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1-(3-Chloro-2-pyridyl)-3-methyl-1H-pyrazole-5-carboxylic acid

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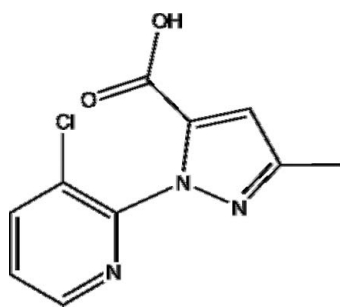
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.033; wR factor = 0.075; data-to-parameter ratio = 13.2.

In the title molecule, $\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$, the dihedral angle between the pyridine and pyrazole rings is $64.01(8)^\circ$. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link molecules, forming extended chains along [001]. These chains are, in turn, linked by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions, forming a two-dimensional network perpendicular to the b axis.

Related literature

The title compound was prepared adventitiously as part of our research program related to metal-organic frameworks. See: Lehn (1995) for background information. For the topologies of metal-organic frameworks, see: Kitakawa *et al.* (2004); Rosi *et al.* (2005); Subramanian & Zaworotko (1994).



Experimental

Crystal data

$\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$
 $M_r = 237.64$
 Orthorhombic, $Pca2_1$
 $a = 8.250(6)$ Å

$b = 11.232(8)$ Å
 $c = 11.942(8)$ Å
 $V = 1106.6(13)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹

$T = 296$ K
 $0.24 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.582$, $T_{\max} = 1.000$

5084 measured reflections
 1943 independent reflections
 1754 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.075$
 $S = 1.04$
 1943 reflections
 147 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.14$ e Å⁻³
 $\Delta\rho_{\min} = -0.13$ e Å⁻³
 Absolute structure: Flack (1983)
 912 Friedel pairs
 Flack parameter: 0.03 (7)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{N1}^{\text{i}}$	0.82	1.93	2.755 (3)	180
$\text{C2}-\text{H2A}\cdots\text{O1}^{\text{ii}}$	0.93	2.36	3.258 (4)	161

Symmetry codes: (i) $-x + \frac{3}{2}, y, z - \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y, z$.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008), PLATON (Spek, 2009) and DIAMOND (Brandenburg & Berndt, 1999); software used to prepare material for publication: SHELXTL.

We acknowledge financial support by the Scientific Research Foundation of the Civil Aviation University of China (No. 08CAUC-S01) and the Natural Science Foundation of Tianjin (09JCYBJC04200).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2933).

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supporting information

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1-(3-Chloro-2-pyridyl)-3-methyl-1H-pyrazole-5-carboxylic acid**Hua Cai, Ying Guo, Jian-Gang Li and Yao Wu****S1. Comment**

Recently, metal-organic frameworks (MOFs) have attracted great attention (Lehn *et al.*, 1995) because of their intriguing topologies (Subramanian *et al.*, 1994; Kitakawa *et al.*, 2004; Rosi *et al.*, 2005). During our efforts to investigate the assembly of metal-organic coordination frameworks, a new compound, (I), was accidentally generated under hydrothermal conditions and the crystal structure of the title compound (I) is described in this paper. The molecular structure of (I) is shown in Fig. 1. The dihedral angle between the pyridine and pyrazole rings is 64.01 (8)°. The dihedral angle between the mean plane of the pyrazole ring and the plane formed by the atoms C10/O1/O2 is 7.47 (18)°. In the crystal structure, O—H...N hydrogen bonds involving the carboxylic acid O atoms and the 3-chloropyridin-2-yl group N atoms, form one-dimensional chains along [001] (Fig. 2). These chains, are in turn, linked by weak intermolecular C—H...O interactions forming a two-dimensional network perpendicular to the b-axis (Fig. 3).

S2. Experimental

A mixture of Zn(OAc)₂·4H₂O (21.8 mg, 0.1 mmol), 1-(3-chloropyridin-2-yl)-3-methyl-pyrazole-5-carboxylic acid (23.8 mg, 0.1 mmol) in water (10 ml) was heated at 433 K for 3 d in a sealed Teflon-lined stainless steel vessel (20 ml) under autogenous pressure. After the reaction mixture was slowly cooled to room temperature at a rate of 5 K h⁻¹, pale-yellow lamellar single crystals suitable for X-ray diffraction were produced.

