

Aquabis(3,5-dimethyl-1*H*-pyrazole- κN^2)(malonato- $\kappa^2 O, O'$)copper(II) dihydrate

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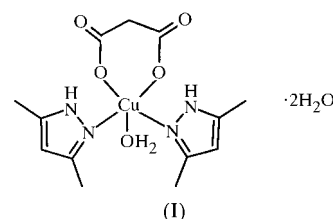
In the neutral title complex, [Cu(C₃H₂O₄)(C₅H₈N₂)₂·(H₂O)]·2H₂O or [Cu(mal)(dmp)₂(H₂O)]·2H₂O (mal is malonate and dmp is 3,5-dimethyl-1*H*-pyrazole), the Cu^{II} ion, in a slightly distorted square-pyramidal geometry, is coordinated by two O atoms of the bidentate malonate, the O atom of the water ligand and two N atoms from the two 3,5-dimethylpyrazole ligands. The mean Cu—N bond length is 2.007 (6) Å, longer than the Cu—O_{mal} bonds [1.950 (5) Å]. The apical position is occupied by a relatively strongly coordinated water molecule [Cu—O_{water} 2.288 (5) Å]. The crystal structure is characterized by the layer motif of a hydrogen-bonded network.

Comment

The self-assembly of ordered supramolecular arrays in the solid state using non-covalent forces, such as hydrogen bonding (Braga & Grepioni, 2000; Fan *et al.*, 1994; Prins *et al.*, 1998) and π - π stacking (Amabilino *et al.*, 1994), is a rapidly expanding field. Co-operative intermolecular interactions that may be encouraged through alignment of molecules in certain ways in the solid state can result in novel magnetic, conductive and non-linear optical properties. Traditionally, organic chemistry (Whitesides *et al.*, 1995) has been the domain of crystal engineering using hydrogen bonding, but transition metal coordination chemistry (our present interest) can also exploit hydrogen bonding if prudent ligand design is practised (Bernhardt, 1999).

The malonate ion (abbreviated as mal) is a versatile ligand frequently used for designing complexes with desired magnetic properties (Ruiz-Perez *et al.*, 2000) and it is also useful as a building block in metal-containing supramolecules. Since the mal ion has four potential H-atom acceptors but no H-atom donors, ligands with H-atom donors may be introduced in order to create potential building blocks for supramolecular assemblies. Therefore, we have synthesized and crystallized the title compound, (I), a new mixed-ligand

copper complex containing mal, water and 3,5-dimethyl-1*H*-pyrazole (abbreviated as dmp), which is an H-atom donor, as well as an important ligand in coordination chemistry (Ardizzoia *et al.*, 1996).



The crystal structure of (I) consists of the neutral [Cu(mal)(dmp)₂(H₂O)] complex and two uncoordinated water molecules. Fig. 1 shows a perspective view of (I) together with the atom-numbering scheme. The geometry of the five-coordinate CuN₂O₃ core is a slightly distorted square pyramid. The basal sites are occupied by two dmp N atoms and two mal carboxylate O atoms. The apical position is occupied by a relatively strongly coordinated water molecule [Cu—O1W 2.288 (5) Å], which is 2.495 (6) Å from the mean basal plane defined by atoms O1, O3, N1 and N3. The coordination geometry around the Cu^{II} ion is similar to that of two reported CuN₂O₃-type complexes, *viz.* [Cu(mal)(phen)(H₂O)] (Kwik *et al.*, 1986) and [Cu(mal)(bpy)(H₂O)] (Lu *et al.*, 1996) (phen is 1,10-phenanthroline and bpy is 2,2'-bipyridine). Although phen and bpy are bidentate N-donor ligands, structurally different from the N-donor dmp ligand in (I), the structural likeness may indicate that dmp has similar π -acceptor properties.

