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Bis(pyrimidine-2-carboxylato- κ^2N,O)-copper(II)

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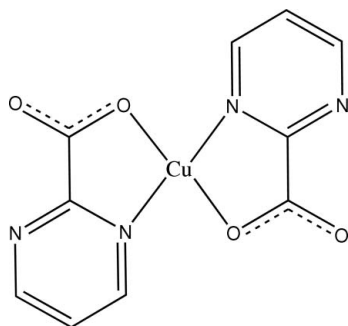
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 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(C-C) = 0.003$ Å; R factor = 0.025; wR factor = 0.072; data-to-parameter ratio = 13.6.

The title compound, $[Cu(C_5H_3N_2O_2)_2]$, was prepared in a water-ethanol solution containing 2-cyanopyrimidine, malonic acid and copper(II) nitrate trihydrate. The Cu^{II} ion, located on an inversion center, is chelated by two pyrimidine-2-carboxylate anions in a CuO_2N_2 square-planar geometry. The uncoordinated carboxylate O atom and pyrimidine N atoms are linked to adjacent pyrimidine rings *via* weak $C-H \cdots O$ and $C-H \cdots N$ hydrogen bonding. $\pi-\pi$ Stacking is observed between nearly parallel pyrimidine rings, the centroid-to-centroid separation being 3.8605 (13) Å.

Related literature

For general background, see: Cheng *et al.* (2000); Xu *et al.* (1996). For related structures, see: Antolić *et al.* (2000) Rodriguez-Dieguez *et al.* (2007).



Experimental

Crystal data

$[Cu(C_5H_3N_2O_2)_2]$
 $M_r = 309.73$
 Monoclinic, $P2_1/c$
 $a = 5.1408$ (8) Å
 $b = 13.2624$ (12) Å
 $c = 7.6735$ (11) Å
 $\beta = 94.025$ (15)°

$V = 521.88$ (12) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.11$ mm⁻¹
 $T = 291$ (2) K
 $0.32 \times 0.20 \times 0.16$ mm

Data collection

Rigaku R-AXIS RAPID IP
 diffractometer
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{min} = 0.545$, $T_{max} = 0.722$

3167 measured reflections
 1196 independent reflections
 1068 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
 $wR(F^2) = 0.072$
 $S = 1.07$
 1196 reflections

88 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.25$ e Å⁻³
 $\Delta\rho_{min} = -0.42$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—O1	1.9367 (14)	Cu—N1	1.9714 (15)
O1—Cu—N1	83.59 (6)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1 \cdots N2 ⁱ	0.93	2.62	3.511 (3)	160
C2—H2 \cdots O2 ⁱ	0.93	2.39	3.193 (3)	145
C3—H3 \cdots O1 ⁱⁱ	0.93	2.57	3.336 (3)	140
C3—H3 \cdots O2 ⁱⁱ	0.93	2.53	3.317 (2)	142

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The work was supported by the ZIJIN project of Zhejiang University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2383).

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supplementary materials

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Bis(pyrimidine-2-carboxylato- κ^2N,O)copper(II)

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Comment

As part of our ongoing investigation on the nature of π - π stacking in metal complexes (Cheng *et al.*, 2000; Xu *et al.*, 1996), the title Cu^{II} compound has recently been prepared and its crystal structure is presented here.

The molecular structure of the title complex is shown in Fig. 1. The Cu^{II} is located an inversion center and chelated by two pyrimidine-2-carboxylate anions in a CuO₂N₂ square-planar coordination geometry (Table 1). The pyrimidine-2-carboxylate anion does not play a role of bridging ligand, this is different from the situation found in pyrimidine-2-carboxylate complex of cobalt(II) and pyrimidine-2-carboxylate complex of iron(II) (Rodríguez-Dieguez *et al.*, 2007), but similar to that found in pyrimidine-2-carboxylate complex of cobalt(III) (Antolić *et al.*, 2000). In the title crystal, two carboxylate-O atoms from adjacent molecules occupy at the axial direction of the Cu^{II} ion (Fig. 1), but the rather longer separation of 2.7300 (15) Å indicates un-coordination. In the title complex, the uncoordinated carboxylate-O atom and uncoordinated pyrimidine-N atom link with the adjacent pyrimidine ring *via* C—H \cdots O and C—H \cdots N hydrogen bonding (Table 2).

π - π stacking is observed between nearly parallel N1-pyrimidine and N1^{iv}-pyrimidine rings [symmetry code: (iv) $x, 1.5 - y, 1/2 + z$] of adjacent complex molecules (Fig. 2). The centroid-to-centroid separation between is 3.8605 (13)°, the dihedral angle is 6.40 (9)°.

Experimental

2-Cyanopyrimidine (0.19 g, 1.8 mmol), copper nitrate trihydrate (0.24 g, 1 mmol) and malonic acid (0.10 g, 1 mmol) were dissolved in a mixture solution of water (15 ml) and ethanol (5 ml). The solution was refluxed for 5 h and then filtered. Single crystals of the title compound were obtained from the filtrate after 8 d.

