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catena-Poly[[[aqua(1,10-phenanthroline-κ^2N,N')-copper(II)]-μ-benzene-1,3-dioxyacetato-κ^2O:O'] dihydrate]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.040
wR factor = 0.105
Data-to-parameter ratio = 15.6

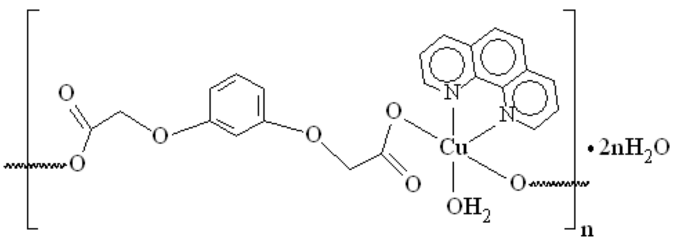
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title one-dimensional coordination polymer {systematic name: *catena*-poly[[[aqua(1,10-phenanthroline-κ^2N,N')copper(II)]-μ-phenylenebis(oxyacetato)-κ^2O:O'] dihydrate]}, $\{[Cu(C_{10}H_8O_6)(C_{12}H_8N_2)(H_2O)]\cdot 2H_2O\}_n$, the Cu^{II} atom has a distorted square-pyramidal coordination geometry, defined by two carboxyl O-atom donors from two benzene-1,3-dioxyacetate groups, two N-atom donors from the 1,10-phenanthroline ligand and one water molecule. The Cu^{II} ions are bridged by benzene-1,3-dioxyacetate dianions (1,3-BDOA^{2-}), resulting in a one-dimensional chain structure. The intrachain Cu$\cdots$Cu separation is 9.769 (4) Å. The chains are linked into a three-dimensional supramolecular network *via* hydrogen bonds and π–π stacking interactions.

Comment

Molecular self-assembly of supramolecular architectures has received much attention during recent decades (Kim *et al.*, 2003; Iglesias *et al.*, 2003; Moulton & Zaworotko, 2001). The structures and properties of such systems depend on the coordination and geometric preferences of both the central metals ions and bridging building blocks as well as the influence of weaker non-covalent interactions, such as hydrogen bonds and π–π stacking interactions. As a building block, phenylenedioxydiacetic acids ($BDOAH_2$) have multiple coordination modes and the capability of forming regular hydrogen bonds by functioning as both hydrogen-bond donors and acceptors. Hence, $BDOAH_2$ are excellent candidates for the construction of supramolecular complexes. Recently, we have reported a series of copper(II) (Gao, Liu, Huo, Zhao & Zhao, 2004*a*,*c*; Liu *et al.*, 2004), zinc(II) (Gao, Li, Liu & Huo, 2004; Gao, Liu, Huo, Zhao & Ng, 2004*a*,*b*), cobalt(II) (Gao, Liu, Huo, Zhao & Zhao, 2004*b*) and cadmium(II) (Gao, Liu, Huo, Zhao & Zhao, 2004*d*; Gao, Liu & Ng, 2004) complexes, which are based on 1,3- or 1,4-BDOA^{2-} dianions and form polymeric chain structures. However, the coordination chemistry of benzene-1,3-dioxyacetic acid has been little documented to date. In the case of the reported polymer $\{[Cu(1,4\text{-}BDOA)(phen)(H_2O)]\cdot H_2O\}_n$, (II) (Gao, Liu, Huo, Zhao & Zhao, 2004*a*), the Cu^{II} atom shows an octahedral geometry. In the present work, we used 1,3-$BDOAH_2$ instead of 1,4-$BDOAH_2$ in the reaction and isolated a new Cu^{II} complex, $\{[Cu(1,3\text{-}BDOA)(phen)(H_2O)]\cdot 2H_2O\}_n$, (I); its crystal structure is reported here.

As illustrated in Fig. 1, the asymmetric unit of complex (I) consists of a mononuclear Cu^{II} complex, $[Cu(1,3\text{-}BDOA)(phen)(H_2O)]$, and two water molecules of crystallization. Each Cu^{II} atom is covalently bonded to two O-atom donors from different monodentate carboxyl groups, two N-atom donors from a phen ligand [mean Cu—N = 2.018 (2) Å] and one water molecule, and displays a distorted square-pyramidal configuration. Atoms N1, N2, O1 and O5^i [symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$] define the basal plane [r.m.s. deviation = 0.11 (3) Å]; the Cu atom is displaced from the mean basal plane by 0.15 (4) Å. Atom O1*w* occupies the apical site, with a Cu—O1*w* bond distance of 2.323 (2) Å. The Cu—O(carboxyl) bond distances are somewhat different, with values of 1.955 (2) and 1.935 (2) Å. The dihedral angle between the planes of the benzene ring and the phen ligand is 71.0 (3)°. Both oxyacetate groups are obviously twisted out of the benzene ring plane, with torsion angles of 75.5 (3) (C19—O4—C21—C22) and −71.6 (3)° (C15—O3—C14—C13). These demonstrate that the two oxyacetate groups have more conformational flexibility than terephthalic acid.



