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catena-Poly[[aquabis(1*H*-imidazole-κN^3)copper(II)]-μ-benzene-1,4-dioxyacetato-κ^2O:O']

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In the title coordination polymer, also called *catena*-poly-[[aquabis(1*H*-imidazole-κN^3)copper(II)]-μ-phenylenedioxydiacetato-κ^2O:O'], [Cu(1,4-BDOA)($C_3H_4N_2$)$_2$(H_2O)]$_n$ (where 1,4-BDOA^{2-} is benzene-1,4-dioxyacetate, $C_{10}H_8O_6$), the Cu^{II} atom is five-coordinate involving two O atoms of the 1,4-BDOA ligand, two N atoms of imidazole ligands and one water molecule, displaying a distorted square-pyramidal coordination geometry. The Cu^{II} atoms are bridged by carboxylate groups, forming a one-dimensional zigzag chain. The adjacent Cu···Cu distance is 12.656 (5) Å. Furthermore, such chains are linked by hydrogen-bond interactions, resulting in a three-dimensional network.

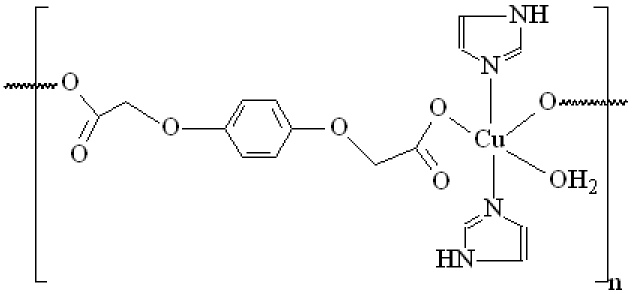
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.054
wR factor = 0.109
Data-to-parameter ratio = 15.7

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

Comment

Phenylenedioxydiacetic acids (BDOAH$_2$), biologically active compounds that are widely used in agriculture, are a family of flexible multidentate carboxylate ligands, which could possess the multiple coordination modes and the capability of forming coordination architectures of diverse sizes and shapes. However, only a few complexes with BDOAH$_2$ ligands have been structurally characterized thus far, and the majority of these contain 1,2-BDOAH$_2$ (Smith *et al.*, 1991; McCann *et al.*, 1994). In particular, the coordination chemistry of (*p*-phenylenedioxy)diacetic acid (or benzene-1,4-dioxyacetic acid) has been documented very little to date. As a contribution to this field, we have previously reported the structures of two one-dimensional chain complexes containing the 1,3-BDOAH$_2$ ligand, {[Zn(1,3-BDOA)(H_2O)$_2$]·2H_2O}$_n$ (Gao *et al.*, 2004) and {[Cu(1,3-BDOA)(bipy)]·H_2O}$_n$, (II), in which the Cu^{II} atom shows a square-pyramidal configuration (Liu *et al.*, 2004).



(I)

In the present report, we have used 1,4-BDOAH$_2$ and imidazole instead of 1,3–BDOAH$_2$ and 2,2-bipy in the reaction and synthesized a new Cu^{II} polymer, *viz*. [Cu(1,4-BDOA)($C_3H_4N_2$)$_2$(H_2O)]$_n$, (I), the crystal structure of which is described here.

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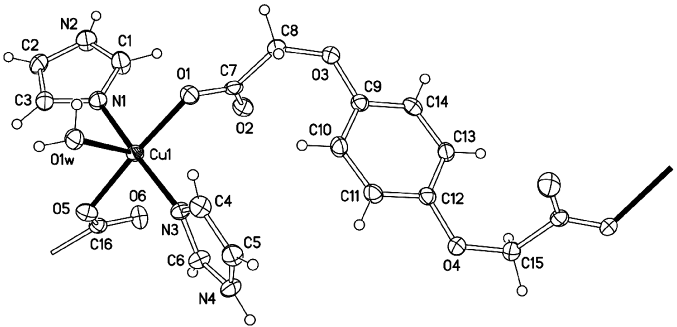

Figure 1
*ORTEP*II plot (Johnson, 1976) of the title complex, with displacement ellipsoids shown at the 30% probability level.

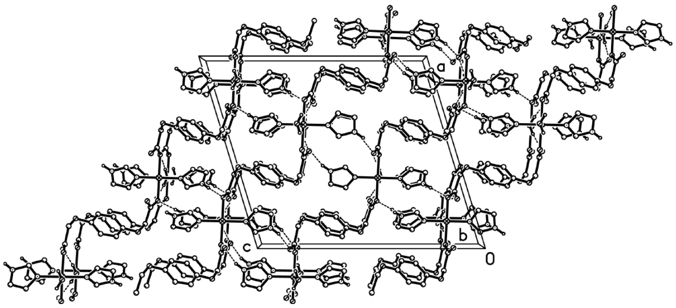

Figure 2
Packing diagram of the title complex. H bonds are indicated by dashed lines and all C—H H atoms are omitted for clarity.

