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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.029

wR factor = 0.067

Data-to-parameter ratio = 14.4

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Aqua(malonato- $\kappa^2\text{O},\text{O}'$ )(pyridine-2-carboxamide- $\kappa^2\text{N}^1,\text{O}$ )copper(II) monohydrate

The title compound,  $[\text{Cu}(\text{mal})(\text{pca})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  [mal is the malonate dianion,  $\text{CH}_2(\text{COO})_2^{2-}$ , and pca is pyridine-2-carboxamide,  $\text{C}_6\text{H}_6\text{N}_2\text{O}$ ], has a five-coordinated Cu atom in a distorted square-pyramidal environment, coordinated by two O atoms of the malonate ion, an O atom and an N atom of pca, and an O atom of water. An uncoordinated water molecule stabilizes the complex by participation in a hydrogen-bonding system. The crystal structure is built from layers parallel to the (111) plane.

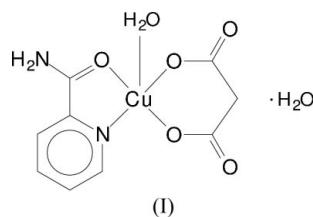
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## Comment

The present work is a continuation of earlier studies of the preparation, properties and structure of copper(II) complexes with pyridine-2-carboxamide (pca) (Sieroń & Bukowska-Strzyżewska, 1997, 1998, 1999) and with malonate (mal) ions (Tosik *et al.*, 1995). Copper(II) malonate complexes provide the framework for supramolecular crystal engineering (Ruiz-Pérez *et al.*, 2000; Shen *et al.*, 2000). The malonate ion is also a ligand often used for designing complexes with desired magnetic properties (Ruiz-Pérez *et al.*, 2003; Pasán *et al.*, 2003).



In the present structure, (I) (Fig. 1), the  $\text{Cu}^{\text{II}}$  atom is bonded to O and N atoms of pca [1.968 (2) and 2.002 (2) Å for Cu—O1 and Cu—N1, respectively], to two carboxylate O atoms from the mal ligand [1.922 (2) and 1.926 (2) Å for Cu—O2 and Cu—O4] in the basal plane, and to a water molecule in the

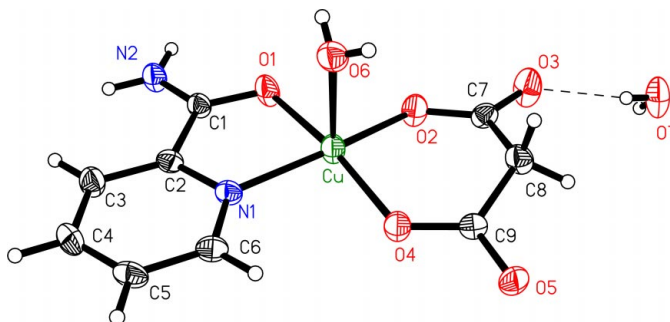
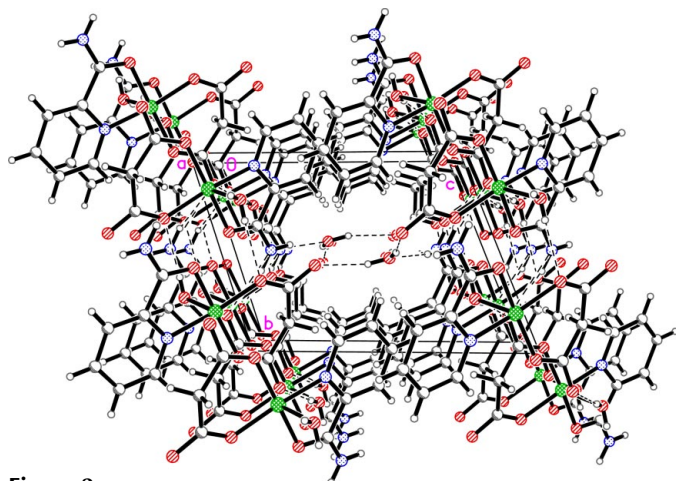
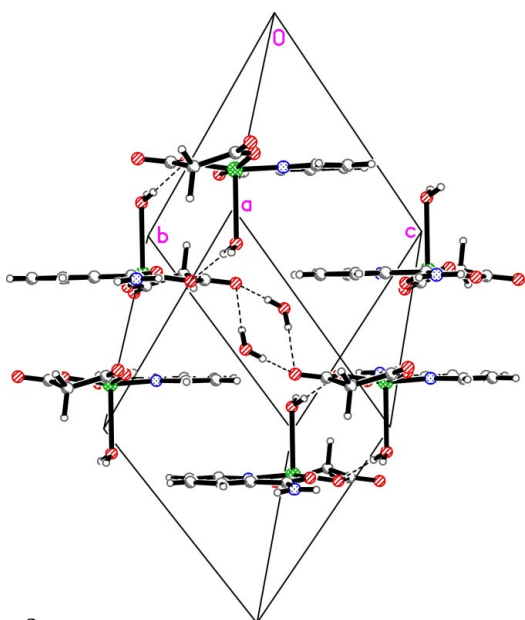


