

Aqua(di-2-pyridylamine- κ^2N,N')-(malonato- κ^2O,O')copper(II) monohydrate

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Received 28 August 2006

Accepted 16 October 2006

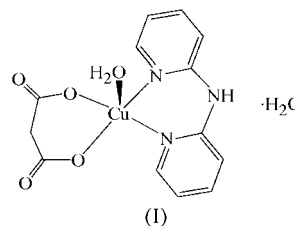
Online 22 November 2006

In the structure of the title complex, $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ or $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, where mal is malonate and dpyam is di-2-pyridylamine, the Cu^{II} atom displays square-pyramidal geometry, being coordinated by two N atoms from the dpyam ligand, two O atoms from the mal group and one O atom of a water ligand. The complex molecules are linked to form a three-dimensional network by hydrogen-bonding interactions between coordinated/uncoordinated water molecules and the uncoordinated malonate N and O atoms of neighboring molecules.

Comment

There has been considerable interest in the design and syntheses of transition metal complexes with the malonate ligand in coordination chemistry, owing to the fact that this type of complex has potential application in molecular-based magnets (Rodríguez-Martín *et al.*, 2001). The malonate dianion generally exhibits bi-, tri- or tetradentate coordination modes (Shen *et al.*, 2000). Although some complexes containing mixed malonate and nitrogen-donor ligands have been synthesized and characterized, complexes containing mixed malonate (mal) and di-2-pyridylamine (dpyam) ligands have not been reported. To the best of our knowledge, there are only four reports on structures with malonate and nitrogen-donor ligands, such as phen (1,10-phenanthroline), bpy (2,2'-bipyridyl) and bpym (2,2'-bipyrimidine), namely $[\text{Cu}(\text{mal})(\text{phen})(\text{H}_2\text{O})]\cdot 1.5\text{H}_2\text{O}$, (II) (Kwik *et al.*, 1986), $[\text{Cu}(\text{mal})(\text{bpym})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (III) (Rodríguez-Martín *et al.*, 2001), $[\text{Cu}(\text{mal})(\text{bpy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (IV) (Suresh & Bhadbhade, 1997), and $[\text{Cu}(\text{mal})(\text{bpy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (V) (Shen *et al.*, 2000). The first three compounds exhibit mononuclear structures, while the last compound involves a dinuclear unit. In this paper, we report the crystal structure of $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (I), in which the three-dimensional network is formed by hydrogen bonds. The dpyam ligand has been

selected primarily because of the fact that it also has an NH hydrogen-bond donor function that might form one-, two- or three-dimensional supramolecular architectures. The structure of complex (I) consists of neutral mononuclear $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]$ units (see Fig. 1) and crystallization water molecules. The Cu atom exhibits a slightly distorted square-pyramidal environment, the geometric τ value (Addison *et al.*, 1984) being only 0.045. The Cu^{II} ion is bonded to two dpyam N atoms and two carboxylate O atoms from the malonate ligand in the basal plane, and to a water molecule in the apical position (Table 1 and Fig. 1). The Cu atom is displaced by 0.257 (1) Å from the mean basal plane towards the apical position. In the Cu unit, the dihedral angle between the N1/Cu1/N2 and O1/Cu1/O2 planes is 21.3°. The dpyam ligands are not planar, with a dihedral angle of 22.9° between the pyridine planes. Other related examples including malonate are compounds (II)–(V). In each of these, the Cu^{II} atom exhibits a slightly distorted square-pyramidal geometry, with τ values of 0.057 for (II), 0.006 for (III), 0.061 for (IV) and 0.040 for (V).



The electronic reflectance spectrum of (I) involves two bands at 15 800 and 11 000 cm^{-1} ; this spectral character of the compound is consistent with the distorted square-pyramidal geometry and $\tau = 0.045$. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy peak and the $d_{xz} \simeq d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The electronic spectrum of (I) is similar to that found in a complex with similar Cu^{II} environment, *viz.* compound (V) (15 400 and 11 000 cm^{-1}). The IR spectrum of (I) exhibits several characteristic strong bands in the range 1670–1600 cm^{-1} , which are attributed to C=O stretching modes. The complex molecules are linked to form a three-dimensional network by hydrogen-bonding interactions between the NH group of the dpyam group and the uncoordinated water molecule, and between the