As illustrated in Fig. 1, the carboxylate group is bound to the Cu^{II} atom in the monodentate fashion. Each Cu^{II} ion displays a five-coordinate distorted square-pyramidal configuration, defined by two N atoms from two imidazole ligands [mean Cu—N = 1.990 (3) Å], two carboxyl O atoms from the 1,4-BDOA ligand and one water molecule. Atoms O1, O5, N1 and N3 define a square plane [r.m.s. = 0.01(4) Å], in which the Cu^{II} deviates by 0.09 (5) Å from the plane, whilst the water molecule (O1*W*) occupies the apical site, with a Cu—O1*W* bond distance of 2.243 (2) Å. The Cu—$O_{carboxyl}$ distances are 1.994 (2) and 2.005 (2) Å, which are longer than the corresponding Cu—O distances of 1.957 (3) and 1.941 (3) Å in (II). This is also reflected by the fact that the two oxyacetate groups are substantially twisted out the benzene ring plane in (I), with the C9—O3—C8—C7 and C12—O4—C15—C16 torsion angles being −71.9 (4) and 74.8 (3)°, respectively, whereas the torsion angles of the two oxyacetate groups and phenyl ring in (II) are 163.4 (3) and −82.0 (3)°, respectively, and suggest the 1,4-$BDOA^{2-}$ ligand has more conformational flexibility than that of the 1,3-$BDOA^{2-}$ ligand.

It should be noted that the O1—C7 [1.263 (4) Å] and O5—C16 [1.278 (4) Å] distances are longer than the O2—C7 [1.237 (4) Å] and O6—C16 [1.222 (4) Å] distances, in accord with greater double-bond character of the latter bonds. The dihedral angles between two imidazole molecules and benzene rings are 30.6 (3) and 83.4 (3)°, and the dihedral angle between the two imidazole ligands is 81.9 (3)°.

Each 1,4-$BDOA^{2-}$ group serves as a bidentate ligand to link two Cu^{II} atoms, giving rise to a one-dimensional zigzag chain structure. In the chain, the adjacent Cu···Cu distance is 12.656 (5) Å, while the interval Cu···Cu distance within the chain is 21.285 (5) Å. Furthermore, the chains are connected through intermolecular hydrogen bonds involving the uncoordinated imidazole N atoms, the coordinated water molecule, carboxyl O atoms and ether O atoms of the 1,4-$BDOA^{2-}$ groups, leading to a three-dimensional hydrogen-bonding network (for details, see Table 2 and Fig. 2).

Experimental

Benzene-1,4-dioxyacetic acid was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). The title complex was prepared by the addition of a stoichiometric amount of $Cu(acetate)_2 \cdot H_2O$ (2.00 g, 10 mmol), NaOH (0.80 g, 20 mmol) and imidazole (1.36 g, 20 mmol) to a hot aqueous solution of 1,4–$BDOAH_2$ (2.26 g, 10 mmol), with subsequent filtration. Blue crystals were obtained at room temperature over several days. Analysis calculated for $C_{16}H_{18}CuN_4O_7$: C 43.49, H 4.11, N 12.68%; found: C 43.31, H 4.02, N 12.75%.

Crystal data

$[Cu(C_{10}H_8O_6)(C_3H_4N_2)_2(H_2O)]$
$M_r = 441.89$
Monoclinic, $P2_1/n$
$a = 16.699 (3)$ Å
$b = 6.0327 (12)$ Å
$c = 18.977 (4)$ Å
$\beta = 107.06 (3)°$
$V = 1827.6 (7)$ Å^3
$Z = 4$
$D_x = 1.606$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10508 reflections
$\theta = 3.2$–27.5°
$\mu = 1.24$ mm^{-1}
$T = 293 (2)$ K
Prism, blue
0.39 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.643$, $T_{max} = 0.807$
11517 measured reflections
4153 independent reflections
3177 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.5°$
$h = -21 \rightarrow 21$
$k = -7 \rightarrow 7$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.109$
$S = 1.05$
4153 reflections
265 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.7112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.987 (3)	O1—C7	1.263 (4)
Cu1—N3	1.994 (2)	O2—C7	1.237 (4)
Cu1—O1	1.994 (2)	O5—C16	1.278 (4)
Cu1—O5	2.005 (2)	O6—C16	1.222 (4)
Cu1—O1*W*	2.243 (2)		
N1—Cu1—N3	173.5 (1)	N3—Cu1—O5	90.6 (1)
N1—Cu1—O1	91.9 (1)	N3—Cu1—O1*W*	91.4 (1)
N1—Cu1—O5	88.8 (1)	O1—Cu1—O5	175.1 (1)
N1—Cu1—O1*W*	95.1 (1)	O1—Cu1—O1*W*	92.63 (9)
N3—Cu1—O1	88.2 (1)	O5—Cu1—O1*W*	92.14 (9)

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{N2-H17}\cdots\mathrm{O2}^{\mathrm{i}}$	0.89 (4)	1.98 (4)	2.829 (4)	160 (4)
$\mathrm{N4-H18}\cdots\mathrm{O5}^{\mathrm{ii}}$	0.89 (3)	1.98 (3)	2.874 (3)	173 (4)
$\mathrm{O1}W-\mathrm{H1}W1\cdots\mathrm{O2}^{\mathrm{iii}}$	0.85 (3)	1.94 (3)	2.780 (3)	169 (3)
$\mathrm{O1}W-\mathrm{H1}W2\cdots\mathrm{O6}^{\mathrm{iii}}$	0.85 (3)	1.91 (3)	2.745 (3)	167 (3)

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

C-bound H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (aliphatic) and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, and were refined in the riding-model approximation. The water H atoms and the imidazole N—H atoms were located in a difference Fourier map and refined with O—H, H···H and N—H distance restraints of 0.85 (1), 1.39 (1) and 0.90 (1) Å, respectively, and with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O,N})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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