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed line indicates a hydrogen bond.



**Figure 2**  
The packing of (I), viewed down the *a* axis. Dashed lines indicate the hydrogen bonds.



**Figure 3**  
Projection of the cell of (I) parallel to the (111) plane, showing the hydrogen bonds as dashed lines.

apical position [2.324 (2) Å for Cu—O6]. The coordinated malonate O4 atom from a different mononuclear unit lies at a distance of 3.273 (2) Å from the Cu atom.

The degree of trigonality  $\tau = 0.08$  [ $\tau$  is defined by Addison *et al.* (1984); for the regular square-pyramidal (SQP) structure, the trigonality parameter is 0, and for the trigonal-bipyramidal (TBP) structure, it increases to 1] indicates a minimal deformation of the observed SQP coordination of the Cu atom towards TBP coordination. The Cu atom deviates by 0.183 (1) Å from the basal plane towards the apical O6 atom. This significant deviation is also evident from the angles O1—Cu—O4 and O2—Cu—N1, with values of 169.16 (8) and 164.33 (8)°, respectively. The dihedral angles between the basal O<sub>3</sub>N plane at the Cu atom and those of the O2—C7—O3 and O4—C9—O5 carboxylate groups are 13.5 (3) and 12.2 (2)°, respectively.

The six-membered chelate malonate ring adopts a slightly distorted boat conformation, with puckering parameters (Cremer & Pople, 1975)  $Q = 0.360$  (2),  $\theta = 86.4$  (3) and  $\varphi = 1.8$  (4)° for the atom sequence Cu—O2—C7—C8—C9—O4. Atoms Cu and C8 lie above the mean plane defined by the remaining four atoms by 0.348 (3) and 0.282 (4) Å, respectively.

The *pca* chelate ring (O1—C1—C2—N1—Cu) and the O2/O4/Cu fragment of the malonate chelate ring are not exactly coplanar; the dihedral angle between them is 15.8 (1)°.

Both uncoordinated mal O atoms act as acceptors for O—H, N—H and C—H donors (Table 2). The coordinated O2 atom forms a hydrogen bond to the water molecule [O6···O2 = 2.930 (2) Å]. These interactions generate an infinite three-dimensional hydrogen-bonding network. The water molecules occupy channels running along the *a* axis and interact with the metal complexes by hydrogen-bond interactions (Fig. 2). The periodic structure is built up from layers of complexes parallel to the (111) plane (Fig. 3). The shortest interlayer metal–metal distances are 4.2279 (6) Å for Cu···Cu<sup>vii</sup> and 4.8098 (6) Å for Cu···Cu<sup>iv</sup> [symmetry codes: (iv) 1 - *x*, 1 - *y*, -*z*; (vii) 1 - *x*, -*y*, -*z*].

## Experimental

Crystals of (I) were grown from an aqueous solution of 2-pyridine-carbonitrile and copper(II) malonate, indicating that the copper-assisted hydrolysis of 2-pyridinecarbonitrile to pyridine-2-carboxamide (Watanabe *et al.*, 1973) had occurred. A pale-blue solution formed when Cu(mal)<sub>2</sub>·4H<sub>2</sub>O (1 mmol) was added to an aqueous solution (50 ml) containing 2-pyridinecarbonitrile (1 mmol). After heating to boiling point, the solution became dark blue. After a few days, blue prismatic crystals of the title compound were obtained.