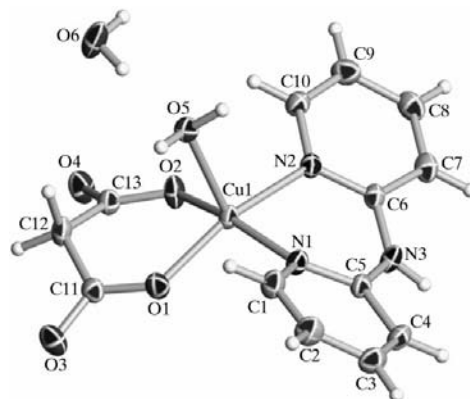


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

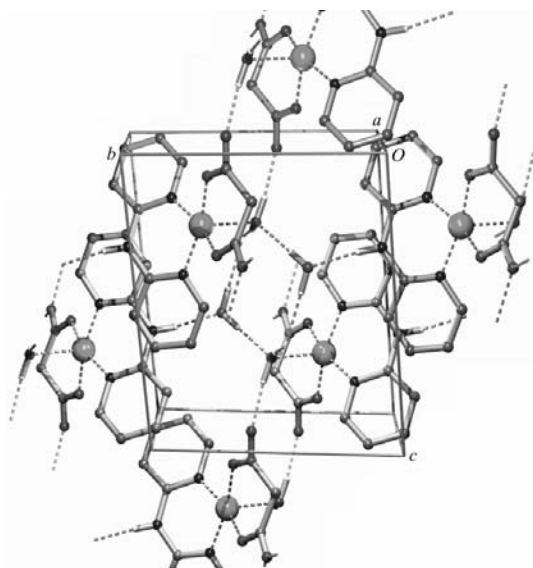


Figure 2
The packing of (I), with hydrogen bonds indicated by dashed lines, showing the three-dimensional structure.

coordinated water molecule and the uncoordinated malonate O atoms (Table 2 and Fig. 2). All available hydrogen-bonding donors take part in hydrogen bonds.

Experimental

A warming solution of copper(II) acetate monohydrate (0.181 g, 1.0 mmol) in water (10 ml) was added to a warming solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 ml), and then solid disodium malonate monohydrate (0.084 g, 0.5 mmol) was added. The resulting green solution was evaporated slowly at room temperature. After several days, blue–green crystals had formed, and these were filtered off, washed with mother liquor and air-dried.

Crystal data

$[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_3) \cdot (\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	$\gamma = 74.8440 (10)^\circ$
$M_r = 372.82$	$V = 730.46 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.2409 (1) \text{ \AA}$	$D_x = 1.695 \text{ Mg m}^{-3}$
$b = 9.6351 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.43800 (1) \text{ \AA}$	$\mu = 1.53 \text{ mm}^{-1}$
$\alpha = 87.8150 (10)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 71.7000 (10)^\circ$	Plate, blue–green
	$0.33 \times 0.32 \times 0.10 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	5409 measured reflections
ω scans	4432 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)	3443 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.599$, $T_{\max} = 0.858$	$R_{\text{int}} = 0.018$
	$\theta_{\max} = 30.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2 + (0.0652P)^2 + 0.0267P)]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
3945 reflections	$\Delta\rho_{\min} = -0.53 \text{ e \AA}^{-3}$
224 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu—O2	1.9368 (15)	Cu—N1	2.0002 (17)
Cu—O1	1.9396 (15)	Cu—O5	2.2722 (15)
Cu—N2	1.9929 (16)		
O2—Cu—O1	91.84 (7)	N2—Cu—N1	88.10 (7)
O2—Cu—N2	87.37 (7)	O2—Cu—O5	97.62 (7)
O1—Cu—N2	166.18 (7)	O1—Cu—O5	94.39 (7)
O2—Cu—N1	163.51 (7)	N2—Cu—O5	99.39 (6)
O1—Cu—N1	88.80 (7)	N1—Cu—O5	98.76 (6)

Table 2

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N3—H5 \cdots O6 ⁱ	0.86	2.04	2.836 (3)	155
O5—H13 \cdots O4 ⁱⁱ	0.85 (3)	1.86 (3)	2.702 (3)	173 (2)
O5—H14 \cdots O3 ⁱⁱⁱ	0.89 (2)	1.82 (2)	2.706 (2)	173 (2)
O6—H15 \cdots O4 ^{iv}	0.89 (2)	2.00 (2)	2.885 (3)	174 (2)
O6—H16 \cdots O5	0.89 (4)	1.99 (4)	2.874 (3)	177 (2)

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

Water H atoms were visible in a difference map and were refined with a DFIX (*SHELXTL*; Sheldrick, 2000b) restraint [$\text{O—H} = 0.90 (1) \text{ \AA}$]. Other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with $\text{C—H} = 0.93\text{--}0.97 \text{ \AA}$ and $\text{N—H} = 0.86 \text{ \AA}$ [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge the Thailand Research Fund (grant Nos. RTA 4880008 and BRG 498007), Khon Kaen University, and the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry, Thailand, for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3018). Services for accessing these data are described at the back of the journal.

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