69 (2)	O7—S1—O2	106.09 (5)
O5 ⁱⁱ —K1—K1 ⁱⁱ	143.23 (2)	O6—S1—O2	99.47 (5)
N1 ⁱⁱ —K1—K1 ⁱⁱ	77.04 (2)	O5—S1—O2	105.75 (5)
O3 ⁱⁱ —K1—K1 ⁱⁱ	44.305 (19)	O7—S1—K2 ^{vii}	117.03 (4)
O1W ⁱⁱⁱ —K1—K1 ⁱⁱ	115.57 (2)	O6—S1—K2 ^{vii}	51.28 (4)
O1 ^{iv} —K1—K1 ⁱⁱ	124.38 (2)	O5—S1—K2 ^{vii}	127.54 (4)
S1 ⁱⁱ —K1—K1 ⁱⁱ	125.061 (11)	O2—S1—K2 ^{vii}	48.78 (3)
O4 ⁱ —K1—K2 ^v	86.50 (2)	O7—S1—K2 ^{ix}	134.65 (4)
O3—K1—K2 ^v	144.54 (2)	O6—S1—K2 ^{ix}	40.71 (4)
O5 ⁱⁱ —K1—K2 ^v	41.328 (19)	O5—S1—K2 ^{ix}	73.18 (4)
N1 ⁱⁱ —K1—K2 ^v	100.27 (2)	O2—S1—K2 ^{ix}	114.92 (3)
O3 ⁱⁱ —K1—K2 ^v	125.21 (2)	K2 ^{vii} —S1—K2 ^{ix}	79.729 (8)
O1W ⁱⁱⁱ —K1—K2 ^v	74.21 (2)	O7—S1—K1 ⁱⁱ	134.83 (4)
O1 ^{iv} —K1—K2 ^v	44.587 (19)	O6—S1—K1 ⁱⁱ	109.13 (4)
S1 ⁱⁱ —K1—K2 ^v	59.892 (7)	O5—S1—K1 ⁱⁱ	37.75 (4)
K1 ⁱⁱ —K1—K2 ^v	168.952 (12)	O2—S1—K1 ⁱⁱ	69.61 (3)
O4 ⁱ —K1—K2 ⁱⁱⁱ	101.95 (2)	K2 ^{vii} —S1—K1 ⁱⁱ	94.176 (9)
O3—K1—K2 ⁱⁱⁱ	86.38 (2)	K2 ^{ix} —S1—K1 ⁱⁱ	79.600 (8)
O5 ⁱⁱ —K1—K2 ⁱⁱⁱ	46.95 (2)	C3—O1—K1 ^{xii}	114.60 (7)
N1 ⁱⁱ —K1—K2 ⁱⁱⁱ	104.70 (2)	C3—O1—K2 ^{vi}	116.45 (7)
O3 ⁱⁱ —K1—K2 ⁱⁱⁱ	161.00 (2)	K1 ^{xii} —O1—K2 ^{vi}	91.63 (3)
O1W ⁱⁱⁱ —K1—K2 ⁱⁱⁱ	30.91 (2)	C3—O1—H1O	104.4 (12)
O1 ^{iv} —K1—K2 ⁱⁱⁱ	106.07 (2)	K1 ^{xii} —O1—H1O	95.2 (12)
S1 ⁱⁱ —K1—K2 ⁱⁱⁱ	48.809 (6)	K2 ^{vi} —O1—H1O	131.0 (12)
K1 ⁱⁱ —K1—K2 ⁱⁱⁱ	129.234 (11)	C6—O2—S1	118.44 (7)

