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Aqua(2,2′-bipyridine)maleatocopper(II) dihydrate

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In the molecule of the title compound, $[Cu(C_{10}H_8N_2)(C_4H_2O_4)(H_2O)]\cdot 2H_2O$, the Cu(II) atom has elongated tetragonal pyramidal geometry, coordinated by one water O atom, two N atoms of the 2,2′-bipyridine ligand and two O atoms of the two carboxylate groups of the maleate dianion. The molecules are linked through hydrogen-bonding and π–π stacking interactions, forming a two-dimensional supramolecular structure.

Comment

Metal–organic coordination complexes containing the maleate ligand have been studied extensively due to their wide range of applications (Maruoka *et al.*, 1993; Chen & Suslick, 1993; Hoskins & Robson, 1990; Kondo *et al.*, 1997). Here, we report the crystal structure of one such complex, the title compound, (I).
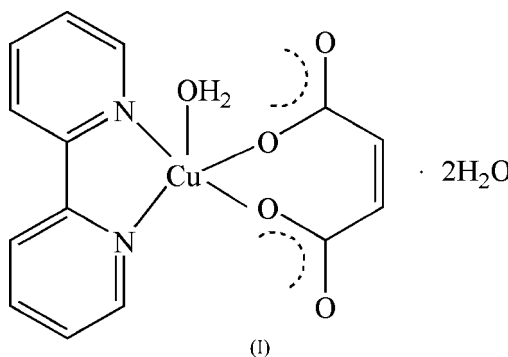
The structure of (I) consists of discrete monomers. The Cu^{II} atom exhibits an elongated tetragonal pyramidal geometry, coordinated by one water O atom, two N atoms of the 2,2′-bipyridine ligand and two O atoms of the two carboxylate groups of the maleate dianion (Table 1, Fig. 1).

The Cu—O(maleate) and Cu—O(water) bonds (Table 1) are slightly longer than the corresponding ones [1.876 (6), 1.894 (6) and 2.150 (6) Å] in $[Cu(pz)_2(male)(H_2O)]\cdot 1.5H_2O$, (II), where pz and male are 3,5-dimethylpyrazole and the maleate anion, respectively (Chen *et al.*, 2003). It is not possible to compare the Cu—O(water) bond in (I) with those [1.975 (2) and 2.414 (2) Å] reported in $\{[Cu(4,4′-bpy)(H_2O)_4](male)\}\cdot 4H_2O$, (III) (Kang *et al.*, 2004), due to the Jahn–Teller distortion for the Cu—O(water) distance of 2.414 (2) Å. The Cu—N bonds (Table 1) are also longer than those in (II) [1.903 (7) and 1.935 (6) Å]. The Cu^{II} atom is displaced by 0.2511 (5) Å from the mean plane through atoms N1, N2, O1 and O3.
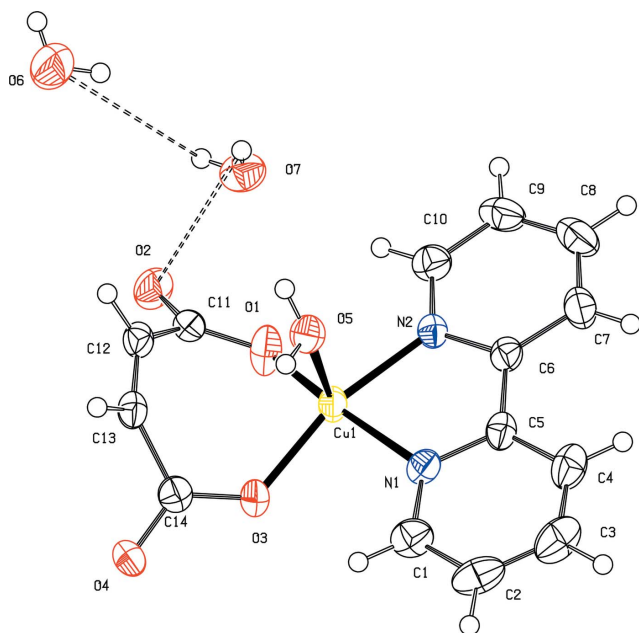
Figure 1
The asymmetric unit, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. Hydrogen bonds are shown as dashed lines.

In the crystal structure, the molecules are packed *via* hydrogen bonds (Fig. 2) between water molecules and the uncoordinated O(maleate) atoms of neighbouring molecules (Table 2), and π–π stacking interactions with centroid–centroid distances of 3.811 (3) and 3.974 (3) Å between the pyridine ring of the molecule at (x, y, z) and those at $(2 - x, -y, 2 - z)$ and $(2 - x, -y, 1 - z)$, respectively, forming a two-dimensional supramolecular structure.