The two dmp ligands are located *cis* with respect to each other in the basal plane, in an antisymmetrical mode. The planes of the two pyrazole rings form dihedral angles of 40.1 (4) and 32.0 (3)° with the basal plane. The six-membered

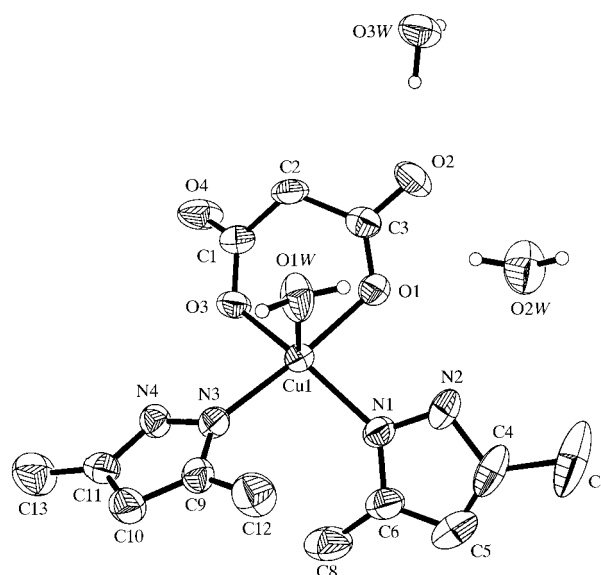


Figure 1

A perspective view of (I) shown with 40% probability displacement ellipsoids. Water H atoms are shown as small spheres of arbitrary radii and the remaining H atoms have been omitted for clarity.

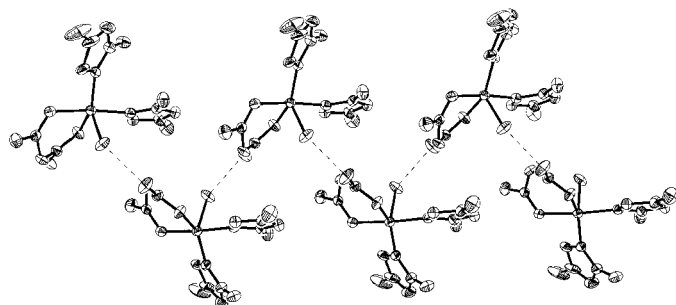


Figure 2
A fragment of a one-dimensional supramolecular chain in (I) viewed along (001). The uncoordinated water molecules have been omitted.

chelate ring of mal is in a boat conformation. Atoms Cu1 and C2 are displaced by 0.71 (1) and 0.32 (1) Å, respectively, from the least-squares plane defined by atoms O1, O3, C1 and C3.

As expected, the molecules of (I) are hydrogen bonded to each other to form a supramolecular array. In this array, H atoms from the coordinated water ligand link to a carbonyl O atom of an adjacent molecule *via* a strong O1W—H1WA···O4 hydrogen bond, with an O···O distance of 2.719 (8) Å (Table 1), leading to the formation of an infinite zigzag supramolecular chain along the (001) direction, as shown in Fig. 2. These supramolecular chains are further joined into an extended two-dimensional supramolecular layer parallel to the [110] plane by a stronger hydrogen-bonded bridge between one carbonyl O atom, one uncoordinated water molecule and the coordinated water molecule, *e.g.* O2···H3WB—O3W···H1WB—O1W, but there is no hydrogen bonding between the layers (Fig. 3). Therefore, the complex crystal may be characterized as a two-dimensional hydrogen-bonded network.

