

Bis(dimethylammonium) di- μ -pyrazole-3,5-dicarboxylato(3-)-bis[aquacopper(II)] monohydrate**Xin-Hua Li**School of Chemistry and Materials Science,
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In the title compound, $(\text{C}_2\text{H}_8\text{N})_2[\text{Cu}_2(\text{C}_5\text{HN}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, the cations, anions and water molecules are linked by hydrogen bonds into a network structure. Two pyrazole-3,5-dicarboxylate trianions and one water molecule are coordinated to the Cu^{II} ion and the geometry is square-pyramidal. Each pair of Cu^{II} ions is bridged by two pyrazole-3,5-dicarboxylate trianions, forming a dinuclear ring.

Received 19 October 2005

Accepted 24 October 2005

Online 27 October 2005

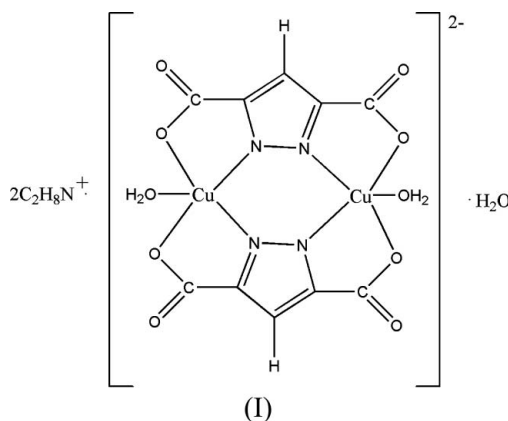
Key indicators

Single-crystal X-ray study
 $T = 298 \text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
 R factor = 0.046
 wR factor = 0.109
 Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The design and synthesis of supramolecular inorganic architectures exhibiting novel properties provide exciting new opportunities (Swiegers & Malefsete, 2002; Johnson & Raymond, 2001; Hof *et al.*, 2002). In the synthesis of supramolecular inorganic architectures by design, the assembly of molecular units in predefined arrangements is a key goal (Desiraju, 1995, 1997; Braga *et al.*, 1998). Directional intermolecular interactions are the primary tools in achieving this goal and hydrogen bonding is currently the best among them (Zaworotko, 1997; Braga & Grepioni, 2000). We report here the structure of the title compound, (I), which consists of dimethylammonium cations, $[\text{Cu}(\text{C}_5\text{HO}_4\text{N}_2)(\text{H}_2\text{O})]_2^{2-}$ anions and solvent water molecules.



The geometry around each Cu^{II} ion in (I) is square-pyramidal, arising from coordination by two pyrazole-3,5-dicarboxylate trianions and a water molecule. A carboxylate O atom and an N atom of one pyrazole-3,5-dicarboxylate trianion are chelated to a Cu^{II} cation, such that each pair of Cu^{II} ions has the same coordination environment bridged by two pyrazole-3,5-dicarboxylate trianions, forming a symmetric dinuclear ring (Fig. 1).

The cations, anions and water molecules of (I) interact through $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2) to generate a three-dimensional network (Fig. 2).

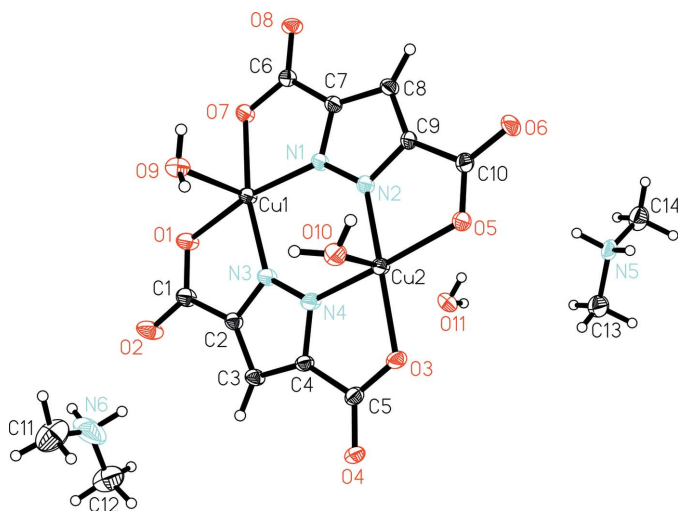


Figure 1
The asymmetric unit of (I), with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level.

Experimental

Copper chloride dihydrate (0.04 g, 0.2 mmol) was dissolved in aqueous dimethylamine (40%, 10 ml), and the solution was mixed with a dimethylformamide solution (10 ml) of pyrazole-3,5-dicarboxylic acid (0.4 g, 2 mmol) and 2,2'-dithiosalicylic acid (0.07 g, 0.2 mmol). The reaction mixture was filtered. Blue block-shaped crystals of (I) separated from the solution after about a month.

