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

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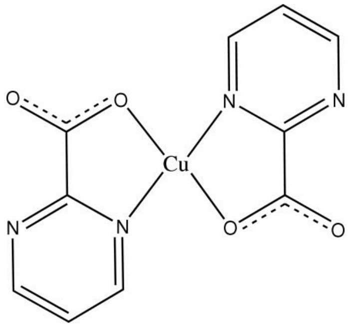
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.025; wR factor = 0.072; data-to-parameter ratio = 13.6.

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···O and C—H···N hydrogen bonding. π–π 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 Rodriquez-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
β = 94.025 (15)°
V = 521.88 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.11 mm^{-1}
T = 291 (2) K
0.32 × 0.20 × 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···A	D—H	H···A	D···A	D—H···A
C1—H1···N2^{i}	0.93	2.62	3.511 (3)	160
C2—H2···O2^{i}	0.93	2.39	3.193 (3)	145
C3—H3···O1^{ii}	0.93	2.57	3.336 (3)	140
C3—H3···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/MSC, 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).

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

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Antolić, S., Kojić-Prodić, B. & Lovrić, J. (2000). *Acta Cryst.* C**56**, e51–e52.
Cheng, D.-P., Zheng, Y., Lin, J., Xu, D. & Xu, Y. (2000). *Acta Cryst.* C**56**, 523–524.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, The Woodlands, Texas, USA.
Rodriquez-Dieguez, A., Cano, J., Kivekas, R., Debdoudi, A. & Colacio, E. (2007). *Inorg. Chem.* **46**, 2503–2510.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Xu, D.-J., Xie, A.-L., Xu, Y.-Z., Zhang, C.-G. & Chen, W.-G. (1996). *J. Coord. Chem.* **39**, 273–280.

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S1. 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 CuO_2N_2 square-planar coordination geometry (Table 1). The pyridine-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) (Rodriquez-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···O and C—H···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)°.

S2. 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.

S3. Refinement

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

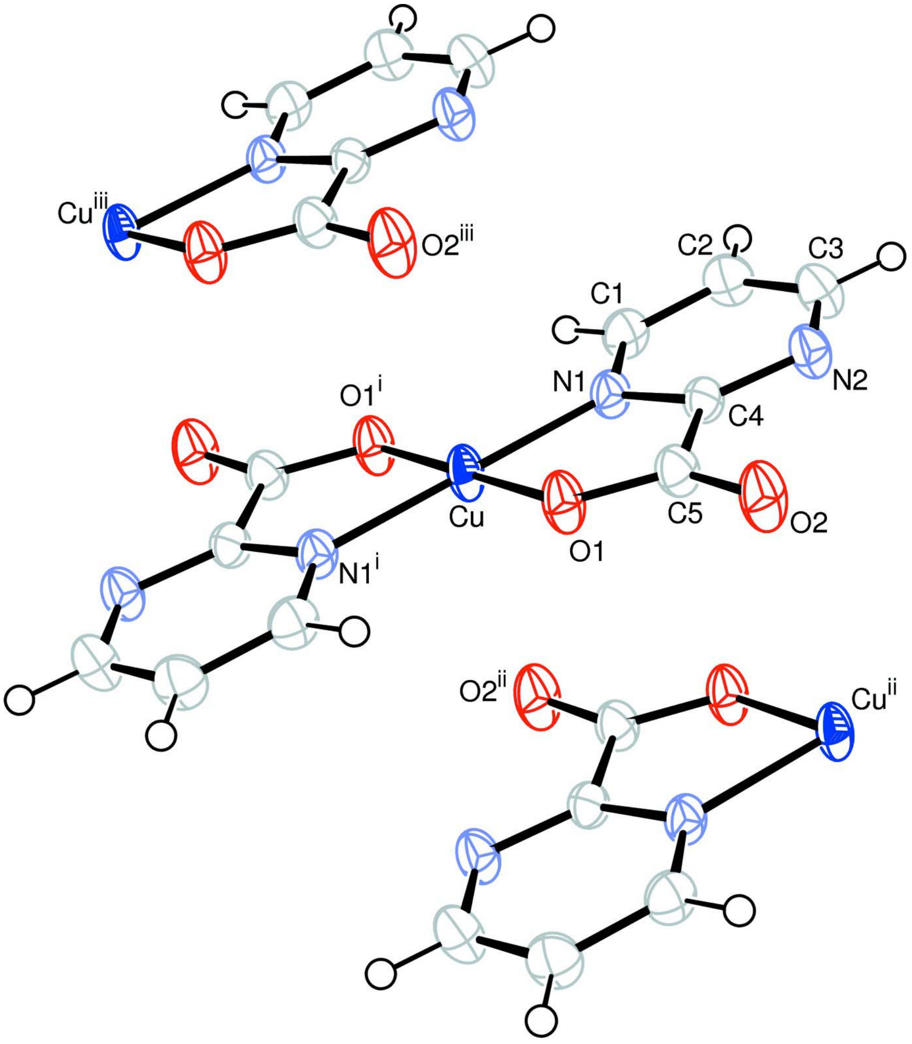

Figure 1

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].

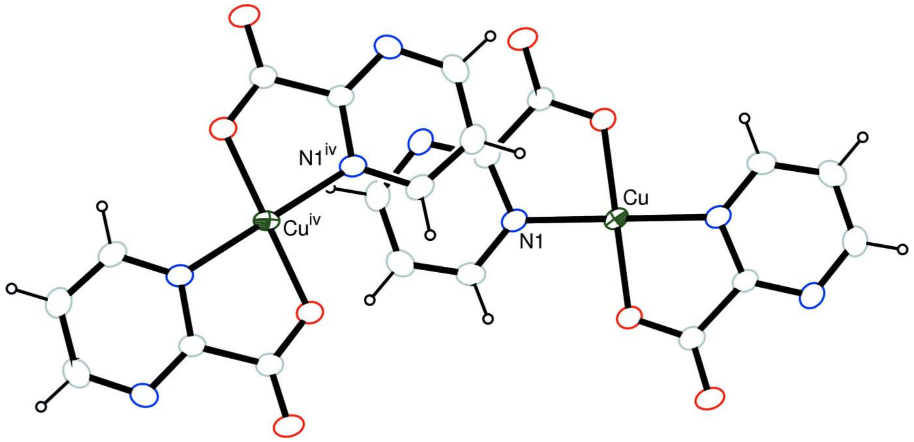

Figure 2

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

$[Cu(C_5H_3N_2O_2)_2]$
$M_r = 309.73$
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) Å^3
$Z = 2$
$F(000) = 310$
$D_x = 1.971$ 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}
$T = 291$ K
Prism, blue
0.32 × 0.20 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm^{-1}
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 $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -6\rightarrow6$
$k = -9\rightarrow17$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.072$
$S = 1.07$
1196 reflections
88 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.1691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å^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)
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 (Å, º)

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 code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N2^{ii}	0.93	2.62	3.511 (3)	160
C2—H2···O2^{ii}	0.93	2.39	3.193 (3)	145
C3—H3···O1^{iii}	0.93	2.57	3.336 (3)	140
C3—H3···O2^{iii}	0.93	2.53	3.317 (2)	142

Symmetry codes: (ii) *x*−1, −*y*+3/2, *z*−1/2; (iii) −*x*+2, *y*+1/2, −*z*+3/2.