

Diaquabis(5-phenyl-1*H*-pyrazole-3-carboxylato)copper(II)

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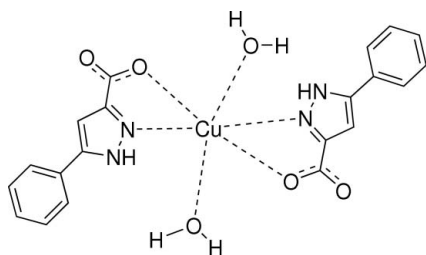
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 Key indicators: single-crystal X-ray study; $T = 292$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.037; wR factor = 0.084; data-to-parameter ratio = 15.0.

In the centrosymmetric title compound, $[\text{Cu}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$, the Cu^{II} ion occupies an inversion centre and exhibits a distorted octahedral geometry. The phenyl and pyrazole rings of the ligand are twisted by an angle of 11.36 (8)°. In the crystal structure, molecules are linked into a two-dimensional network parallel to the (010) plane by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For ligand preparation, see: Crane *et al.* (1999); Gharbaoui *et al.* (2007). For general background, see: van Herk *et al.* (2003); Knopp (1999).



Experimental

Crystal data

$[\text{Cu}(\text{C}_{10}\text{H}_7\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2]$
 $M_r = 473.92$
 Monoclinic, $P2_1/n$
 $a = 5.0443$ (6) Å
 $b = 32.161$ (4) Å
 $c = 6.3234$ (8) Å
 $\beta = 106.293$ (1)°

$V = 984.6$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.16$ mm⁻¹
 $T = 292$ (2) K
 $0.35 \times 0.25 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.690$, $T_{\text{max}} = 0.829$

8611 measured reflections
 2254 independent reflections

1907 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.084$
 $S = 1.08$
 2254 reflections
 150 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.9572 (17)	Cu1—O3	2.5400 (19)
Cu1—O1	1.9968 (14)		
N1—Cu1—N1 ⁱ	180	N1—Cu1—O3	87.85 (7)
N1—Cu1—O1 ⁱ	98.56 (6)	N1 ⁱ —Cu1—O3	92.15 (7)
N1—Cu1—O1	81.44 (6)	O1 ⁱ —Cu1—O3	91.56 (6)
O1 ⁱ —Cu1—O1	180	O1—Cu1—O3	88.44 (6)

Symmetry code: (i) $-x + 1, -y, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H1W}\cdots\text{O2}^{\text{ii}}$	0.83 (3)	1.88 (3)	2.679 (3)	161 (3)
$\text{N2}-\text{H2}\cdots\text{O3}^{\text{iii}}$	0.86	1.93	2.719 (3)	152
$\text{O3}-\text{H2W}\cdots\text{O1}^{\text{iv}}$	0.83 (3)	2.04 (3)	2.773 (3)	149 (3)

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

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); 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); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2551).

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supplementary materials

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Diaquabis(5-phenyl-1*H*-pyrazole-3-carboxylato)copper(II)

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Comment

Nicotinic acid as a hypolipidemic agent appears to have good potential to increase HDL cholesterol levels to a greater extent (Knopp, 1999). However, it has severe skin flushing side effect. In the search for novel agonists for nicotinic acid receptor, substituted pyrazole-3-carboxylic acids were found have substantial affinity for cloned G protein-coupled nicotinic acid receptor (van Herk *et al.*, 2003). We report here the crystal structure of the title Cu^{II} complex with 5-phenyl-1*H*-pyrazole-3-carboxylic acid.

The asymmetric unit contains one-half of a formula unit (Fig. 1). The Cu^{II} ion occupies an inversion centre and exhibits a distorted octahedral geometry. The phenyl (C5—C10) and pyrazole (N1/N2/C2/C3/C4) rings form a dihedral angle of 11.36 (8)°. The dihedral angle between the Cu1/O1/C1/C2/N1 and N1/N2/C2/C3/C4 planes is 3.8 (1)°.

The molecules are linked into a two-dimensional network parallel to the (0 1 0) plane by O—H⋯O and N—H⋯O hydrogen bonds (Table 2).

