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Poly[[aquatetraimidazoledi-μ-phthalato-dicopper(II)] monohydrate]

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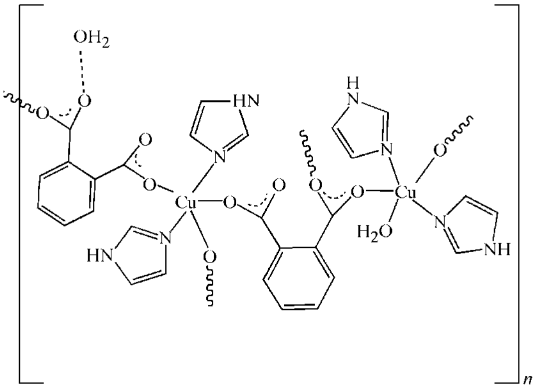
The title complex, $\{[Cu_2(C_8H_4O_4)_2(C_3H_4N_2)_4(H_2O)]\cdot H_2O\}_n$, is a three-dimensional polymer formed through bridging by phthalate dianions of two different Cu^{II} cations and a network of O(N)—H···O hydrogen bonds. The Cu—O and Cu—N interaction distances are in the ranges 2.0020 (16)–2.4835 (17) and 1.968 (2)–1.9855 (19) Å, respectively. The structure is composed of alternating polymer chains parallel to the *c* axis, with a shortest Cu···Cu distance of 6.3000 (5) Å.

Comment

There has been considerable interest in the design and synthesis of transition metal complexes with carboxylate ligands in coordination chemistry, owing to the fact that this type of complex has potential applications in molecular-based magnets, catalysis, supramolecular chemistry and biological systems (Li *et al.*, 2002; Shi *et al.*, 2000; Devereux *et al.*, 2000). It is known that the phthalate dianion is a versatile ligand able to chelate to, as well as bridge, metal ions. The variety of its coordination modes provides the possibility of preparing new metal phthalates with diverse topological structures and interesting physical properties (Biagini Cingi *et al.*, 1979; Squire *et al.*, 1995; Whitcomb & Rogers, 1997).

Several structures of Cu^{II} complexes with the phthalate ligand (pht) have been reported, *viz.* $[Cu(pht)(4\text{-MeIm})_2(H_2O)]_n$ (4-MeIm is 4-methylimidazole; Baca, Malinovskii *et al.*, 2004), $\{[Cu(pht)(phen)_2(H_2O)]\cdot H_2O\}_n$ (phen is 1,10-phenanthroline; Ye *et al.*, 2005), $[CuNa_2(pht)_2(H_2O)_2]_n$ (Liu *et al.*, 2003), $[Cu(pht)(1\text{-MeIm})_2]_n$ (Baca, Filippova *et al.*, 2004) and $[Cu(pht)_2(pic)_4(H_2O)]$ (pic is 4-methylpyridine; Gerbeleu *et al.*, 1999). In these structures, the Cu^{II} ions are all found to have the same stereochemistry. To the best of our knowledge, different Cu^{II} coordination sites have only been found in one structure, *viz.* $\{[Cu(dien)]_2[Cu(dien)(H_2O)]TCB(ClO_4)_2\cdot H_2O\}_n$ (TCB is tetracarboxylatobenzene and dien is 3-azapentane-1,5-diamine; Zou *et al.*, 1998). We report here another novel three-dimensional copper phthalate compound, $\{[Cu_2(pht)_2(Im)_4(H_2O)]\cdot H_2O\}_n$, (I), in which two different copper(II) environments are observed.



(I)

The molecular structure of (I) (Fig. 1 and Table 1) can be described as a three-dimensional network of Cu^{II} ions, which are linked by phthalate dianions into columns, lying approximately parallel to the *c* axis, crosslinked by an extensive network of hydrogen bonds; this network includes water molecules of crystallization (Fig. 2 and Table 2).