S3. Refinement

Although all H atoms were visible in difference Fourier maps, they were placed in calculated positions, with C-H distances in the range 0.93–0.96 Å and an O-H distance of 0.82 Å, and included in the final refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{C}_{\text{methyl}})$

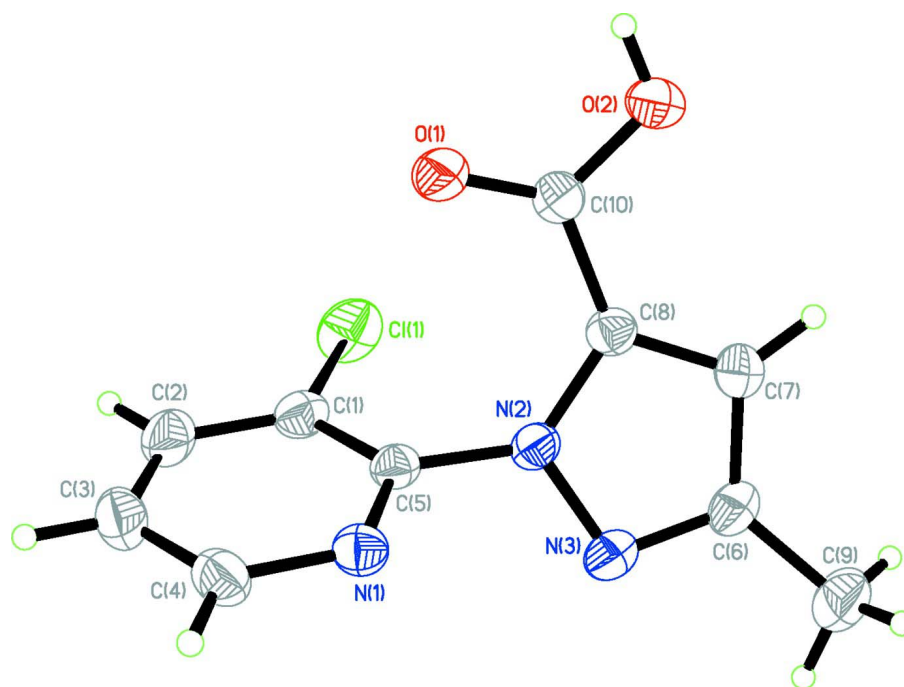


Figure 1

The molecular structure of (I) showing 30% probability ellipsoids.

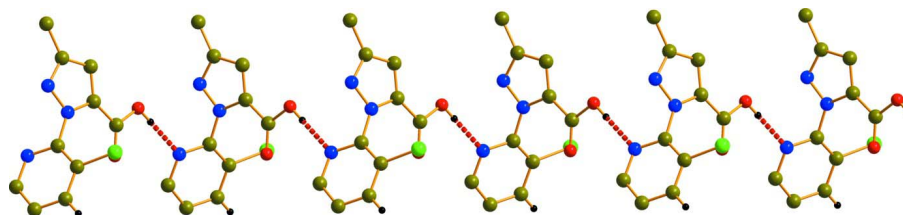


Figure 2

The one-dimensional chain structure of (I), showing O—H...N hydrogen bonds as red dashed lines.

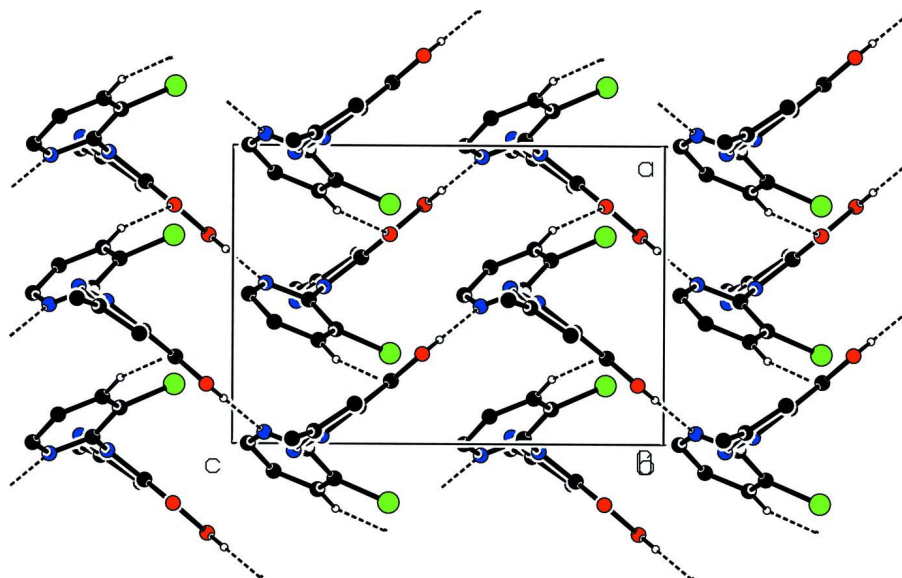


Figure 3

Part of the crystal structure with hydrogen bonds shown as dashed lines.

