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Pyridine-4-carboxamidoxime *N*-oxide

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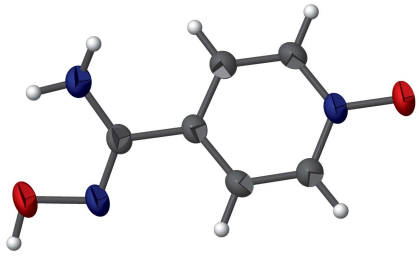
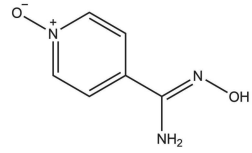
Our work in the area of synthesis of metal–organic frameworks (MOFs) based on organic *N*-oxides led to the crystallization of pyridine-4-carboxamidoxime *N*-oxide. Herein we report the first crystal structure of the title compound, $C_6H_7N_3O_2$ [systematic name: (*Z*)-4-(*N*′-hydroxycarbamimidoyl)pyridine *N*-oxide]. The hydroxycarbamimidoyl group is essentially coplanar with the aromatic ring, r.m.s.d. = 0.112 Å. The compound crystallizes in hydrogen-bonding layers built from the formation of strong O—H···O hydrogen bonds between the oxime oxygen atom and the oxygen atom of the *N*-oxide, and the formation of N—H···O hydrogen bonds between one amine nitrogen atom and the *N*-oxide oxygen atom. These combined build $R_4^3(24)$ ring motifs in the crystal. The crystal structure has no π–π interactions.

3D view



Chemical scheme



Structure description

Since their first reported syntheses (Meisenheimer *et al.*, 1926), pyridine *N*-oxide and related compounds have garnered much interest in chemistry. We are particularly interested in their uses in coordination polymers and as potential catalysts. The utility of these aromatic *N*-oxides to facilitate organic oxotransfer reactions has been well documented over the years (see, for example: Espenson, 2003). Many of these reactions are actually catalyzed by transition-metal interactions with the *N*-oxide ligands (see, for example: Moustafa *et al.*, 2014). Others have reported their use as coordination polymers (Ren *et al.*, 2018). We have also previously reported *N*-oxides used in coordination polymers of Mn (Kang *et al.*, 2017 and Lynch *et al.*, 2018). In this work, the syntheses of metal complexes of the title compound were attempted (Mn, Cu, Ce, Nd, Er, and Pr) by mixing the halide or nitrate salts of the metals with the title compound in methanol; unfortunately, all resulting crystals were of the uncomplexed ligand.

Herein we report the first crystal structure of pyridine-4-carboxamidoxime *N*-oxide (Fig. 1), which crystallizes in the monoclinic space group $P2_1/c$. The molecule is nearly

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···O1^{i}	0.91 (3)	1.77 (3)	2.6747 (19)	172 (2)
N3—H3A···O1^{ii}	0.91 (2)	2.00 (2)	2.899 (2)	167 (2)

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

planar with a r.m.s.d. of 0.112 Å for all non-hydrogen atoms, with the carbamimidoyl group slightly rotated by 15.09 (8)° with respect to the pyridine ring plane. N1—O1 has a distance of 1.3226 (18) Å and is consistent with normal *N*-oxide distances. The crystal structure contains a strong intermolecular hydrogen bond between O2···O1^{i} which forms a chain running parallel to the *b* axis; the O2···O1^{i} separation is 2.6747 (19) Å. Another hydrogen bond is formed between N3···O1^{ii} which links neighboring chains together; the N3···O1^{ii} separation is 2.899 (2) Å [symmetry codes: (i) x, $y+1$, z; (ii) x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$, see Table 1].

These hydrogen bonds link four molecules together and form an $R_4^3(24)$ ring motif in the crystal. Each molecule is also part of four different $R(24)$ synthons, generating sheets of hydrogen-bonding molecules parallel to the (100) face of the unit cell (Fig. 2). There are no other short contacts or π–π interactions observed in the crystal.

Synthesis and crystallization

An amount of 0.025 g of pyridine-4-carboxamidoxime *N*-oxide (Alfa Aesar) was weighed and dissolved in a 25 ml beaker in enough methanol to form a solution that allowed to slowly evaporate at room temperature. The clear crystals were analyzed on a Rigaku Xtal Miniflex.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