Refinement

H atoms were placed in calculated positions with C—H = 0.93 Å and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

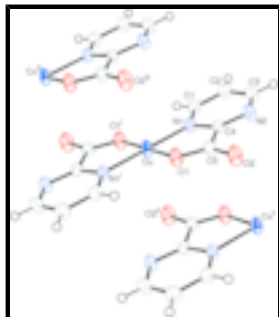


Fig. 1. The molecular structure of the title compound with 30% probability displacement (arbitrary spheres for H atoms) [symmetry codes: (ii) $x - 1, y, z$; (iii) $1 - x, 1/2 + y, 1.5 - z$].

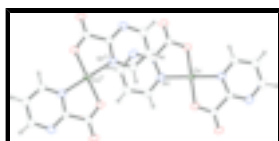


Fig. 2. π - π stacking between nearly parallel pyrimidine rings [symmetry code: (iv) $x, 1.5 - y, 1/2 + z$].

Bis(pyrimidine-2-carboxylato- κ^2N,O)copper(II)

Crystal data

[Cu(C₅H₃N₂O₂)₂]

$M_r = 309.73$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.1408$ (8) Å

$b = 13.2624$ (12) Å

$c = 7.6735$ (11) Å

$\beta = 94.025$ (15)°

$V = 521.88$ (12) Å³

$Z = 2$

$F_{000} = 310$

$D_x = 1.971$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2068 reflections

$\theta = 3.5$ – 25.0 °

$\mu = 2.11$ mm⁻¹

$T = 291$ (2) K

Prism, blue

$0.32 \times 0.20 \times 0.16$ mm

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 10.0 pixels mm⁻¹

$T = 291$ (2) K

ω scans

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.545$, $T_{\max} = 0.722$

3167 measured reflections

1196 independent reflections

1068 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 27.5$ °

$\theta_{\text{min}} = 3.1$ °

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 17$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.025$	H-atom parameters constrained
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.1691P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1196 reflections	$(\Delta/\sigma)_{\max} < 0.001$
88 parameters	$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
	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 $F^2 > \sigma(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu	0.5000	0.5000	0.5000	0.02825 (13)
N1	0.6118 (3)	0.64215 (11)	0.51341 (19)	0.0256 (3)
N2	0.9563 (3)	0.74012 (12)	0.6465 (2)	0.0305 (3)
O1	0.8109 (3)	0.47785 (10)	0.6527 (2)	0.0326 (3)
O2	1.1774 (3)	0.55441 (11)	0.7517 (2)	0.0405 (4)
C1	0.4897 (3)	0.72551 (15)	0.4523 (3)	0.0299 (4)
H1	0.3330	0.7201	0.3847	0.036*
C2	0.5948 (4)	0.81889 (15)	0.4891 (3)	0.0340 (4)
H2	0.5094	0.8774	0.4505	0.041*
C3	0.8314 (4)	0.82293 (14)	0.5852 (3)	0.0352 (4)
H3	0.9074	0.8856	0.6084	0.042*
C4	0.8391 (3)	0.65348 (13)	0.6096 (2)	0.0247 (4)
C5	0.9575 (3)	0.55522 (14)	0.6793 (2)	0.0281 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.02102 (19)	0.02422 (19)	0.0376 (2)	-0.00481 (11)	-0.01119 (13)	0.00144 (12)

supplementary materials

N1	0.0194 (6)	0.0268 (7)	0.0296 (7)	-0.0016 (6)	-0.0045 (5)	-0.0006 (6)
N2	0.0276 (7)	0.0265 (8)	0.0361 (8)	-0.0041 (6)	-0.0069 (6)	-0.0030 (6)
O1	0.0252 (7)	0.0260 (6)	0.0445 (8)	-0.0032 (5)	-0.0132 (6)	0.0037 (6)
O2	0.0279 (7)	0.0349 (8)	0.0554 (9)	-0.0024 (6)	-0.0201 (6)	0.0024 (7)
C1	0.0232 (8)	0.0328 (10)	0.0326 (9)	0.0030 (7)	-0.0047 (7)	0.0020 (8)
C2	0.0337 (9)	0.0282 (9)	0.0395 (10)	0.0048 (8)	-0.0027 (8)	0.0030 (8)
C3	0.0403 (10)	0.0250 (9)	0.0395 (10)	-0.0038 (8)	-0.0037 (8)	-0.0029 (8)
C4	0.0194 (7)	0.0270 (9)	0.0270 (8)	-0.0008 (6)	-0.0032 (6)	-0.0026 (6)
C5	0.0244 (8)	0.0281 (9)	0.0308 (9)	-0.0009 (7)	-0.0061 (7)	-0.0013 (7)