1-(3-Chloro-2-pyridyl)-3-methyl-1H-pyrazole-5-carboxylic acid

Crystal data

$C_{10}H_8ClN_3O_2$

$M_r = 237.64$

Orthorhombic, $Pca2_1$

Hall symbol: $P\ 2c\ -2ac$

$a = 8.250\ (6)\ \text{\AA}$

$b = 11.232\ (8)\ \text{\AA}$

$c = 11.942\ (8)\ \text{\AA}$

$V = 1106.6\ (13)\ \text{\AA}^3$

$Z = 4$

$F(000) = 488$

$D_x = 1.426\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2602 reflections

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

$\mu = 0.33\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.24 \times 0.20 \times 0.18\ \text{mm}$

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.582$, $T_{\max} = 1.000$

5084 measured reflections

1943 independent reflections

1754 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -9 \rightarrow 8$

$k = -11 \rightarrow 13$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.075$

$S = 1.04$

1943 reflections

147 parameters

1 restraint

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

$$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.1923P]$$

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

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

$$\Delta\rho_{\max} = 0.14 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983) 912 Friedel pairs

Absolute structure parameter: 0.03 (7)

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. 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.19679 (9)	0.18938 (6)	0.13597 (6)	0.0748 (2)
O1	0.7978 (2)	0.17726 (13)	0.1372 (2)	0.0622 (5)
O2	0.6983 (2)	0.34151 (14)	0.05851 (17)	0.0664 (5)
H2	0.6504	0.2936	0.0186	0.100*
N1	0.9622 (2)	0.18043 (16)	0.42451 (15)	0.0446 (5)
N2	0.9738 (2)	0.33015 (15)	0.29058 (16)	0.0414 (4)
N3	1.0231 (2)	0.42331 (17)	0.35467 (17)	0.0490 (5)
C1	1.1171 (3)	0.1403 (2)	0.26170 (19)	0.0484 (6)
C2	1.1532 (3)	0.0288 (2)	0.3012 (2)	0.0606 (7)
H2A	1.2178	-0.0224	0.2594	0.073*
C3	1.0928 (3)	-0.0067 (2)	0.4034 (3)	0.0625 (7)
H3	1.1145	-0.0823	0.4314	0.075*
C4	0.9994 (3)	0.0727 (2)	0.4629 (2)	0.0544 (6)
H4	0.9607	0.0501	0.5329	0.065*
C5	1.0179 (2)	0.21361 (19)	0.32469 (18)	0.0396 (5)
C6	0.9573 (3)	0.5193 (2)	0.3074 (2)	0.0502 (6)
C7	0.8657 (3)	0.4882 (2)	0.2137 (2)	0.0508 (6)
H7	0.8092	0.5395	0.1668	0.061*
C8	0.8758 (3)	0.36675 (19)	0.20469 (19)	0.0421 (5)
C9	0.9834 (4)	0.6389 (2)	0.3575 (3)	0.0786 (9)
H9A	1.0755	0.6363	0.4066	0.118*
H9B	0.8889	0.6617	0.3992	0.118*
H9C	1.0026	0.6958	0.2991	0.118*
C10	0.7890 (3)	0.28386 (18)	0.1310 (2)	0.0435 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0825 (5)	0.0840 (5)	0.0578 (4)	0.0041 (4)	0.0284 (4)	-0.0126 (4)
O1	0.0816 (12)	0.0439 (10)	0.0612 (10)	-0.0104 (8)	-0.0217 (10)	0.0019 (10)
O2	0.0833 (13)	0.0539 (10)	0.0618 (12)	-0.0028 (9)	-0.0294 (11)	0.0010 (9)

N1	0.0460 (11)	0.0480 (11)	0.0399 (11)	-0.0015 (8)	0.0012 (9)	0.0004 (8)
N2	0.0477 (11)	0.0391 (10)	0.0376 (10)	-0.0016 (8)	0.0009 (9)	-0.0041 (8)
N3	0.0497 (11)	0.0477 (11)	0.0496 (11)	-0.0037 (9)	-0.0004 (10)	-0.0108 (9)
C1	0.0471 (13)	0.0541 (14)	0.0441 (13)	0.0011 (11)	0.0002 (10)	-0.0101 (11)
C2	0.0564 (14)	0.0555 (15)	0.0701 (17)	0.0155 (12)	-0.0069 (14)	-0.0158 (13)
C3	0.0659 (17)	0.0482 (13)	0.0734 (18)	0.0074 (14)	-0.0155 (15)	0.0052 (13)
C4	0.0598 (15)	0.0549 (16)	0.0484 (13)	-0.0030 (13)	-0.0059 (11)	0.0096 (11)
C5	0.0368 (11)	0.0429 (12)	0.0391 (12)	-0.0007 (9)	-0.0034 (9)	-0.0053 (9)
C6	0.0511 (13)	0.0416 (13)	0.0578 (15)	-0.0040 (11)	0.0021 (12)	-0.0096 (11)
C7	0.0562 (14)	0.0425 (13)	0.0539 (13)	0.0012 (11)	-0.0029 (12)	0.0017 (11)
C8	0.0451 (12)	0.0438 (13)	0.0373 (11)	-0.0019 (10)	0.0012 (9)	-0.0007 (10)
C9	0.088 (2)	0.0546 (16)	0.093 (2)	0.0004 (16)	-0.0138 (19)	-0.0207 (16)
C10	0.0493 (12)	0.0425 (12)	0.0386 (11)	-0.0034 (10)	0.0030 (11)	0.0035 (12)