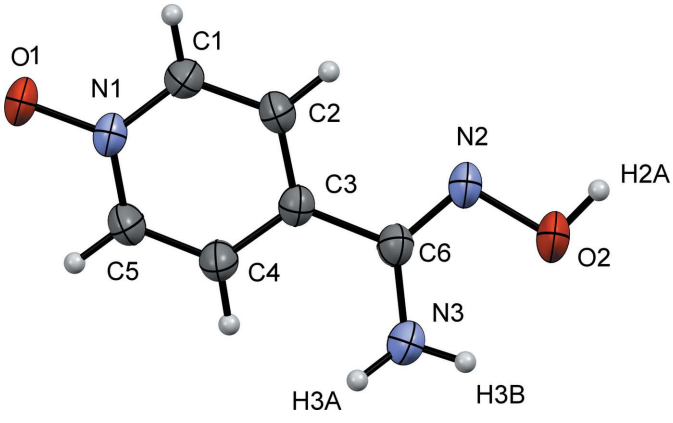


Figure 1
A view of the molecular structure of the title compound, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_7N_3O_2$
M_r	153.15
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	170
a, b, c (Å)	7.4130 (8), 9.2858 (7), 10.1238 (10)
β (°)	102.841 (10)
V (Å^3)	679.45 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.35 × 0.2 × 0.2
Data collection	
Diffractometer	Rigaku XtaLAB mini
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018)
T_{min}, T_{max}	0.940, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5858, 1238, 961
R_{int}	0.034
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.101, 1.04
No. of reflections	1238
No. of parameters	113
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.15

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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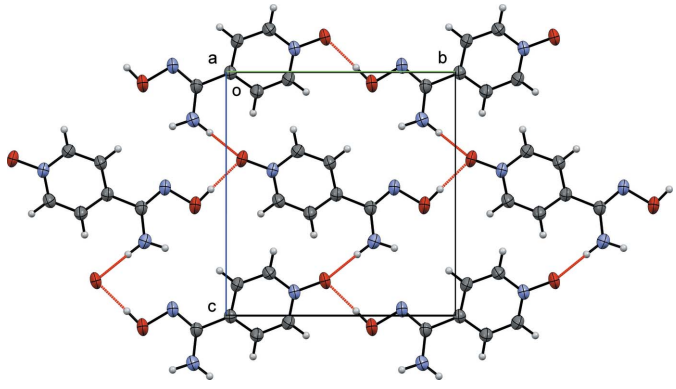

Figure 2
Crystal packing diagram of title compound viewed along [100]. Hydrogen bonds are colored red.

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full crystallographic data

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(*Z*)-4-(*N*′-Hydroxycarbamimidoyl)pyridine *N*-oxide

Crystal data

$C_6H_7N_3O_2$
M_r = 153.15
Monoclinic, $P2_1/c$
a = 7.4130 (8) Å
b = 9.2858 (7) Å
c = 10.1238 (10) Å
β = 102.841 (10)°
V = 679.45 (11) Å^3
Z = 4
$F(000)$ = 320
D_x = 1.497 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3017 reflections
θ = 2.1–32.6°
μ = 0.12 mm^{-1}
T = 170 K
Block, clear dark colourless
0.35 × 0.2 × 0.2 mm

Data collection

Rigaku XtaLAB mini diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite Monochromator monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω–scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
T_{min} = 0.940, T_{max} = 1.000
5858 measured reflections
1238 independent reflections
961 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 25.4°, θ_{min} = 2.8°
h = −8→8
k = −11→11
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.101
S = 1.04
1238 reflections
113 parameters
3 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.2172P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: SHELXL-2018/1 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.007 (2)