Experimental

5-Phenyl-1*H*-pyrazole-3-carboxylic acid was synthesized according to the reported procedure (Gharbaoui *et al.*, 2007; Crane *et al.*, 1999). 5-Phenyl-1*H*-pyrazole-3-carboxylic acid (1.0 g, 5.3 mmol) and Cu(OAc)₂·2H₂O (0.75 g, 2.7 mmol) were heated in H₂O (200 ml) for 4 h with stirring. The resulting precipitate was filtered off to obtain the title compound (1.0 g, 80%). Single crystals suitable for X-ray diffraction were obtained by recrystallization from dimethylformamide-water (1:1 v/v) solution.

Refinement

The water H atoms were located and isotropically refined, with the O—H and H⋯H distances restrained to 0.84 (1) and 1.37 (2) Å, respectively. The remaining H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

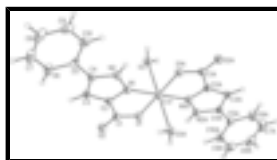


Fig. 1. The molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atomic numbering. Atoms labelled with the suffix A are generated by the symmetry operation $(-x + 1, -y, -z)$.

Diaquabis(5-phenyl-1H-pyrazole-3-carboxylato)copper(II)

Crystal data

[Cu(C₁₀H₇N₂O₂)₂(H₂O)₂]

$M_r = 473.92$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 5.0443$ (6) Å

$b = 32.161$ (4) Å

$c = 6.3234$ (8) Å

$\beta = 106.293$ (1)°

$V = 984.6$ (2) Å³

$Z = 2$

$F_{000} = 486$

$D_x = 1.599$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2772 reflections

$\theta = 2.5$ – 26.6 °

$\mu = 1.16$ mm⁻¹

$T = 292$ (2) K

Block, blue

$0.35 \times 0.25 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 292$ (2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.690$, $T_{\max} = 0.829$

8611 measured reflections

2254 independent reflections

1907 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 2.5$ °

$h = -6 \rightarrow 6$

$k = -41 \rightarrow 39$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.084$

$S = 1.08$

2254 reflections

150 parameters

3 restraints

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H atoms treated by a mixture of
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.72P]$$

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

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

$\Delta\rho_{\text{max}} = 0.34$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.0000	0.0000	0.03166 (13)
O1	0.3462 (3)	0.01796 (5)	0.2440 (2)	0.0325 (3)
O2	0.3301 (4)	0.07235 (5)	0.4604 (3)	0.0404 (4)
O3	0.0850 (4)	0.03336 (6)	-0.2706 (3)	0.0380 (4)
N1	0.6670 (4)	0.05536 (5)	0.0513 (3)	0.0294 (4)
N2	0.8212 (4)	0.08034 (5)	-0.0348 (3)	0.0301 (4)
H2	0.8956	0.0730	-0.1359	0.036*
C1	0.4084 (4)	0.05525 (7)	0.3144 (3)	0.0288 (5)
C2	0.5895 (4)	0.07783 (7)	0.2015 (3)	0.0277 (4)
C3	0.6964 (4)	0.11779 (7)	0.2111 (4)	0.0302 (5)
H3	0.6732	0.1395	0.3017	0.036*
C4	0.8454 (4)	0.11852 (6)	0.0569 (4)	0.0282 (4)
C5	1.0091 (5)	0.15138 (7)	-0.0085 (4)	0.0328 (5)
C6	1.0740 (6)	0.18727 (8)	0.1155 (5)	0.0473 (6)
H6	1.0067	0.1911	0.2368	0.057*
C7	1.2389 (7)	0.21770 (9)	0.0605 (6)	0.0641 (9)
H7	1.2821	0.2417	0.1454	0.077*
C8	1.3376 (6)	0.21240 (9)	-0.1183 (6)	0.0642 (9)
H8	1.4482	0.2328	-0.1543	0.077*
C9	1.2744 (6)	0.17720 (10)	-0.2448 (5)	0.0565 (8)
H9	1.3419	0.1738	-0.3663	0.068*
C10	1.1097 (5)	0.14664 (8)	-0.1918 (4)	0.0438 (6)
H10	1.0662	0.1229	-0.2786	0.053*
H1W	0.138 (6)	0.0417 (9)	-0.376 (4)	0.069 (10)*
H2W	-0.041 (5)	0.0163 (8)	-0.312 (5)	0.075 (11)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0386 (2)	0.0297 (2)	0.0341 (2)	-0.00911 (17)	0.02227 (17)	-0.00583 (17)
O1	0.0365 (9)	0.0338 (8)	0.0339 (8)	-0.0071 (7)	0.0207 (7)	-0.0019 (7)
O2	0.0523 (11)	0.0407 (9)	0.0388 (9)	-0.0031 (8)	0.0301 (8)	-0.0036 (7)

