metal-organic papers

μ-1,1′-Methylenedi-1H-imidazole-κ^2N^3:$N^{3'}$-bis[aqua(pyridine-2,6-dicarboxylato)copper(II)] tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.082
Data-to-parameter ratio = 14.0

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

The title compound, [Cu$_2$(C$_7$H$_3$NO$_4$)$_2$(C$_7$H$_8$N$_4$)(H$_2$O)$_2$]·4H$_2$O, has a dinuclear structure in which each Cu^{II} atom is five-coordinate in a distorted square-based pyramidal geometry and the 1,1′-methylenedi-1H-imidazole ligand adopts a bis-monodentate bridging mode, linking the Cu^{II} atoms. A twofold rotation axis passes through the C atom linking the imidazole rings. The molecules are connected by O—H···O hydrogen bonds [O···O = 2.748 (3)–2.973 (3) Å].

Comment

Alkyl-linked bis-imidazole ligands are known to be a kind of bridging ligand in which the flexible nature of the spacers allows the ligands to bend and rotate when coordinating to metal centers to accommodate the coordination geometries of the metal ions (Duncan *et al.*, 1996; Wu *et al.*, 1997; Ballester *et al.*, 1998; Ma *et al.*, 2004). The crystal structures of some metal complexes with the ligand bis(1-imidazolyl)methane, *L*, have been reported (Cui *et al.*, 2005). In a further study of the coordination chemistry of this ligand, we report here the crystal structure of the title compound, (I).

(I)
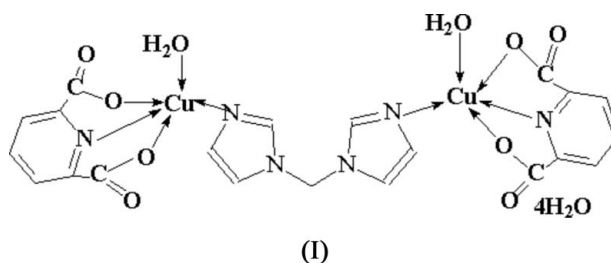
The asymmetric unit of (I) contains one copper(II), one PDC (H$_2$PDC is pyridine-2,6-dicarboxylate acid) ligand, half of an *L* ligand, one coordinated water molecule and two uncoordinated water molecules. A twofold rotation axis passes through atom C10. The Cu^{II} center is five-coordinate in a distorted square-based pyramidal geometry (Fig.1). Selected geometric parameters are given in Table 1. Each Cu^{II} center is coordinated by two carboxylate O atoms and one N atom from a tridentate PDC ligand and another N atom from an *L* ligand together with one water O atom. Two carboxylate O atoms and two N atoms define the basal plane, and the water O atom occupies the apical position. Each *L* ligand bridges two copper atoms related by a twofold axis to give a dinuclear structure. The dihedral angle between the two symmetry-related imidazole rings is 97.2 (4)°. There are extensive hydrogen-bonding interactions (Table 2) involving the carboxylate O atoms of the PDC ligands as well as coordinated and unco-ordinated water molecules.
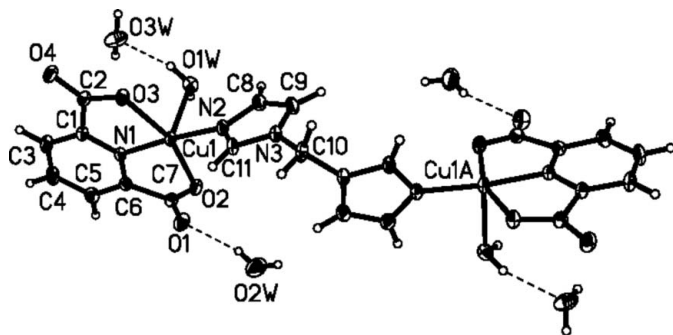
Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering. The suffix A denotes an atom related by the symmetry code $(1 - x, y, \frac{1}{2} - z)$. Dashed lines indicate hydrogen bonds.

Experimental

Bis(1-imidazolyl)methane (L) was prepared according to the reported procedure (Schütze & Schubert, 1959). A mixture of Cu(NO₃)₂·3H₂O (120.5 mg, 0.5 mmol), pyridine-2,6-dicarboxylic acid (167 mg, 1 mmol), NaOH (80 mg, 2 mmol), L (74 mg, 0.5 mmol) and water (18 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated to 433 K for 60 h. The reaction mixture was cooled to room temperature over a period of 60 h. Blue prismatic crystals of compound (I) suitable for X-ray difraction analysis were obtained in a yield of 37%. Analysis calculated for $C_{21}H_{26}Cu_2N_6O_{14}$: C 35.35, H 3.67, N 11.78%; found: C 34.49, H 3.59, N 11.48%.

Crystal data

$[Cu_2(C_7H_3NO_4)_2(C_7H_8N_4)(H_2O)_2]·4H_2O$	$D_x = 1.785$ Mg m⁻³
$M_r = 713.56$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 920
$a = 35.376\ (7)$ Å	reflections
$b = 5.1136\ (10)$ Å	$\theta = 4.5–25.5°$
$c = 14.868\ (3)$ Å	$\mu = 1.69$ mm⁻¹
$\beta = 99.15\ (3)°$	$T = 293\ (2)$ K
$V = 2655.4\ (9)$ Å³	Prism, blue
$Z = 4$	$0.20 \times 0.18 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2962 independent reflections
	2526 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.026$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
	$h = -45 \rightarrow 45$
$T_{min} = 0.729$, $T_{max} = 0.774$	$k = -6 \rightarrow 6$
11796 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 4.4628P]$
$wR(F^2) = 0.082$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.002$
2962 reflections	$\Delta\rho_{max} = 0.40$ e Å⁻³
211 parameters	$\Delta\rho_{min} = -0.26$ e Å⁻³
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.9137 (18)	Cu1—O3	2.0537 (16)
Cu1—N2	1.9492 (18)	Cu1—O1W	2.2820 (19)
Cu1—O2	2.0240 (17)		
N1—Cu1—N2	173.90 (8)	O2—Cu1—O3	159.25 (7)
N1—Cu1—O2	80.27 (7)	N1—Cu1—O1W	93.92 (7)
N2—Cu1—O2	98.58 (7)	N2—Cu1—O1W	92.16 (7)
N1—Cu1—O3	79.60 (7)	O2—Cu1—O1W	96.04 (7)
N2—Cu1—O3	100.91 (7)	O3—Cu1—O1W	90.28 (7)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1W—H1WA⋯O3ⁱ	0.84 (1)	1.91 (2)	2.748 (3)	170 (3)
O1W—H1WB⋯O3W	0.84 (1)	2.03 (3)	2.802 (3)	154 (3)
O2W—H2WA⋯O1	0.80	2.08	2.806 (3)	150
O2W—H2WB⋯O2Wⁱⁱ	0.81	2.44	2.912 (5)	118
O3W—H3WA⋯O4ⁱ	0.83 (1)	1.99 (3)	2.819 (3)	173 (3)
O3W—H3WB⋯O4ⁱⁱⁱ	0.83 (1)	2.18 (3)	2.973 (3)	159 (3)

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

Water H atoms were located in a difference Fourier map. H atoms attached to O1W and O3W were refined isotropically with O—H and H⋯H restraints of 0.84 (1) and 1.37 (2) Å, respectively, whereas those attached to O2W were allowed to ride on it, with $U_{iso}(H) = 1.5U_{eq}(O2W)$. The remaining H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and included in the final cycles of refinement using a riding model, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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