The Cu1 ion adopts a distorted square-pyramidal N_2O_3 environment, with the basal plane defined by atoms O1 and O3 from two phthalate ligands, and atoms N1 and N3 from two imidazole ligands; there is a long Cu—O8(carboxylate) apical interaction (Table 1). The Cu2 ion is also coordinated in a square-pyramidal geometry, in this case by two imidazole ligands (N5 and N7), a phthalate ligand (O7) and a water

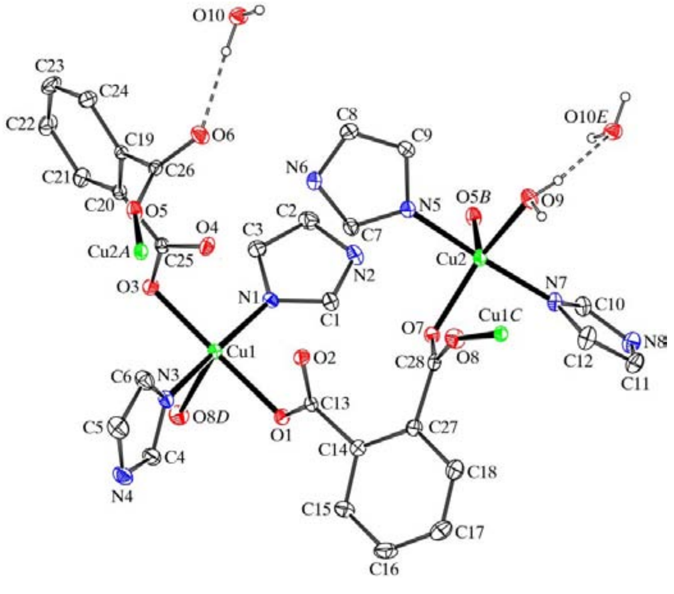


Figure 1
The asymmetric unit plus additional atoms showing the polymeric links of (I), with displacement ellipsoids at the 30% probability level. Dashed lines represent hydrogen bonds. [Symmetry codes: (*A*) $x - 1, y, z$; (*B*) $x + 1, y, z$; (*C*) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$; (*D*) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (*E*) $-x + 1, -y + 1, -z + 1$.]

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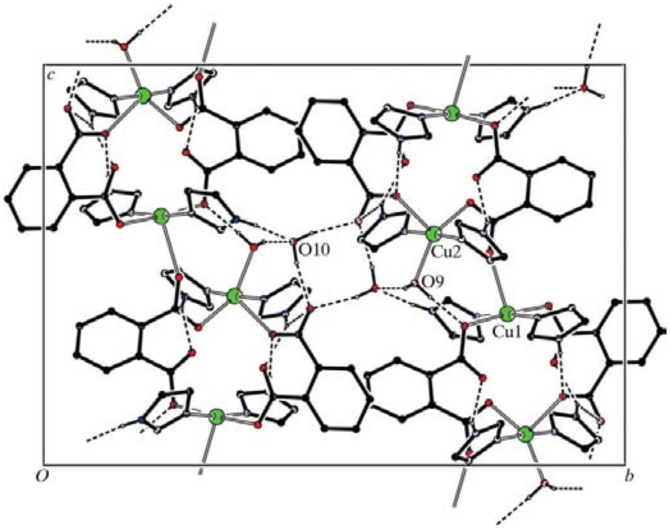

Figure 2
A packing diagram of (I), with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted (see Table 2).

molecule (O9) in the basal plane, with the apical position occupied by carboxylate atom O5. The equatorial Cu—N, Cu—O(pht) and Cu—O(water) distances are in agreement with the corresponding distances observed in $[Cu(pht)(4\text{-}MeIm)_2(H_2O)]_n$ (Baca, Malinovskii *et al.*, 2004) and $[Cu(pht)_2(pic)_4(H_2O)]$ (Gerbeleu *et al.*, 1999). The axial Cu2—O5 distance is longer than that in the related complex $[Cu(pht)_2(pic)_4(H_2O)]$ [2.240 (4) Å], but shorter than that in $[Cu(pht)(4\text{-}MeIm)_2(H_2O)]_n$ [2.353 (2) Å]. The C—O bond distances of the carboxylate groups are normal, with coordinated C—O bond distances slightly longer [by 0.004 (3)–0.050 (3) Å] than the uncoordinated C—O bond distances.