K2 ^v —K1—K2 ⁱⁱⁱ	61.786 (6)	C6—O2—K2 ^{vii}	134.86 (7)
O7—K2—O6 ^{vi}	96.93 (3)	S1—O2—K2 ^{vii}	105.02 (4)
O7—K2—O1W	163.59 (3)	C7—O3—K1	120.18 (8)
O6 ^{vi} —K2—O1W	98.84 (3)	C7—O3—K1 ⁱⁱ	120.90 (8)
O7—K2—O2 ^{vii}	80.73 (3)	K1—O3—K1 ⁱⁱ	90.00 (3)
O6 ^{vi} —K2—O2 ^{vii}	142.83 (3)	C7—O4—K1 ^x	133.68 (8)
O1W—K2—O2 ^{vii}	83.96 (3)	S1—O5—K1 ⁱⁱ	123.68 (5)
O7—K2—O5 ^{viii}	83.24 (3)	S1—O5—K2 ^{viii}	138.63 (5)
O6 ^{vi} —K2—O5 ^{viii}	81.17 (3)	K1 ⁱⁱ —O5—K2 ^{viii}	97.65 (3)
O1W—K2—O5 ^{viii}	103.61 (3)	S1—O6—K2 ^{ix}	118.92 (5)
O2 ^{vii} —K2—O5 ^{viii}	134.52 (3)	S1—O6—K2 ^{vii}	105.82 (5)
O7—K2—O6 ^{vii}	82.98 (3)	K2 ^{ix} —O6—K2 ^{vii}	110.96 (3)
O6 ^{vi} —K2—O6 ^{vii}	93.96 (2)	S1—O7—K2	163.84 (6)
O1W—K2—O6 ^{vii}	91.42 (3)	C6—N1—C2	117.72 (11)
O2 ^{vii} —K2—O6 ^{vii}	48.87 (3)	C6—N1—K1 ⁱⁱ	119.90 (8)
O5 ^{viii} —K2—O6 ^{vii}	164.72 (3)	C2—N1—K1 ⁱⁱ	119.70 (8)
O7—K2—O1 ^{ix}	101.29 (3)	N1—C2—C3	121.82 (11)
O6 ^{vi} —K2—O1 ^{ix}	143.63 (3)	N1—C2—C7	116.38 (11)
O1W—K2—O1 ^{ix}	68.03 (3)	C3—C2—C7	121.79 (11)
O2 ^{vii} —K2—O1 ^{ix}	71.74 (3)	O1—C3—C2	121.99 (11)
O5 ^{viii} —K2—O1 ^{ix}	70.16 (3)	O1—C3—C4	119.11 (11)
O6 ^{vii} —K2—O1 ^{ix}	119.21 (3)	C2—C3—C4	118.90 (11)
O7—K2—S1 ^{vii}	78.73 (2)	C5—C4—C3	118.94 (11)
O6 ^{vi} —K2—S1 ^{vii}	116.72 (2)	C5—C4—H4	120.5
O1W—K2—S1 ^{vii}	90.11 (2)	C3—C4—H4	120.5
O2 ^{vii} —K2—S1 ^{vii}	26.201 (18)	C4—C5—C6	117.37 (11)
O5 ^{viii} —K2—S1 ^{vii}	155.84 (2)	C4—C5—H5	121.3
O6 ^{vii} —K2—S1 ^{vii}	22.895 (18)	C6—C5—H5	121.3
O1 ^{ix} —K2—S1 ^{vii}	97.67 (2)	N1—C6—C5	125.24 (11)
O7—K2—S1 ^{vi}	109.94 (2)	N1—C6—O2	115.26 (11)
O6 ^{vi} —K2—S1 ^{vi}	20.38 (2)	C5—C6—O2	119.36 (11)
O1W—K2—S1 ^{vi}	84.12 (2)	O3—C7—O4	124.78 (11)
O2 ^{vii} —K2—S1 ^{vi}	127.21 (2)	O3—C7—C2	118.96 (11)
O5 ^{viii} —K2—S1 ^{vi}	98.27 (2)	O4—C7—C2	116.25 (11)
O6 ^{vii} —K2—S1 ^{vi}	80.302 (19)	K2—O1W—K1 ^{xiii}	116.56 (4)
O1 ^{ix} —K2—S1 ^{vi}	145.27 (2)	K2—O1W—H1W	132.9 (13)
S1 ^{vii} —K2—S1 ^{vi}	102.902 (10)	K1 ^{xiii} —O1W—H1W	94.4 (14)
O7—K2—K1 ^{xi}	116.69 (2)	K2—O1W—H2W	108.4 (13)
O6 ^{vi} —K2—K1 ^{xi}	99.86 (2)	K1 ^{xiii} —O1W—H2W	96.0 (14)
O1W—K2—K1 ^{xi}	64.86 (2)	H1W—O1W—H2W	102.0 (15)
O2 ^{vii} —K2—K1 ^{xi}	114.43 (2)		
O7—S1—O2—C6	55.28 (10)	K1 ⁱⁱ —S1—O7—K2	142.06 (18)
O6—S1—O2—C6	175.77 (9)	C6—N1—C2—C3	-0.18 (17)
O5—S1—O2—C6	-66.14 (10)	K1 ⁱⁱ —N1—C2—C3	-161.62 (9)
K2 ^{vii} —S1—O2—C6	167.38 (11)	C6—N1—C2—C7	-179.2 (1)
K2 ^{ix} —S1—O2—C6	-144.57 (8)	K1 ⁱⁱ —N1—C2—C7	19.36 (14)
K1 ⁱⁱ —S1—O2—C6	-77.22 (8)	K1 ^{xii} —O1—C3—C2	101.95 (11)