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O3	0.0416 (10)	0.0443 (10)	0.0361 (9)	-0.0093 (8)	0.0239 (8)	-0.0051 (8)
N1	0.0332 (10)	0.0304 (10)	0.0301 (9)	-0.0060 (7)	0.0177 (8)	-0.0028 (7)
N2	0.0334 (10)	0.0325 (10)	0.0311 (10)	-0.0064 (8)	0.0203 (8)	-0.0029 (8)
C1	0.0276 (11)	0.0349 (12)	0.0264 (11)	0.0006 (9)	0.0115 (9)	0.0032 (9)
C2	0.0286 (11)	0.0311 (11)	0.0260 (10)	0.0004 (8)	0.0119 (9)	-0.0003 (8)
C3	0.0315 (11)	0.0298 (11)	0.0320 (12)	0.0002 (9)	0.0133 (9)	-0.0033 (9)
C4	0.0282 (10)	0.0277 (11)	0.0296 (11)	0.0005 (8)	0.0094 (9)	0.0016 (9)
C5	0.0285 (11)	0.0303 (11)	0.0402 (12)	0.0008 (9)	0.0108 (9)	0.0071 (10)
C6	0.0478 (15)	0.0366 (14)	0.0641 (18)	-0.0063 (11)	0.0264 (13)	-0.0051 (12)
C7	0.0610 (19)	0.0357 (15)	0.104 (3)	-0.0135 (13)	0.0363 (19)	-0.0046 (15)
C8	0.0521 (18)	0.0476 (17)	0.101 (3)	-0.0060 (14)	0.0345 (18)	0.0248 (17)
C9	0.0530 (17)	0.0655 (19)	0.0588 (18)	-0.0018 (14)	0.0287 (14)	0.0232 (15)
C10	0.0481 (15)	0.0462 (15)	0.0411 (14)	-0.0060 (11)	0.0189 (12)	0.0055 (11)

Geometric parameters (\AA , $^\circ$)

Cu1—N1	1.9572 (17)	C3—C4	1.388 (3)
Cu1—N1 ⁱ	1.9573 (17)	C3—H3	0.93
Cu1—O1 ⁱ	1.9968 (14)	C4—C5	1.470 (3)
Cu1—O1	1.9968 (14)	C5—C6	1.382 (3)
Cu1—O3	2.5400 (19)	C5—C10	1.398 (3)
O1—C1	1.287 (3)	C6—C7	1.390 (4)
O2—C1	1.231 (3)	C6—H6	0.93
O3—H1W	0.827 (10)	C7—C8	1.368 (5)
O3—H2W	0.825 (10)	C7—H7	0.93
N1—C2	1.336 (3)	C8—C9	1.371 (5)
N1—N2	1.336 (2)	C8—H8	0.93
N2—C4	1.349 (3)	C9—C10	1.387 (3)
N2—H2	0.86	C9—H9	0.93
C1—C2	1.496 (3)	C10—H10	0.93
C2—C3	1.388 (3)		
N1—Cu1—N1 ⁱ	180	C3—C2—C1	135.23 (19)
N1—Cu1—O1 ⁱ	98.56 (6)	C4—C3—C2	105.36 (19)
N1 ⁱ —Cu1—O1 ⁱ	81.44 (6)	C4—C3—H3	127.3
N1—Cu1—O1	81.44 (6)	C2—C3—H3	127.3
N1 ⁱ —Cu1—O1	98.56 (6)	N2—C4—C3	106.56 (18)
O1 ⁱ —Cu1—O1	180	N2—C4—C5	121.60 (19)
N1—Cu1—O3	87.85 (7)	C3—C4—C5	131.8 (2)
N1 ⁱ —Cu1—O3	92.15 (7)	C6—C5—C10	118.6 (2)
O1 ⁱ —Cu1—O3	91.56 (6)	C6—C5—C4	120.2 (2)
O1—Cu1—O3	88.44 (6)	C10—C5—C4	121.2 (2)
C1—O1—Cu1	115.29 (13)	C5—C6—C7	120.6 (3)
Cu1—O3—H1W	107 (2)	C5—C6—H6	119.7
Cu1—O3—H2W	110 (2)	C7—C6—H6	119.7
H1W—O3—H2W	111 (2)	C8—C7—C6	120.1 (3)
C2—N1—N2	106.51 (17)	C8—C7—H7	120.0
C2—N1—Cu1	114.33 (14)	C6—C7—H7	120.0