### Crystal data

[Cu(C <sub>3</sub> H <sub>3</sub> O <sub>4</sub> )(C <sub>6</sub> H <sub>6</sub> N <sub>2</sub> O)·(H <sub>2</sub> O)]·H <sub>2</sub> O	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 323.76	<i>D<sub>x</sub></i> = 1.749 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.0566 (5) Å	Cell parameters from 4631 reflections
<i>b</i> = 8.7694 (7) Å	$\theta$ = 2.1–29.1°
<i>c</i> = 10.4093 (7) Å	$\mu$ = 1.81 mm <sup>-1</sup>
$\alpha$ = 68.540 (7)°	<i>T</i> = 293 K
$\beta$ = 81.355 (5)°	Prism, blue
$\gamma$ = 63.933 (7)°	0.50 × 0.15 × 0.03 mm
<i>V</i> = 614.78 (9) Å <sup>3</sup>	

### Data collection

Kuma KM-4 CCD diffractometer	2131 reflections with $I > 2\sigma(I)$
$\omega$ scans	<i>R</i> <sub>int</sub> = 0.031
Absorption correction: numerical ( <i>XRED</i> ; Stoe & Cie, 1999)	$\theta_{\text{max}}$ = 27.5°
<i>T</i> <sub>min</sub> = 0.729, <i>T</i> <sub>max</sub> = 0.947	<i>h</i> = -10 → 10
4723 measured reflections	<i>k</i> = -11 → 8
2828 independent reflections	<i>l</i> = -13 → 13

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.92	$(\Delta/\sigma)_{\text{max}} < 0.001$
2828 reflections	$\Delta\rho_{\text{max}} = 0.88 \text{ e \AA}^{-3}$
196 parameters	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

**Table 1**  
Selected geometric parameters (Å, °).

Cu—O1	1.9679 (17)	O2—C7	1.260 (3)
Cu—O2	1.9223 (16)	O3—C7	1.232 (3)
Cu—O4	1.9244 (17)	O4—C9	1.267 (3)
Cu—O6	2.3239 (18)	O5—C9	1.236 (3)
Cu—N1	2.0023 (18)		
O1—Cu—O2	86.50 (7)	O2—Cu—O6	100.56 (7)
O1—Cu—O4	169.20 (8)	O2—Cu—N1	164.35 (8)
O1—Cu—O6	96.63 (7)	O4—Cu—O6	93.78 (7)
O1—Cu—N1	81.30 (7)	O4—Cu—N1	95.75 (7)
O2—Cu—O4	94.43 (7)	O6—Cu—N1	90.60 (7)

**Table 2**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H1...O5 <sup>i</sup>	0.86	2.11	2.939 (2)	161
N2—H2...O7 <sup>ii</sup>	0.86	1.99	2.837 (3)	168
O6—H61...O5 <sup>iii</sup>	0.82	2.06	2.865 (3)	170
O6—H62...O2 <sup>iv</sup>	0.82	2.12	2.930 (2)	171
O7—H71...O3	0.82	1.96	2.742 (2)	160
O7—H72...O3 <sup>v</sup>	0.82	2.18	2.983 (3)	164
C3—H3...O7 <sup>ii</sup>	0.93	2.41	3.293 (3)	159
C5—H5...O3 <sup>vi</sup>	0.93	2.46	3.389 (3)	174
C8—H81...O5 <sup>iii</sup>	0.97	2.51	3.357 (3)	146

Symmetry codes: (i)  $x - 1, 1 + y, z$ ; (ii)  $x - 1, y, 1 + z$ ; (iii)  $2 - x, -y, -z$ ; (iv)  $1 - x, 1 - y, -z$ ; (v)  $1 - x, 1 - y, -1 - z$ ; (vi)  $x, y - 1, 1 + z$ .

The water H atoms were located in a difference Fourier map and refined with O—H distances restrained to 0.82 Å. All remaining H atoms were positioned geometrically and allowed to ride on the parent atoms with *SHELXL97* (Sheldrick, 1997) defaults for bond lengths (C—H = 0.93 or 0.97 Å, and N—H = 0.86 Å). The isotropic displacement parameters of all H atoms were refined freely.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003; cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *PLATON* (Spek, 1990).

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