O7—S1—O2—K2 ^{vii}	-112.10 (5)	K2 ^{vi} —O1—C3—C2	-152.82 (9)
O6—S1—O2—K2 ^{vii}	8.39 (5)	K1 ^{xii} —O1—C3—C4	-77.87 (12)
O5—S1—O2—K2 ^{vii}	126.48 (5)	K2 ^{vi} —O1—C3—C4	27.36 (14)
K2 ^{ix} —S1—O2—K2 ^{vii}	48.05 (4)	N1—C2—C3—O1	-179.28 (11)
K1 ⁱⁱ —S1—O2—K2 ^{vii}	115.40 (3)	C7—C2—C3—O1	-0.31 (18)
O7—S1—O5—K1 ⁱⁱ	-133.28 (6)	N1—C2—C3—C4	0.54 (18)
O6—S1—O5—K1 ⁱⁱ	90.99 (7)	C7—C2—C3—C4	179.51 (11)
O2—S1—O5—K1 ⁱⁱ	-17.12 (7)	O1—C3—C4—C5	179.41 (11)
K2 ^{vii} —S1—O5—K1 ⁱⁱ	32.58 (8)	C2—C3—C4—C5	-0.41 (18)
K2 ^{ix} —S1—O5—K1 ⁱⁱ	94.73 (5)	C3—C4—C5—C6	-0.03 (18)
O7—S1—O5—K2 ^{viii}	43.85 (10)	C2—N1—C6—C5	-0.32 (18)
O6—S1—O5—K2 ^{viii}	-91.88 (9)	K1 ⁱⁱ —N1—C6—C5	161.09 (9)
O2—S1—O5—K2 ^{viii}	160.01 (7)	C2—N1—C6—O2	175.49 (10)
K2 ^{vii} —S1—O5—K2 ^{viii}	-150.29 (5)	K1 ⁱⁱ —N1—C6—O2	-23.10 (13)
K2 ^{ix} —S1—O5—K2 ^{viii}	-88.14 (7)	C4—C5—C6—N1	0.42 (19)
K1 ⁱⁱ —S1—O5—K2 ^{viii}	177.13 (12)	C4—C5—C6—O2	-175.23 (11)
O7—S1—O6—K2 ^{ix}	-129.41 (6)	S1—O2—C6—N1	94.96 (11)
O5—S1—O6—K2 ^{ix}	5.50 (8)	K2 ^{vii} —O2—C6—N1	-102.36 (12)
O2—S1—O6—K2 ^{ix}	117.46 (5)	S1—O2—C6—C5	-88.96 (12)
K2 ^{vii} —S1—O6—K2 ^{ix}	125.55 (7)	K2 ^{vii} —O2—C6—C5	73.72 (14)
K1 ⁱⁱ —S1—O6—K2 ^{ix}	45.88 (6)	K1—O3—C7—O4	-88.64 (13)
O7—S1—O6—K2 ^{vii}	105.04 (6)	K1 ⁱⁱ —O3—C7—O4	160.99 (9)
O5—S1—O6—K2 ^{vii}	-120.05 (5)	K1—O3—C7—C2	89.91 (11)
O2—S1—O6—K2 ^{vii}	-8.09 (5)	K1 ⁱⁱ —O3—C7—C2	-20.46 (14)
K2 ^{ix} —S1—O6—K2 ^{vii}	-125.55 (7)	K1 ^x —O4—C7—O3	-30.63 (18)
K1 ⁱⁱ —S1—O6—K2 ^{vii}	-79.67 (4)	K1 ^x —O4—C7—C2	150.78 (8)
O6—S1—O7—K2	-44.2 (2)	N1—C2—C7—O3	0.67 (17)
O5—S1—O7—K2	-179.00 (19)	C3—C2—C7—O3	-178.36 (11)
O2—S1—O7—K2	65.0 (2)	N1—C2—C7—O4	179.34 (10)
K2 ^{vii} —S1—O7—K2	13.6 (2)	C3—C2—C7—O4	0.31 (17)
K2 ^{ix} —S1—O7—K2	-89.3 (2)		