Each phthalate dianion acts as a bidentate ligand, bridging two different Cu^{II} ions through O atoms from both carboxylate groups (1,6-bridging mode). On the basis of this coordination mode of the phthalate ligand, including the weak interaction between atoms Cu1 and O8, an infinite polymeric network is formed parallel to the *c* axis (Fig. 2), with a shortest inter-column Cu⋯Cu distance of 6.3000 (5) Å. All available H atoms are involved in hydrogen-bond interactions (Table 2). The coordinated and solvent water molecules (atoms O9 and O10), and the uncoordinated imidazole N atoms (atoms N2, N4, N6 and N8) are linked through hydrogen bonds to uncoordinated carboxylate O atoms (atoms O2, O4 and O6). Thus, the alternating infinite chains are linked to each other through these hydrogen-bond interactions to form a stable three-dimensional coordination polymer.

Experimental

Basic copper(II) carbonate (0.220 g, 1 mmol) was added to a solution of *o*-phthalic acid (0.167 g, 1 mmol) and imidazole (0.14 g, 2 mmol) in water (15 ml). The resulting mixture was stirred and heated at 328 K for 30 min. The resulting solution was cooled to room temperature and filtered. Blue single crystals were obtained from the filtrate after a period of two weeks.

Crystal data

$[Cu_2(C_8H_4O_4)_2(C_3H_4N_2)_4(H_2O)]\cdot H_2O$
$M_r = 763.66$
Monoclinic, $P2_1/c$
$a = 8.8863$ (4) Å
$b = 22.3787$ (10) Å
$c = 16.1281$ (7) Å
$\beta = 106.4700$ (10)°
$V = 3075.7$ (2) Å^3
$Z = 4$
$D_x = 1.649$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 1.45$ mm^{-1}
$T = 292$ (2) K
Irregular, blue
0.30 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.670$, $T_{\max} = 0.893$
35554 measured reflections
7066 independent reflections
5531 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.090$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 0.95$
7066 reflections
457 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.968 (2)	Cu2—N7	1.961 (2)
Cu1—N1	1.9855 (19)	Cu2—N5	1.967 (2)
Cu1—O3	2.0020 (16)	Cu2—O7	2.0137 (16)
Cu1—O1	2.0712 (16)	Cu2—O9	2.0483 (17)
Cu1—O8^{i}	2.4835 (17)	Cu2—O5^{ii}	2.3070 (16)
O1—C13	1.278 (3)	O5—C26	1.252 (3)
O3—C25	1.267 (3)	O7—C28	1.273 (3)
N3—Cu1—N1	172.39 (8)	N5—Cu2—O7	93.16 (7)
N3—Cu1—O3	90.38 (8)	N5—Cu2—O9	87.10 (8)
N3—Cu1—O1	87.67 (8)	N7—Cu2—O5^{ii}	92.49 (7)
O3—Cu1—O1	175.61 (6)	N5—Cu2—O5^{ii}	88.26 (8)
N7—Cu2—N5	176.65 (8)		

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

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O9—H9*A*⋯O10^{iii}	0.81 (3)	2.02 (3)	2.804 (3)	164 (3)
O9—H9*B*⋯O1^{iv}	0.82 (2)	1.94 (2)	2.729 (2)	162 (3)
N2—H2*A*⋯O5^{ii}	0.86 (3)	2.00 (3)	2.832 (3)	163 (3)
N4—H4*A*⋯O10^{v}	0.83 (3)	1.98 (3)	2.787 (3)	163 (3)
N6—H6*A*⋯O4	0.85 (3)	2.09 (2)	2.805 (3)	140 (3)
N6—H6*A*⋯O6	0.85 (3)	2.46 (3)	3.078 (3)	130 (3)
N8—H8*A*⋯O2^{ii}	0.85 (2)	2.01 (2)	2.713 (3)	139 (3)
O10—H10*A*⋯O6^{vi}	0.815 (18)	1.878 (18)	2.686 (2)	171 (3)
O10—H10*B*⋯O6	0.82 (2)	2.00 (2)	2.809 (3)	170 (3)

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

All the water and N-bound H atoms were located in difference Fourier maps and their positional parameters were refined with O—H and N—H distances restrained to 0.82 (2) and 0.86 (2) Å, respectively. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H bond lengths of 0.93 Å and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3009). Services for accessing these data are described at the back of the journal.

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