Special details

Refinement. All carbon-bound H atoms were positioned geometrically and refined as riding, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). N—H and O—H hydrogen atoms were refined with free coordinates and isotropic displacement parameters.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.7185 (2)	0.20253 (15)	0.40257 (15)	0.0361 (4)
C1	0.6365 (3)	0.31255 (19)	0.32458 (18)	0.0392 (5)
H1	0.565809	0.293556	0.235921	0.047*
O1	0.6953 (2)	0.06920 (13)	0.35596 (13)	0.0498 (4)
C2	0.6543 (2)	0.45181 (18)	0.37200 (17)	0.0371 (5)
H2	0.596971	0.528186	0.315518	0.044*
N2	0.7210 (2)	0.73345 (15)	0.47364 (16)	0.0434 (4)
O2	0.7388 (2)	0.86472 (14)	0.54650 (15)	0.0628 (5)
H2A	0.713 (3)	0.933 (3)	0.481 (2)	0.084 (8)*
C3	0.7554 (2)	0.48156 (17)	0.50187 (16)	0.0311 (4)
N3	0.8319 (3)	0.64526 (18)	0.69433 (16)	0.0450 (5)
H3A	0.807 (3)	0.572 (2)	0.748 (2)	0.066 (7)*
H3B	0.805 (3)	0.7337 (18)	0.722 (2)	0.059 (7)*
C4	0.8403 (3)	0.36626 (19)	0.57809 (18)	0.0382 (5)
H4	0.912748	0.382572	0.666750	0.046*
C5	0.8210 (3)	0.22887 (19)	0.52697 (19)	0.0407 (5)
H5	0.881159	0.151356	0.580441	0.049*
C6	0.7673 (2)	0.62923 (18)	0.55763 (17)	0.0337 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0481 (9)	0.0226 (7)	0.0376 (8)	0.0000 (7)	0.0092 (7)	−0.0035 (6)
C1	0.0496 (11)	0.0309 (10)	0.0334 (9)	0.0011 (8)	0.0016 (8)	−0.0018 (8)
O1	0.0790 (10)	0.0213 (7)	0.0470 (8)	−0.0002 (6)	0.0098 (7)	−0.0077 (6)
C2	0.0468 (11)	0.0263 (9)	0.0359 (10)	0.0036 (8)	0.0044 (8)	0.0038 (7)
N2	0.0670 (11)	0.0213 (8)	0.0419 (9)	−0.0020 (7)	0.0119 (8)	−0.0021 (7)
O2	0.1140 (14)	0.0213 (7)	0.0520 (9)	−0.0023 (8)	0.0158 (9)	−0.0038 (7)
C3	0.0334 (9)	0.0255 (9)	0.0348 (9)	−0.0015 (7)	0.0083 (8)	−0.0008 (7)
N3	0.0656 (11)	0.0286 (9)	0.0387 (9)	−0.0060 (8)	0.0068 (8)	−0.0042 (7)
C4	0.0446 (11)	0.0299 (9)	0.0360 (10)	0.0018 (8)	0.0002 (8)	−0.0005 (8)
C5	0.0517 (11)	0.0288 (10)	0.0377 (10)	0.0064 (8)	0.0018 (9)	0.0036 (8)
C6	0.0382 (10)	0.0265 (9)	0.0365 (10)	−0.0046 (7)	0.0088 (8)	−0.0013 (8)

Geometric parameters (Å, º)

N1—C1	1.350 (2)	O2—H2A	0.91 (3)
N1—O1	1.3226 (18)	C3—C4	1.386 (2)
N1—C5	1.341 (2)	C3—C6	1.478 (2)
C1—H1	0.9500	N3—H3A	0.912 (16)
C1—C2	1.376 (2)	N3—H3B	0.903 (15)
C2—H2	0.9500	N3—C6	1.368 (2)
C2—C3	1.389 (2)	C4—H4	0.9500
N2—O2	1.4156 (19)	C4—C5	1.372 (2)
N2—C6	1.284 (2)	C5—H5	0.9500

O1—N1—C1	119.59 (15)	C4—C3—C6	121.51 (15)
O1—N1—C5	120.50 (15)	H3A—N3—H3B	114 (2)
C5—N1—C1	119.91 (15)	C6—N3—H3A	116.5 (14)
N1—C1—H1	119.6	C6—N3—H3B	111.1 (14)
N1—C1—C2	120.77 (16)	C3—C4—H4	119.6
C2—C1—H1	119.6	C5—C4—C3	120.77 (16)
C1—C2—H2	119.8	C5—C4—H4	119.6
C1—C2—C3	120.47 (16)	N1—C5—C4	120.90 (16)
C3—C2—H2	119.8	N1—C5—H5	119.5
C6—N2—O2	108.89 (15)	C4—C5—H5	119.5
N2—O2—H2A	103.8 (16)	N2—C6—C3	117.52 (15)
C2—C3—C6	121.33 (15)	N2—C6—N3	124.75 (16)
C4—C3—C2	117.14 (16)	N3—C6—C3	117.71 (15)
N1—C1—C2—C3	−0.7 (3)	C2—C3—C6—N3	165.27 (17)
C1—N1—C5—C4	1.7 (3)	O2—N2—C6—C3	179.01 (15)
C1—C2—C3—C4	1.8 (3)	O2—N2—C6—N3	−3.0 (3)
C1—C2—C3—C6	−176.45 (16)	C3—C4—C5—N1	−0.5 (3)
O1—N1—C1—C2	178.21 (17)	C4—C3—C6—N2	165.18 (17)
O1—N1—C5—C4	−177.58 (17)	C4—C3—C6—N3	−13.0 (3)
C2—C3—C4—C5	−1.2 (3)	C5—N1—C1—C2	−1.1 (3)
C2—C3—C6—N2	−16.6 (3)	C6—C3—C4—C5	177.05 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O1^{i}	0.91 (3)	1.77 (3)	2.6747 (19)	172 (2)
N3—H3*A*···O1^{ii}	0.91 (2)	2.00 (2)	2.899 (2)	167 (2)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, −*y*+1/2, *z*+1/2.