N2—N1—Cu1	138.77 (14)	C7—C8—C9	120.4 (3)
N1—N2—C4	111.41 (17)	C7—C8—H8	119.8
N1—N2—H2	124.3	C9—C8—H8	119.8
C4—N2—H2	124.3	C8—C9—C10	120.1 (3)
O2—C1—O1	125.27 (19)	C8—C9—H9	120.0
O2—C1—C2	120.58 (19)	C10—C9—H9	120.0
O1—C1—C2	114.14 (18)	C9—C10—C5	120.3 (3)
N1—C2—C3	110.16 (18)	C9—C10—H10	119.9
N1—C2—C1	114.60 (18)	C5—C10—H10	119.9
N1—Cu1—O1—C1	2.75 (15)	O1—C1—C2—C3	176.1 (2)
N1 ⁱ —Cu1—O1—C1	-177.25 (15)	N1—C2—C3—C4	0.0 (2)
O3—Cu1—O1—C1	-85.31 (15)	C1—C2—C3—C4	-178.6 (2)
O1 ⁱ —Cu1—N1—C2	175.94 (15)	N1—N2—C4—C3	-0.1 (2)
O1—Cu1—N1—C2	-4.06 (15)	N1—N2—C4—C5	179.06 (19)
O3—Cu1—N1—C2	84.69 (16)	C2—C3—C4—N2	0.1 (2)
O1 ⁱ —Cu1—N1—N2	4.4 (2)	C2—C3—C4—C5	-179.0 (2)
O1—Cu1—N1—N2	-175.6 (2)	N2—C4—C5—C6	-167.6 (2)
O3—Cu1—N1—N2	-86.8 (2)	C3—C4—C5—C6	11.3 (4)
C2—N1—N2—C4	0.1 (2)	N2—C4—C5—C10	10.3 (3)
Cu1—N1—N2—C4	172.02 (17)	C3—C4—C5—C10	-170.8 (2)
Cu1—O1—C1—O2	178.61 (18)	C10—C5—C6—C7	-0.8 (4)
Cu1—O1—C1—C2	-1.0 (2)	C4—C5—C6—C7	177.2 (3)
N2—N1—C2—C3	0.0 (2)	C5—C6—C7—C8	0.3 (5)
Cu1—N1—C2—C3	-174.22 (15)	C6—C7—C8—C9	0.2 (5)
N2—N1—C2—C1	178.84 (17)	C7—C8—C9—C10	-0.1 (5)
Cu1—N1—C2—C1	4.7 (2)	C8—C9—C10—C5	-0.5 (4)
O2—C1—C2—N1	178.0 (2)	C6—C5—C10—C9	0.9 (4)
O1—C1—C2—N1	-2.4 (3)	C4—C5—C10—C9	-177.1 (2)
O2—C1—C2—C3	-3.5 (4)		

Symmetry codes: (i) $-x+1, -y, -z$.

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>
O3—H1W \cdots O2 ⁱⁱ	0.83 (3)	1.88 (3)	2.679 (3)	161 (3)
N2—H2 \cdots O3 ⁱⁱⁱ	0.86	1.93	2.719 (3)	152
O3—H2W \cdots O1 ^{iv}	0.83 (3)	2.04 (3)	2.773 (3)	149 (3)

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

Fig. 1

