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catena-Poly[[[aqua(1,10-phenanthroline-κ^2N,N')-copper(II)]-μ-benzene-1,4-dioxyacetato-$\kappa^3O,O':O''$] monohydrate]

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Key indicators

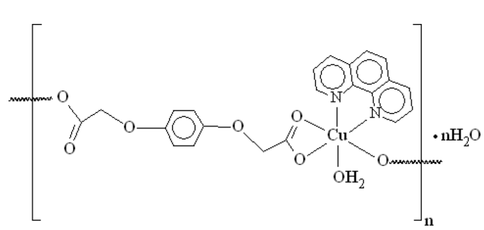
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 15.5

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

Each Cu^{II} atom in the title coordination polymer, $\{[Cu(1,4\text{-}BDOA)(phen)(H_2O)]\cdot H_2O\}_n$ [where 1,4-$BDOA^{2-}$ is the benzene-1,4-dioxyacetate dianion ($C_{10}H_8O_6^{2-}$) and phen is 1,10-phenanthroline ($C_{12}H_8N_2$)], shows a distorted octahedral coordination geometry, defined by three carboxyl O-atom donors from the benzene-1,4-dioxyacetate ligand, two N-atom donors from the phen ligand and one water molecule. The Cu^{II} ions are bridged by carboxylate groups, forming a one-dimensional chain structure. The Cu···Cu separation within the polymer is 11.325 (2) Å. Furthermore, the chains are linked into a three-dimensional supramolecular network *via* hydrogen bonds and π–π stacking interactions.

Comment

The rational design and construction of aromatic carboxylate coordination polymers is a rapidly developing research area of supramolecular chemistry, within which ligand design is an important aspect in adjusting the coordination framework and functionalities of the compounds formed. In contrast with the extensively studied coordination compounds with rigid ligands such as terephthalic acid and benzene tetracarboxylic acid (Lee *et al.*, 2003; Gomez-Lor *et al.*, 2002; Gutschke *et al.*, 2001), the coordination chemistry and structural properties of flexible multidentate ligands with versatile binding modes, such as benzene-1,4-dioxyacetic acid, have received little attention to date. As a contribution to this work, we have reported the structures of a number of mononuclear complexes incorporating this ligand, namely $[MnCl(1,10\text{-phenanthroline})_2(H_2O)]_2(1,4\text{-}BDOA)\cdot 2H_2O$ (Gao, Liu, Huo *et al.*, 2004), $[Mn(H_2O)_6](1,4\text{-}BDOA)$ (Liu, Huo, Gao, Zhao & Ng, 2004), $[Co(H_2O)_6](1,4\text{-}BDOA)$ (Liu, Gao *et al.*, 2004), $[Co(\text{triethanolamine})_2](1,4\text{-}BDOA)$ (Gao, Liu, Huo & Ng, 2004) and polymeric $\{[Cu(1,3\text{-}BDOA)(bipy)]\cdot H_2O\}_n$ (bipy is 2,2′-bipyridine), in which the Cu^{II} atom exhibits a square-pyramidal geometry and possesses an infinite zigzag chain structure (Liu, Huo, Gao, Zhao *et al.*, 2004). In the present work, we have isolated a new Cu^{II} complex, $\{[Cu(1,4\text{-}BDOA)(phen)(H_2O)]\cdot H_2O\}_n$, (I), where 1,4-$BDOA^{2-}$ is the benzene-1,4-dioxyacetate dianion, and report its crystal structure here.



(I)

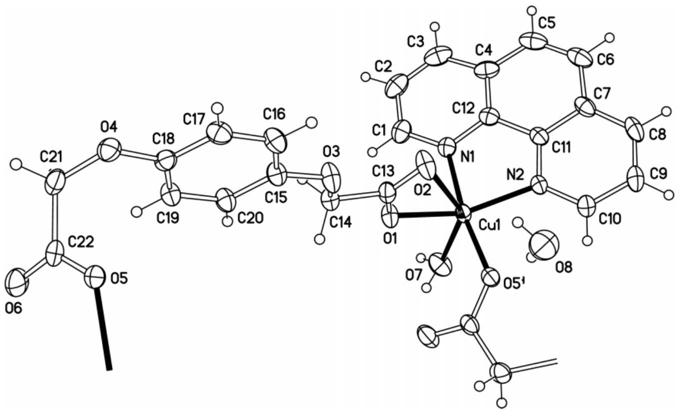


Figure 1
A view of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$].

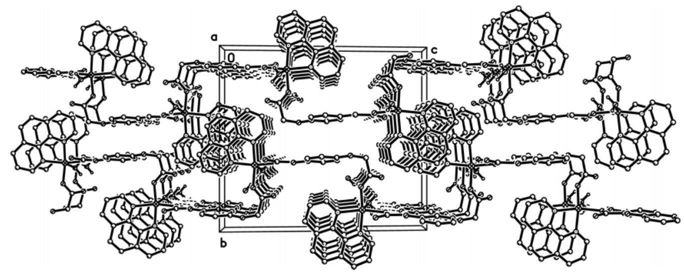


Figure 2
A packing diagram for (I), viewed down the *c* axis.