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x, -y+1, -z+1$; (iii) $x-1, -y+1/2, z-1/2$; (iv) $-x, y+1/2, -z+1/2$; (v) $x-1, y, z-1$; (vi) $-x+1, y-1/2, -z+3/2$; (vii) $-x+1, -y+1, -z+1$; (viii) $-x+1, -y+1, -z+2$; (ix) $-x+1, y+1/2, -z+3/2$; (x) $x, -y+1/2, z+1/2$; (xi) $x+1, y, z+1$; (xii) $-x, y-1/2, -z+1/2$; (xiii) $x+1, -y+1/2, z+1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O4	0.843 (19)	1.760 (19)	2.5429 (13)	153.6 (17)
C4—H4 \cdots O5 ⁱ	0.95	2.64	3.3682 (16)	133
C5—H5 \cdots O6 ^{vii}	0.95	2.35	3.2943 (15)	175
O1W—H1W \cdots O3 ^{xiv}	0.83 (2)	1.97 (2)	2.7852 (13)	165 (2)
O1W—H2W \cdots O4 ^{xiii}	0.83 (2)	2.09 (2)	2.8910 (14)	161 (2)

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (vii) $-x+1, -y+1, -z+1$; (xiii) $x+1, -y+1/2, z+1/2$; (xiv) $x+1, y, z$.

3-Hydroxy-6-oxo-1,6-dihydropyridine-2-carboxylic acid (II)

Crystal data

$C_6H_5NO_4$	$D_x = 1.693 \text{ Mg m}^{-3}$
$M_r = 155.11$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
Orthorhombic, $Abm2$	Cell parameters from 3820 reflections
$a = 10.2045 (6) \text{ \AA}$	$\theta = 4.3\text{--}78.5^\circ$
$b = 6.1282 (4) \text{ \AA}$	$\mu = 1.27 \text{ mm}^{-1}$
$c = 9.7293 (6) \text{ \AA}$	$T = 90 \text{ K}$
$V = 608.42 (7) \text{ \AA}^3$	Plate, colourless
$Z = 4$	$0.14 \times 0.10 \times 0.02 \text{ mm}$
$F(000) = 320$	

Data collection

Bruker D8 Venture dual source diffractometer	4025 measured reflections
Radiation source: microsource	700 independent reflections
Detector resolution: $7.41 \text{ pixels mm}^{-1}$	690 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.025$
Absorption correction: multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	$\theta_{\text{max}} = 77.8^\circ$, $\theta_{\text{min}} = 4.3^\circ$
$T_{\text{min}} = 0.799$, $T_{\text{max}} = 0.971$	$h = -11 \rightarrow 12$
	$k = -7 \rightarrow 7$
	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.050P)^2 + 0.0512P]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\text{max}} = 0.024$
700 reflections	$\Delta\rho_{\text{max}} = 0.20 \text{ e \AA}^{-3}$
74 parameters	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
4 restraints	Absolute structure: Refined as a perfect inversion twin
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.5
Secondary atom site location: difference Fourier map	

Special details

Experimental. The crystal was mounted using polyisobutene oil on the tip of a fine glass fibre, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid-nitrogen based cryostat (Hope, 1994; Parkin & Hope, 1998).