(I)

The O1—C13 [1.269 (3) Å] and O5—C22 [1.264 (3) Å] distances are longer than the O2—C13 [1.229 (3) Å] and O6—C22 [1.231 (3) Å] distances, suggesting greater double-bond character of the latter bonds. These reflect the fact that each benzene-1,3-dioxyacetate ligand serves as a bis-monodentate bridging group to link two Cu^{II} ions, giving rise to a one-dimensional chain structure (see Fig. 2). The antiparallel phen ligands lie on alternate sides of the chain. The polymeric chains run along the *c* axis of the unit cell and show a corrugated arrangement. In the chain, the shortest adjacent Cu···Cu distance is 9.769 (4) Å. The shortest intrachain Cu···Cu distance in (I) is significantly shorter than that reported in (II) [11.325 (2) Å], in which copper centres are joined by 1,4-BDOA^{2-} ligands in monodentate and bidentate chelating modes, to generate a one-dimensional chain structure.

The polymeric chains in (I) are connected through an extensive network of hydrogen bonds among the carboxylate O atoms, the ether O atom and the water molecules, with the O···O distances ranging from 2.726 (3) to 3.249 (2) Å, and the O—H···O angles ranging from 141 (3) to 175 (3)° (Table 2), leading to a two-dimensional hydrogen-bonding layer architecture parallel to the crystallographic *bc* plane. Individual layers are stacked in an offset manner along the **a** direction, through π–π stacking interactions between phen ligands at 3.593 (3) Å. With the help of the hydrogen-bonding and π–π stacking interactions, a three-dimensional supramolecular network structure is constructed, as shown in Fig. 3.

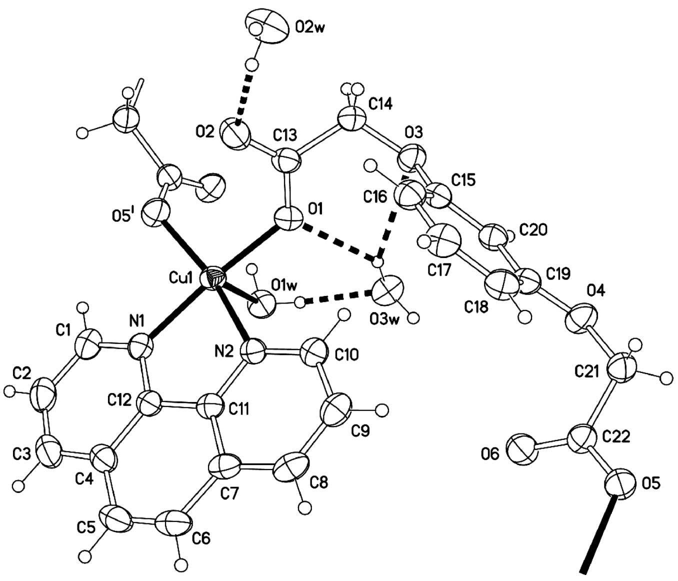


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title complex, showing displacement ellipsoids at the 30% probability level. Intermolecular hydrogen bonds are shown as dashed lines.

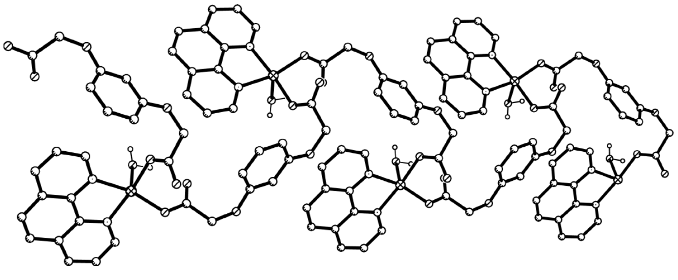


Figure 2
One-dimensional chain structure of the title complex. H atoms have been omitted.