Experimental

Cu(NO$_3$)$_2$·3H$_2$O (0.241 g, 1.0 mmol) was added slowly to an aqueous solution of maleic acid (0.116 g, 1.0 mmol, 15 ml), and the reaction mixture was stirred for 1 h at 353 K. An ethanol solution (5 ml) of 2,2′-bipyridine (0.156 g, 1.0 mmol) was then added with continuous stirring. NaOH solution (0.1 mol/l) was added until a pH of 7 was obtained. After 1 h, the reaction mixture was cooled to room temperature and then filtered. Blue single crystals were obtained from the filtrate after two weeks (yield 139.9 mg, 36%, m.p. 525 K).

Crystal data

[Cu(C$_{10}$H$_8$N$_2$)(C$_4$H$_2$O$_4$)-(H$_2$O)]·2H$_2$O	D_x = 1.661 Mg m^{-3}
M_r = 387.83	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3123
a = 8.9793 (18) Å	reflections
b = 22.487 (5) Å	θ = 2.6–27.8°
c = 7.7187 (15) Å	μ = 1.45 mm^{-1}
β = 95.62 (3)°	T = 292 (2) K
V = 1551.0 (5) Å^3	Block, blue
Z = 4	0.20 × 0.06 × 0.06 mm
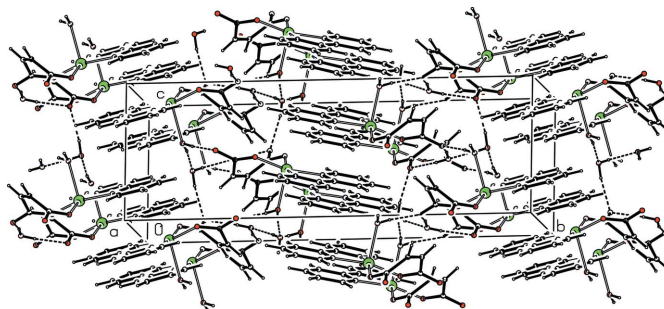
Figure 2
A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Data collection

Bruker SMART CCD area-detector diffractometer	3528 independent reflections
φ and ω scans	2257 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	R_{int} = 0.073
(*SADABS*; Bruker, 2000)	θ_{max} = 27.5°
T_{min} = 0.760, T_{max} = 0.918	$h = -11 \rightarrow 11$
10456 measured reflections	$k = -28 \rightarrow 24$
	$l = -9 \rightarrow 6$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.052	
$wR(F^2)$ = 0.123	
S = 0.97	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
3528 reflections	where $P = (F_o^2 + 2F_c^2)/3$
241 parameters	$(\Delta/\sigma)_{max}$ = 0.001
	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
	$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.931 (3)	Cu1—N1	2.003 (3)
Cu1—O3	1.931 (3)	Cu1—N2	2.003 (3)
Cu1—O5	2.261 (3)		
O1—Cu1—O3	93.44 (12)	O1—Cu1—O5	107.62 (12)
O3—Cu1—N1	91.72 (12)	O3—Cu1—O5	100.11 (12)
O1—Cu1—N2	90.55 (12)	N1—Cu1—O5	86.57 (12)
N1—Cu1—N2	80.53 (13)	N2—Cu1—O5	93.38 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5a$\cdots$O7^i	0.80 (3)	1.96 (3)	2.752 (5)	172 (5)
O7—H7b$\cdots$O6	0.75 (3)	2.07 (4)	2.819 (6)	174 (5)
O6—H6a$\cdots$O4^{ii}	0.75 (4)	2.18 (4)	2.889 (5)	159 (7)
O7—H7a$\cdots$O2	0.83 (4)	2.03 (4)	2.850 (5)	169 (5)
O5—H5b$\cdots$O4^{iii}	0.80 (3)	1.99 (3)	2.783 (4)	174 (4)
O6—H6b$\cdots$O2^{iv}	0.79 (4)	2.14 (4)	2.903 (5)	162 (6)

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

Atoms H5a, H5b, H6a, H6b, H7a and H7b were located in a difference map and refined isotropically [O—H = 0.75 (3)–0.83 (4) Å and U_{iso}(H) = 0.043 (17)–0.10 (3) Å^2]. The remaining H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve

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structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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