Diffraction data were collected with the crystal at 90K, which is standard practice in this laboratory for the majority of flash-cooled crystals.

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

Refinement. Refined as a two-component perfect inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.3327 (2)	0.250000	0.44103 (19)	0.0146 (4)	0.953 (3)
H1N	0.421 (3)	0.25000 (2)	0.3976 (15)	0.017*	0.953 (3)

C2	0.3260 (2)	0.250000	0.5827 (2)	0.0131 (5)	0.953 (3)
C3	0.2033 (3)	0.250000	0.6458 (3)	0.0148 (5)	0.953 (3)
O1	0.19022 (19)	0.250000	0.7831 (2)	0.0188 (4)	0.953 (3)
H1O	0.269 (4)	0.25000 (2)	0.8219 (19)	0.028*	0.953 (3)
C4	0.0919 (3)	0.250000	0.5626 (3)	0.0194 (6)	0.953 (3)
H4	0.007769	0.250000	0.604343	0.023*	0.953 (3)
C5	0.1011 (2)	0.250000	0.4226 (3)	0.0191 (5)	0.953 (3)
H5	0.024166	0.250000	0.367711	0.023*	0.953 (3)
C6	0.2280 (2)	0.250000	0.3592 (3)	0.0154 (5)	0.953 (3)
O2	0.2369 (2)	0.250000	0.22580 (18)	0.0186 (4)	0.953 (3)
H2O	0.326 (3)	0.25000 (2)	0.200 (1)	0.028*	0.953 (3)
C7	0.4488 (2)	0.250000	0.6616 (2)	0.0158 (5)	0.953 (3)
O3	0.55590 (18)	0.250000	0.59684 (19)	0.0182 (4)	0.953 (3)
O4	0.43850 (17)	0.250000	0.7906 (2)	0.0224 (5)	0.953 (3)
N1'	0.3327 (2)	0.250000	0.55897 (19)	0.0131 (5)	0.047 (3)
H1'N	0.421 (3)	0.25000 (2)	0.6024 (16)	0.016*	0.047 (3)
C2'	0.3260 (2)	0.250000	0.4173 (2)	0.0146 (4)	0.047 (3)
C3'	0.2033 (3)	0.250000	0.3542 (3)	0.0154 (5)	0.047 (3)
O1'	0.19022 (19)	0.250000	0.2169 (2)	0.0186 (4)	0.047 (3)
H1'O	0.269 (4)	0.25000 (2)	0.178 (2)	0.028*	0.047 (3)
C4'	0.0919 (3)	0.250000	0.4374 (3)	0.0191 (5)	0.047 (3)
H4'	0.007769	0.250000	0.395657	0.023*	0.047 (3)
C5'	0.1011 (2)	0.250000	0.5774 (3)	0.0194 (6)	0.047 (3)
H5'	0.024166	0.250000	0.632289	0.023*	0.047 (3)
C6'	0.2280 (2)	0.250000	0.6408 (3)	0.0148 (5)	0.047 (3)
O2'	0.2369 (2)	0.250000	0.77420 (18)	0.0188 (4)	0.047 (3)
H2'O	0.326 (4)	0.25000 (2)	0.8001 (11)	0.028*	0.047 (3)
C7'	0.4488 (2)	0.250000	0.3384 (2)	0.0158 (5)	0.047 (3)
O3'	0.55590 (18)	0.250000	0.40316 (19)	0.0182 (4)	0.047 (3)
O4'	0.43850 (17)	0.250000	0.2094 (2)	0.0224 (5)	0.047 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0142 (9)	0.0190 (8)	0.0105 (11)	0.000	0.0000 (9)	0.000
C2	0.0127 (12)	0.0155 (9)	0.0112 (10)	0.000	-0.0016 (9)	0.000
C3	0.0151 (10)	0.0180 (11)	0.0113 (11)	0.000	0.0040 (8)	0.000
O1	0.0167 (9)	0.0274 (9)	0.0123 (8)	0.000	0.0041 (7)	0.000
C4	0.0159 (12)	0.0222 (10)	0.0202 (13)	0.000	0.0025 (10)	0.000
C5	0.0150 (11)	0.0259 (10)	0.0166 (10)	0.000	-0.0017 (9)	0.000
C6	0.0150 (12)	0.017 (1)	0.0141 (12)	0.000	-0.0031 (9)	0.000
O2	0.0163 (9)	0.0295 (8)	0.0101 (8)	0.000	0.0003 (6)	0.000
C7	0.0167 (10)	0.0196 (12)	0.0112 (14)	0.000	-0.0002 (9)	0.000
O3	0.0141 (8)	0.0268 (7)	0.0137 (8)	0.000	-0.0008 (6)	0.000
O4	0.0148 (12)	0.0368 (11)	0.0157 (9)	0.000	-0.0014 (7)	0.000
N1'	0.0127 (12)	0.0155 (9)	0.0112 (10)	0.000	-0.0016 (9)	0.000
C2'	0.0142 (9)	0.0190 (8)	0.0105 (11)	0.000	0.0000 (9)	0.000
C3'	0.0150 (12)	0.017 (1)	0.0141 (12)	0.000	-0.0031 (9)	0.000