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

Cu—O1	1.9367 (14)	O1—C5	1.281 (2)
Cu—O1 ⁱ	1.9367 (14)	O2—C5	1.224 (2)
Cu—N1 ⁱ	1.9714 (15)	C1—C2	1.373 (3)
Cu—N1	1.9714 (15)	C1—H1	0.9300
N1—C1	1.339 (2)	C2—C3	1.378 (3)
N1—C4	1.346 (2)	C2—H2	0.9300
N2—C4	1.319 (2)	C3—H3	0.9300
N2—C3	1.341 (2)	C4—C5	1.520 (2)
O1—Cu—O1 ⁱ	180.0	C2—C1—H1	119.8
O1—Cu—N1 ⁱ	96.41 (6)	C1—C2—C3	117.70 (18)
O1 ⁱ —Cu—N1 ⁱ	83.59 (6)	C1—C2—H2	121.1
O1—Cu—N1	83.59 (6)	C3—C2—H2	121.1
O1 ⁱ —Cu—N1	96.41 (6)	N2—C3—C2	122.61 (17)
N1 ⁱ —Cu—N1	180.0	N2—C3—H3	118.7
C1—N1—C4	117.84 (16)	C2—C3—H3	118.7
C1—N1—Cu	130.04 (13)	N2—C4—N1	125.53 (16)
C4—N1—Cu	111.96 (12)	N2—C4—C5	120.37 (15)
C4—N2—C3	115.95 (15)	N1—C4—C5	114.10 (15)
C5—O1—Cu	115.23 (12)	O2—C5—O1	125.42 (17)
N1—C1—C2	120.31 (17)	O2—C5—C4	120.11 (16)
N1—C1—H1	119.8	O1—C5—C4	114.46 (15)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 \cdots N2 ⁱⁱ	0.93	2.62	3.511 (3)	160
C2—H2 \cdots O2 ⁱⁱ	0.93	2.39	3.193 (3)	145
C3—H3 \cdots O1 ⁱⁱⁱ	0.93	2.57	3.336 (3)	140
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Symmetry codes: (ii) $x-1, -y+3/2, z-1/2$; (iii) $-x+2, y+1/2, -z+3/2$.

Fig. 1

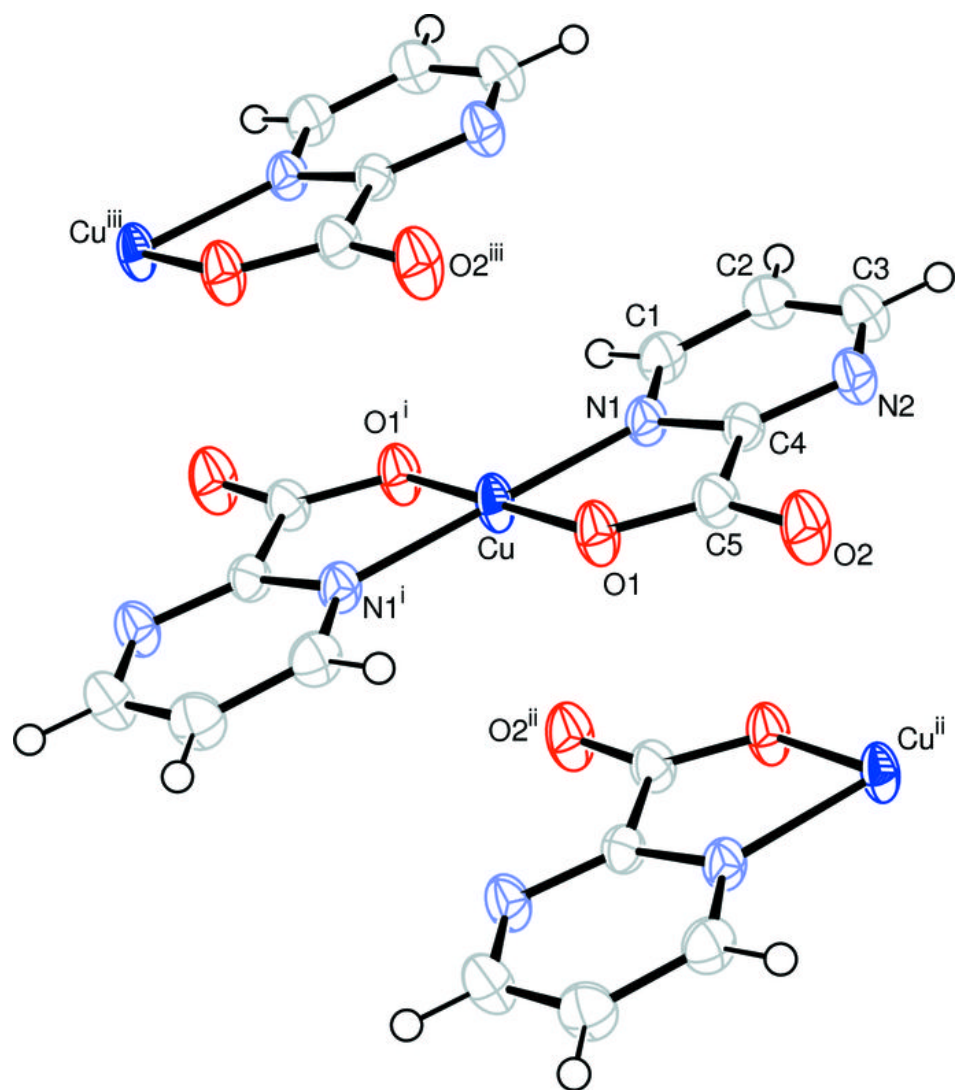


Fig. 2