Crystal data

$(C_2H_8N)_2[Cu_2(C_5HN_2O_4)_2(H_2O)_2] \cdot H_2O$	$Z = 2$
$M_r = 579.47$	$D_x = 1.788 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.2094 (7) \text{ \AA}$	Cell parameters from 5717 reflections
$b = 10.6365 (8) \text{ \AA}$	$\theta = 1.9\text{--}25.1^\circ$
$c = 12.6853 (10) \text{ \AA}$	$\mu = 2.05 \text{ mm}^{-1}$
$\alpha = 109.775 (1)^\circ$	$T = 298 (2) \text{ K}$
$\beta = 111.109 (1)^\circ$	Block, blue
$\gamma = 91.252 (2)^\circ$	$0.48 \times 0.25 \times 0.22 \text{ mm}$
$V = 1076.14 (14) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	3760 independent reflections
ω scans	3371 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.015$
$T_{\text{min}} = 0.540$, $T_{\text{max}} = 0.632$	$\theta_{\text{max}} = 25.1^\circ$
5717 measured reflections	$h = -10 \rightarrow 10$
	$k = -11 \rightarrow 12$
	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 2.5226P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 1.38 \text{ e \AA}^{-3}$
3760 reflections	$\Delta\rho_{\text{min}} = -1.51 \text{ e \AA}^{-3}$
310 parameters	
H atoms treated by a mixture of independent and constrained refinement	

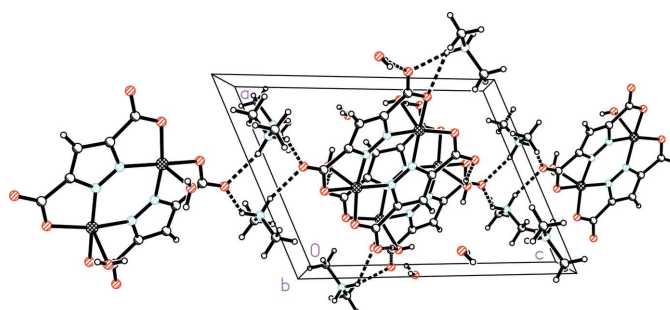


Figure 2
A perspective view of the molecular packing of (I), with hydrogen bonds shown as dashed lines.

Table 1

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

Cu1—N3	1.920 (3)	Cu2—N2	1.922 (3)
Cu1—N1	1.920 (3)	Cu2—N4	1.923 (3)
Cu1—O1	2.009 (3)	Cu2—O3	2.007 (3)
Cu1—O7	2.016 (3)	Cu2—O5	2.022 (3)
Cu1—O9	2.282 (3)	Cu2—O10	2.304 (3)
N3—Cu1—N1	93.04 (13)	N2—Cu2—N4	92.85 (13)
N3—Cu1—O1	79.95 (12)	N2—Cu2—O3	167.80 (13)
N1—Cu1—O1	167.82 (14)	N4—Cu2—O3	80.07 (12)
N3—Cu1—O7	168.19 (14)	N2—Cu2—O5	79.99 (12)
N1—Cu1—O7	79.95 (12)	N4—Cu2—O5	168.30 (14)
O1—Cu1—O7	105.18 (11)	O3—Cu2—O5	105.26 (11)
N3—Cu1—O9	99.99 (14)	N2—Cu2—O10	100.07 (13)
N1—Cu1—O9	97.68 (13)	N4—Cu2—O10	100.35 (14)
O1—Cu1—O9	93.37 (12)	O3—Cu2—O10	91.02 (12)
O7—Cu1—O9	90.41 (11)	O5—Cu2—O10	90.07 (11)

Table 2

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O9—H9B \cdots O6 ⁱ	0.82	2.03	2.820 (4)	162
O10—H10B \cdots O11 ⁱⁱ	0.82	1.97	2.785 (5)	177
O11—H11D \cdots O4 ⁱⁱⁱ	0.81 (3)	1.91 (3)	2.702 (4)	166 (5)
O11—H11E \cdots O8 ^{iv}	0.81 (3)	2.02 (3)	2.819 (4)	166 (5)
O9—H9A \cdots O11 ⁱⁱ	0.82	2.02	2.843 (4)	175
O10—H10A \cdots O8 ⁱ	0.82	1.98	2.787 (4)	170
N5—H5B \cdots O6 ^v	0.90	1.92	2.759 (4)	155
N5—H5A \cdots O3 ⁱⁱⁱ	0.90	2.65	3.336 (4)	134
N5—H5A \cdots O4 ⁱⁱⁱ	0.90	1.97	2.773 (4)	148
N6—H6B \cdots O2	0.90	2.00	2.731 (6)	138
N6—H6A \cdots O2 ^{vi}	0.90	2.07	2.945 (10)	164

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

The uncoordinated water H atoms were refined subject to the restraint $O\text{---}H = 0.82 (3) \text{ \AA}$. H atoms attached to C atoms were included in the refinement in calculated positions in the riding-model approximation [$C\text{---}H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for Csp^2 , and $C\text{---}H = 0.96 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for Csp^3]. All other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $0.82 (O\text{---}H)$ and $0.90 \text{ \AA} (N\text{---}H)$ with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(\text{parent atom})$. The maximum and minimum electron-density peaks are located 0.95 and 0.36 \AA from atoms H6B and N6, respectively.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

We acknowledge financial support from the Zhejiang Provincial Natural Science Foundation of China (grant No. Y404294) and the '151' Distinguished Person Foundation of Zhejiang Province.

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