O1'	0.0163 (9)	0.0295 (8)	0.0101 (8)	0.000	0.0003 (6)	0.000
C4'	0.0150 (11)	0.0259 (10)	0.0166 (10)	0.000	-0.0017 (9)	0.000
C5'	0.0159 (12)	0.0222 (10)	0.0202 (13)	0.000	0.0025 (10)	0.000
C6'	0.0151 (10)	0.0180 (11)	0.0113 (11)	0.000	0.0040 (8)	0.000
O2'	0.0167 (9)	0.0274 (9)	0.0123 (8)	0.000	0.0041 (7)	0.000
C7'	0.0167 (10)	0.0196 (12)	0.0112 (14)	0.000	-0.0002 (9)	0.000
O3'	0.0141 (8)	0.0268 (7)	0.0137 (8)	0.000	-0.0008 (6)	0.000
O4'	0.0148 (12)	0.0368 (11)	0.0157 (9)	0.000	-0.0014 (7)	0.000

Geometric parameters (Å, °)

N1—C6	1.333 (3)	N1'—C6'	1.333 (3)
N1—C2	1.381 (3)	N1'—C2'	1.381 (3)
N1—H1N	0.99 (3)	N1'—H1'N	0.99 (4)
C2—C3	1.394 (3)	C2'—C3'	1.394 (3)
C2—C7	1.470 (3)	C2'—C7'	1.470 (3)
C3—O1	1.342 (3)	C3'—O1'	1.342 (3)
C3—C4	1.395 (4)	C3'—C4'	1.395 (4)
O1—H1O	0.89 (4)	O1'—H1'O	0.89 (4)
C4—C5	1.365 (3)	C4'—C5'	1.365 (3)
C4—H4	0.9500	C4'—H4'	0.9500
C5—C6	1.434 (3)	C5'—C6'	1.434 (3)
C5—H5	0.9500	C5'—H5'	0.9500
C6—O2	1.301 (3)	C6'—O2'	1.301 (3)
O2—H2O	0.94 (4)	O2'—H2'O	0.94 (4)
C7—O4	1.259 (3)	C7'—O4'	1.259 (3)
C7—O3	1.262 (3)	C7'—O3'	1.262 (3)
C6—N1—C2	123.81 (19)	C6'—N1'—C2'	123.81 (19)
C6—N1—H1N	118.1	C6'—N1'—H1'N	118.1
C2—N1—H1N	118.1	C2'—N1'—H1'N	118.1
N1—C2—C3	119.0 (2)	N1'—C2'—C3'	119.0 (2)
N1—C2—C7	118.6 (2)	N1'—C2'—C7'	118.6 (2)
C3—C2—C7	122.41 (19)	C3'—C2'—C7'	122.41 (19)
O1—C3—C2	121.8 (2)	O1'—C3'—C2'	121.8 (2)
O1—C3—C4	119.8 (2)	O1'—C3'—C4'	119.8 (2)
C2—C3—C4	118.4 (2)	C2'—C3'—C4'	118.4 (2)
C3—O1—H1O	109.5	C3'—O1'—H1'O	109.5
C5—C4—C3	121.5 (2)	C5'—C4'—C3'	121.5 (2)
C5—C4—H4	119.2	C5'—C4'—H4'	119.2
C3—C4—H4	119.2	C3'—C4'—H4'	119.2
C4—C5—C6	119.5 (2)	C4'—C5'—C6'	119.5 (2)
C4—C5—H5	120.3	C4'—C5'—H5'	120.3
C6—C5—H5	120.3	C6'—C5'—H5'	120.3
O2—C6—N1	122.7 (2)	O2'—C6'—N1'	122.7 (2)
O2—C6—C5	119.5 (2)	O2'—C6'—C5'	119.5 (2)
N1—C6—C5	117.8 (2)	N1'—C6'—C5'	117.8 (2)
C6—O2—H2O	109.5	C6'—O2'—H2'O	109.5