Experimental

1,3-BDOAH$_2$ was prepared following the method described for the synthesis of 1,2-BDOAH$_2$ by Mirci (1990). The title complex was prepared by the addition of a stoichiometric amount of Cu(OAc)$_2$·H$_2$O (4.00 g, 20 mmol), NaOH (1.60 g, 40 mmol) and 1,10-phenanthroline (3.98 g, 20 mmol) to a hot aqueous solution of 1,3-BDOAH$_2$ (4.52 g, 20 mmol), with subsequent filtration. Blue crystals were obtained from the filtered solution at room temperature over a period of five days. Analysis calculated for $C_{22}H_{22}CuN_2O_9$: C 50.62, H 4.25, N 5.37%; found: C 50.82, H 4.18, N 5.41%.

Crystal data

$[Cu(C_{10}H_8O_6)(C_{12}H_8N_2)(H_2O)]\cdot 2H_2O$
M_r = 521.97
Monoclinic, $P2_1/n$
a = 9.0034 (10) Å
b = 19.4609 (19) Å
c = 12.7448 (13) Å
β = 93.005 (5)°
V = 2230.0 (4) Å^3
Z = 4

D_x = 1.555 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 20 290 reflections
θ = 3.4–27.5°
μ = 1.04 mm^{-1}
T = 293 (2) K
Prism, blue
0.38 × 0.24 × 0.18 mm

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Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.694$, $T_{\max} = 0.835$
21 197 measured reflections
5070 independent reflections
4250 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 27.4°$
$h = -11 \rightarrow 11$
$k = -23 \rightarrow 25$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.105$
$S = 1.04$
5070 reflections
325 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.6427P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.014 (2)	O1—C13	1.269 (3)
Cu1—N2	2.021 (2)	O2—C13	1.229 (3)
Cu1—O1	1.955 (2)	O5—C22	1.264 (3)
Cu1—O5$^{\rm i}$	1.935 (2)	O6—C22	1.231 (3)
Cu1—O1*w*	2.323 (2)		
N1—Cu1—N2	81.67 (7)	O1—Cu1—O1*w*	88.02 (6)
N1—Cu1—O1*w*	94.47 (6)	O5$^{\rm i}$—Cu1—N1	90.23 (7)
N2—Cu1—O1*w*	100.24 (6)	O5$^{\rm i}$—Cu1—N2	162.71 (7)
O1—Cu1—N1	172.78 (7)	O5$^{\rm i}$—Cu1—O1	96.28 (7)
O1—Cu1—N2	91.22 (7)	O5$^{\rm i}$—Cu1—O1*w*	95.58 (7)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*1···O3*w*	0.85 (3)	1.93 (3)	2.775 (3)	175 (3)
O1*w*—H1*w*2···O6$^{\rm i}$	0.85 (3)	1.97 (3)	2.781 (2)	158 (3)
O2*w*—H2*w*1···O2	0.85 (3)	1.95 (3)	2.774 (3)	162 (3)
O2*w*—H2*w*2···O6$^{\rm ii}$	0.85 (3)	2.04 (3)	2.856 (2)	161 (4)
O3*w*—H3*w*1···O2*w*$^{\rm iii}$	0.85 (3)	1.89 (3)	2.726 (3)	170 (3)
O3*w*—H3*w*2···O1	0.85 (3)	2.22 (2)	2.928 (2)	141 (3)
O3*w*—H3*w*2···O3	0.85 (3)	2.49 (2)	3.249 (2)	148 (3)

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

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

Data collection: *RAPID-AUTO* (Rigaku Corporation, 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; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

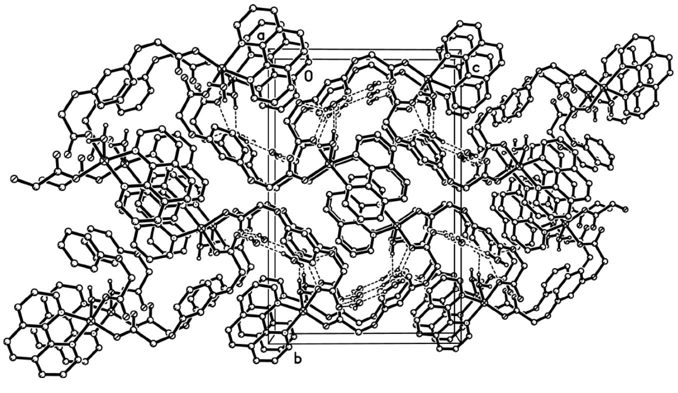

Figure 3
Packing diagram of the title complex. H atoms have been omitted. Dashed lines indicate hydrogen bonds.

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