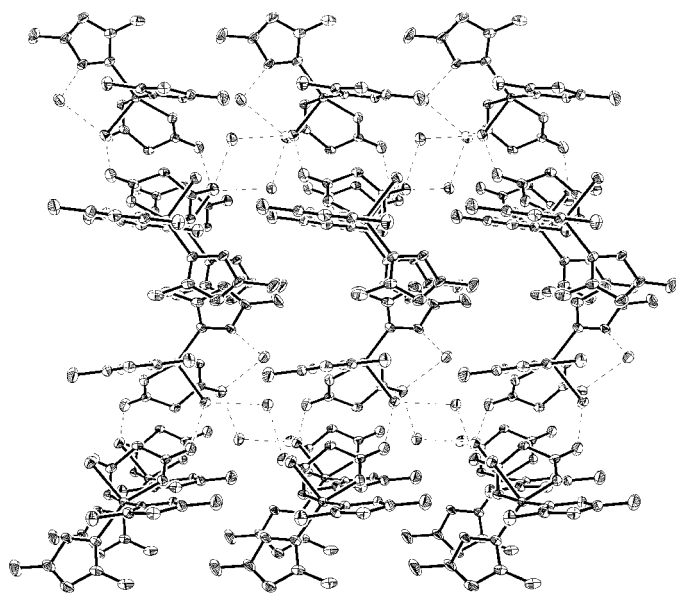


Figure 3
A view of the hydrogen-bonded supramolecular plane parallel to [110], showing the layer structure.

An important point to emerge from the above crystal analysis is that metal complexes containing mal may assemble into interesting hydrogen-bonded supramolecular networks due to the potential boat shape and four H-atom acceptors of mal, if ligands with H-atom donors are introduced to the mal-containing metal complex. These complexes can be useful new building blocks for crystal engineering.

Experimental

To an aqueous solution of H₂mal (100 ml, 1 mmol l⁻¹), Cu(OH)₂ powder (1 mmol) and solid dmp (2 mmol) were added slowly with stirring. The mixture was stirred for 15 min at 323 K. Blue polyhedral crystals of (I) appeared within 3 d (70% yield).

Crystal data

[Cu(C₃H₂O₄)(C₅H₈N₂)₂·
(H₂O)]·2H₂O
M_r = 411.90
Orthorhombic, *Pca*2₁
a = 24.000 (7) Å
b = 8.531 (3) Å
c = 9.369 (2) Å
V = 1918.2 (10) Å³
Z = 4

D_x = 1.426 Mg m⁻³
Mo *K*α radiation
Cell parameters from 25
reflections
θ = 7.5–15.0°
μ = 1.18 mm⁻¹
T = 293 (2) K
Prism, blue
0.46 × 0.36 × 0.32 mm

Data collection

Siemens *P4* diffractometer
ω scans
Absorption correction: empirical
via *ψ* scan (North *et al.*, 1968)
T_{min} = 0.523, *T_{max}* = 0.686
2821 measured reflections
2705 independent reflections
1654 reflections with *I* > 2σ(*I*)

R_{int} = 0.033
θ_{max} = 29°
h = -1 → 32
k = 0 → 11
l = 0 → 12
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.059
wR (*F*²) = 0.157
S = 1.03
2705 reflections
226 parameters
H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0781*P*)²]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.36 e Å⁻³
Δρ_{min} = -0.43 e Å⁻³
Absolute structure: Flack (1983)
Flack parameter = -0.01 (3)

Table 1
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>
O1W—H1WA···O4 ⁱ	1.13	1.77	2.719 (8)	139
O1W—H1WB···O3W ⁱⁱ	0.83	2.22	2.815 (7)	129
O2W—H2WA···O2	0.90	2.23	2.816 (10)	122
O2W—H2WA···O1	0.90	2.40	3.059 (9)	130
O2W—H2WB···O4 ⁱⁱⁱ	0.88	2.35	2.965 (9)	127
O3W—H3WA···O4 ^{iv}	0.94	2.28	3.041 (10)	138
O3W—H3WB···O2	0.94	1.82	2.762 (9)	175
N2—H2···O1	1.00	2.20	2.812 (9)	118
N4—H4···O3	0.93	2.24	2.731 (9)	112

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

H atoms attached to C atoms were placed in their optimized positions with *U*_{iso} fixed at 0.08 Å²; the N—H and water H atoms were located in difference Fourier maps and were included in fixed positions. Although the Flack parameter (Flack, 1983) is zero within one s.u., note that this is based on only a few Bijvoet pairs and may be unreliable.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1196). Services for accessing these data are described at the back of the journal.

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