O4—C7—O3	124.8 (2)	O4'—C7'—O3'	124.8 (2)
O4—C7—C2	116.7 (2)	O4'—C7'—C2'	116.7 (2)
O3—C7—C2	118.53 (19)	O3'—C7'—C2'	118.53 (19)
C6—N1—C2—C3	0.000 (1)	C6'—N1'—C2'—C3'	0.000 (1)
C6—N1—C2—C7	180.000 (1)	C6'—N1'—C2'—C7'	180.000 (1)
N1—C2—C3—O1	180.000 (1)	N1'—C2'—C3'—O1'	180.000 (1)
C7—C2—C3—O1	0.000 (1)	C7'—C2'—C3'—O1'	0.000 (1)
N1—C2—C3—C4	0.000 (1)	N1'—C2'—C3'—C4'	0.000 (1)
C7—C2—C3—C4	180.000 (1)	C7'—C2'—C3'—C4'	180.000 (1)
O1—C3—C4—C5	180.000 (1)	O1'—C3'—C4'—C5'	180.000 (1)
C2—C3—C4—C5	0.000 (1)	C2'—C3'—C4'—C5'	0.000 (1)
C3—C4—C5—C6	0.000 (1)	C3'—C4'—C5'—C6'	0.000 (1)
C2—N1—C6—O2	180.000 (1)	C2'—N1'—C6'—O2'	180.000 (1)
C2—N1—C6—C5	0.000 (1)	C2'—N1'—C6'—C5'	0.000 (1)
C4—C5—C6—O2	180.000 (1)	C4'—C5'—C6'—O2'	180.000 (1)
C4—C5—C6—N1	0.000 (1)	C4'—C5'—C6'—N1'	0.000 (1)
N1—C2—C7—O4	180.000 (1)	N1'—C2'—C7'—O4'	180.000 (1)
C3—C2—C7—O4	0.000 (1)	C3'—C2'—C7'—O4'	0.000 (1)
N1—C2—C7—O3	0.000 (1)	N1'—C2'—C7'—O3'	0.000 (1)
C3—C2—C7—O3	180.000 (1)	C3'—C2'—C7'—O3'	180.000 (1)

Hydrogen-bond geometry (\AA , $^\circ$)

The $D\cdots A$ distance for $C4-H4\cdots O2^{iii}$ is rather long, but within the bounds noted by Desiraju & Steiner (1999).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N \cdots O4 ⁱ	0.99	1.77	2.755 (3)	169
O1—H1O \cdots O4	0.89	1.76	2.535 (3)	145
C5—H5 \cdots O1 ⁱⁱ	0.95	2.34	3.269 (3)	166
C4—H4 \cdots O2 ⁱⁱⁱ	0.95	2.76	3.712 (4)	180
O2—H2O \cdots O3 ⁱ	0.94	1.57	2.459 (3)	156
O2—H2O \cdots O4 ⁱ	0.94	2.56	3.372 (3)	144

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