The asymmetric unit of (I) consists of a mononuclear complex, [Cu(1,4-BDOA)(phen)(H_2O)], and one water molecule of crystallization (Fig. 1). The 1,4-BDOA ligand acts as both a bidentate chelating ligand, through atoms O1 and O2, and a monodentate bridging ligand, through atom O5. Each Cu^{II} atom is six-coordinate in a distorted octahedral environment, of which the equatorial plane is defined by atoms O1 and O2 from the 1,4-BDOA ligand, atom N2 from the phen ligand and the coordinated water molecule [r.m.s. deviation 0.06 (2) Å; deviation of the Cu atom from this plane 0.04 (2) Å]. The axial positions are occupied by atom $O5^i$ from the 1,4-BDOA group [symmetry code: (i) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$] and the phen atom N1 [$O5^i$—Cu1—N1 171.94 (6)°]. The phen molecule acts as a terminal ligand, with a typical mean Cu—N distance [2.020 (2) Å]. It should be noted that the Cu—O2 distance of 2.812 (2) Å is considerably longer, indicative of weaker interaction with the Cu (Billing *et al.*, 1970). The O1—C13 [1.265 (2) Å] and O5—C22 [1.278 (2) Å] distances are longer than the O2—C13 [1.234 (2) Å] and O6—C22 [1.234 (2) Å] distances, in accord with the greater double-bond character of the latter bonds.

The bridging of the the Cu^{II} ions by the carboxylate groups of the 1,4-BDOA ligand results in the formation of a one-dimensional chain along the *c* axis. The antiparallel phen ligands lie on alternate sides of the chain. The shortest Cu···Cu distance in the chain is 11.325 (2) Å, slightly longer than the value of 11.284 (3) Å in the one-dimensional copper polymer with the terephthalate ligand (Bian *et al.*, 2003).

The bidentate oxyacetate group and the benzene ring are almost coplanar, with a C15—O3—C14—C13 torsion angle of 172.1 (2)°. In contrast, the monodentate oxyacetate group is twisted out of the benzene ring plane, with a C18—O4—C21—C22 torsion angle of −70.2 (2)°. The benzene ring is nearly perpendicular to the plane of the phen ligand, with a dihedral angle of 87.3 (1)°. In addition, the chains are connected through extensive hydrogen bonds, involving the coordinated and uncoordinated water molecules and the 1,4-BDOA groups, with O···O distances ranging from 2.689 (2) to 3.179 (2) Å and O—H···O angles ranging from 132 (2) to 170 (3)° (Table 2). There are face-to-face π–π stacking interactions between the benzene rings, at 3.611 (3) Å. With the help of such interactions, the polymeric chains assemble to form a three-dimensional supramolecular network (Fig. 2).

Experimental

Benzene-1,4-dioxyacetic acid was prepared according to 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)$_2$·H_2O (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 1,4-BDOAH_2 (4.52 g, 20 mmol), with subsequent filtration. Blue crystals of (I) were obtained after allowing the mixture to stand at room temperature for several days. Analysis, calculated for $C_{22}H_{20}N_2O_8Cu$: C 52.43, H 4.00, N 5.56%; found: C 52.65, H 4.08, N 5.70%.

Crystal data

[Cu($C_{10}H_8O_6$)($C_{12}H_8N_2$)(H_2O)]·H_2O
M_r = 503.95
Monoclinic, $P2_1/c$
a = 7.2444 (14) Å
b = 16.089 (3) Å
c = 18.276 (4) Å
β = 98.85 (3)°
V = 2104.8 (7) Å^3
Z = 4
D_x = 1.590 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 433 reflections
θ = 3.2–27.5°
μ = 1.09 mm^{-1}
T = 293 (2) K
Prism, blue
0.39 × 0.25 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.676, T_{max} = 0.819
20 006 measured reflections
4809 independent reflections
4031 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 20$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 1.04
4809 reflections
310 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.5695P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	2.004 (2)	Cu1—O7	2.280 (2)
Cu1—N2	2.036 (2)	O1—C13	1.265 (2)
Cu1—O1	1.968 (1)	O2—C13	1.234 (2)
Cu1—O2	2.812 (2)	O5—C22	1.278 (2)
Cu1—O5^{ii}	1.949 (1)	O6—C22	1.234 (2)
N1—Cu1—N2	81.40 (6)	O1—Cu1—O7	92.94 (6)
N1—Cu1—O2	91.24 (7)	O5^{ii}—Cu1—N1	171.94 (6)
N1—Cu1—O7	93.30 (6)	O5^{ii}—Cu1—N2	90.54 (6)
N2—Cu1—O2	103.54 (6)	O5^{ii}—Cu1—O1	95.13 (6)
N2—Cu1—O7	112.00 (7)	O5^{ii}—Cu1—O2	90.49 (6)
O1—Cu1—N1	92.12 (6)	O5^{ii}—Cu1—O7	89.86 (6)
O1—Cu1—N2	154.45 (6)	O7—Cu1—O2	144.46 (6)
O1—Cu1—O2	51.65 (6)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H23A···O2^{iv}	0.85 (3)	1.98 (3)	2.731 (2)	147 (3)
O7—H23A···O3^{iv}	0.85 (3)	2.55 (2)	3.179 (2)	132 (2)
O7—H23B···O6^{ii}	0.85 (3)	1.92 (3)	2.689 (2)	151 (2)
O8—H24A···O5^{ii}	0.85 (3)	2.17 (3)	3.013 (2)	170 (3)
O8—H24B···O7^{iii}	0.86 (3)	2.19 (3)	3.040 (3)	168 (3)

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

The H atoms of the 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 with $U_{iso}(H) = 1.5U_{eq}(O)$. C-bound H atoms were placed in calculated positions, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and were refined in the riding-model approximation.

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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