Geometric parameters (Å, °)

C11—C1	1.729 (3)	C2—H2A	0.9300
O1—C10	1.202 (2)	C3—C4	1.376 (4)
O2—C10	1.314 (3)	C3—H3	0.9300
O2—H2	0.8200	C4—H4	0.9300
N1—C4	1.330 (3)	C6—C7	1.394 (4)
N1—C5	1.331 (3)	C6—C9	1.486 (4)
N2—N3	1.359 (2)	C7—C8	1.371 (3)
N2—C8	1.369 (3)	C7—H7	0.9300
N2—C5	1.418 (3)	C8—C10	1.468 (3)
N3—C6	1.333 (3)	C9—H9A	0.9600
C1—C2	1.371 (4)	C9—H9B	0.9600
C1—C5	1.383 (3)	C9—H9C	0.9600
C2—C3	1.377 (4)		
C10—O2—H2	109.5	C1—C5—N2	123.0 (2)
C4—N1—C5	118.9 (2)	N3—C6—C7	111.0 (2)
N3—N2—C8	111.56 (16)	N3—C6—C9	120.1 (2)
N3—N2—C5	118.17 (18)	C7—C6—C9	128.9 (2)
C8—N2—C5	130.08 (18)	C8—C7—C6	106.2 (2)
C6—N3—N2	105.21 (18)	C8—C7—H7	126.9
C2—C1—C5	119.0 (2)	C6—C7—H7	126.9
C2—C1—C11	120.47 (19)	N2—C8—C7	106.01 (19)
C5—C1—C11	120.49 (18)	N2—C8—C10	123.1 (2)
C1—C2—C3	119.4 (2)	C7—C8—C10	130.4 (2)
C1—C2—H2A	120.3	C6—C9—H9A	109.5
C3—C2—H2A	120.3	C6—C9—H9B	109.5
C4—C3—C2	118.2 (2)	H9A—C9—H9B	109.5
C4—C3—H3	120.9	C6—C9—H9C	109.5
C2—C3—H3	120.9	H9A—C9—H9C	109.5
N1—C4—C3	122.7 (3)	H9B—C9—H9C	109.5
N1—C4—H4	118.6	O1—C10—O2	124.5 (2)
C3—C4—H4	118.6	O1—C10—C8	124.4 (3)

N1—C5—C1	121.6 (2)	O2—C10—C8	111.10 (19)
N1—C5—N2	115.29 (19)		
C8—N2—N3—C6	-0.9 (2)	C8—N2—C5—C1	69.0 (3)
C5—N2—N3—C6	-176.4 (2)	N2—N3—C6—C7	0.2 (3)
C5—C1—C2—C3	-1.3 (3)	N2—N3—C6—C9	178.8 (2)
C11—C1—C2—C3	177.8 (2)	N3—C6—C7—C8	0.6 (3)
C1—C2—C3—C4	-0.8 (4)	C9—C6—C7—C8	-177.9 (3)
C5—N1—C4—C3	-0.4 (4)	N3—N2—C8—C7	1.3 (2)
C2—C3—C4—N1	1.7 (4)	C5—N2—C8—C7	176.0 (2)
C4—N1—C5—C1	-1.9 (3)	N3—N2—C8—C10	-172.2 (2)
C4—N1—C5—N2	-179.44 (19)	C5—N2—C8—C10	2.6 (4)
C2—C1—C5—N1	2.8 (3)	C6—C7—C8—N2	-1.1 (2)
C11—C1—C5—N1	-176.29 (17)	C6—C7—C8—C10	171.7 (2)
C2—C1—C5—N2	-179.9 (2)	N2—C8—C10—O1	-1.5 (4)
C11—C1—C5—N2	1.0 (3)	C7—C8—C10—O1	-173.2 (3)
N3—N2—C5—N1	60.9 (3)	N2—C8—C10—O2	177.4 (2)
C8—N2—C5—N1	-113.5 (3)	C7—C8—C10—O2	5.7 (4)
N3—N2—C5—C1	-116.5 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots N1 ⁱ	0.82	1.93	2.755 (3)	180
C2—H2A \cdots O1 ⁱⁱ	0.93	2.36	3.258 (4)	161

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