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catena-Poly[[[aquadipyridinecopper(II)]-μ-1,3-phenylenedioxydiacetato-κ^2*O*:*O*′] dihydrate]

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Key indicators

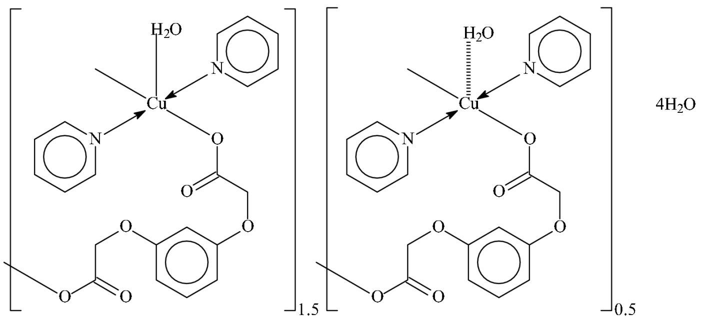
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.135
Data-to-parameter ratio = 16.1

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

The crystal structure of the title compound, $\{[Cu_2(C_{10}H_8O_6)_2(C_5H_5N)_4(H_2O)_2]\cdot 4H_2O\}_n$, consists of linear chains built from $Cu(C_{10}H_8O_6)(C_5H_5N)_2(H_2O)$ units (where the Cu*B* atom lies on a general position) bridged through the dicarboxylate dianion to two other $Cu(C_{10}H_8O_6)(C_5H_5N)_2(H_2O)$ units (the Cu*A* and Cu*C* atoms lie on different inversion centers). The Cu*A* and Cu*C* atoms of the two units at the inversion centers are disordered over two sites, and the disorder is such that these atoms are five-coordinate in one component as both are coordinated by water molecules, whereas the Cu*A*′ and Cu*C*′ component atoms are only four-coordinate, as the metal–water distance exceeds 3 Å. The compound is formally a co-crystal, namely *catena*-poly[[[aquabis(pyridine-κN)copper(II)]-μ-1,3-phenylenedioxydiacetato-κ^2-*O:O*′] dihydrate]–*catena*-poly[[[bisN)copper(II)]-μ-1,3-phenylenedioxydiacetato-κ^2-O:O] trihydrate] (1.5/0.5).

Comment

We have reported several metal 1,3-phenylenedi(oxyacetates), *e.g.* the diaquazinc (Gao, Li *et al.*, 2004), the hexaaquamagnesium (Liu *et al.*, 2004), the hexaaquachromium (Gao *et al.*, 2004*a*) and the hexakis(imidazole)nickel (Gao, Liu, Dong *et al.*, 2004) carboxylates; among these, the carboxylate group is bonded directly to the metal atom only in the zinc compound. The present study of the *N*-heterocyclic adduct of copper 1,3-phenylenedi(oxyacetate) represents an extension to the study on copper 1,4-phenylenedi(oxyacetate), which was isolated as an adduct with imidazole. The Cu atom is coordinated by a water molecule and two imidazole rings to confer a square-pyramidal geometry at the metal atom. The compound adopts a linear-chain motif arising from the bridging nature of the carboxylate unit (Gao *et al.*, 2004*b*).



(I)

The title compound, (I), has an empirical formulation corresponding to $[Cu(C_{10}H_8O_6)(C_5H_5N)_2(H_2O)]\cdot 2H_2O$. It

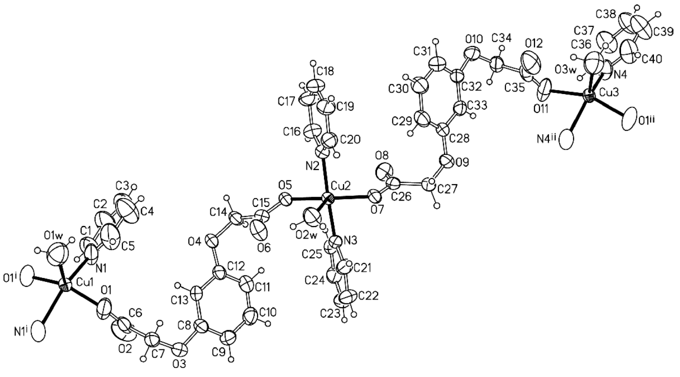


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. The disordered Cu1′ and Cu3′ atoms have been omitted. H atoms are drawn as spheres of arbitrary radii.

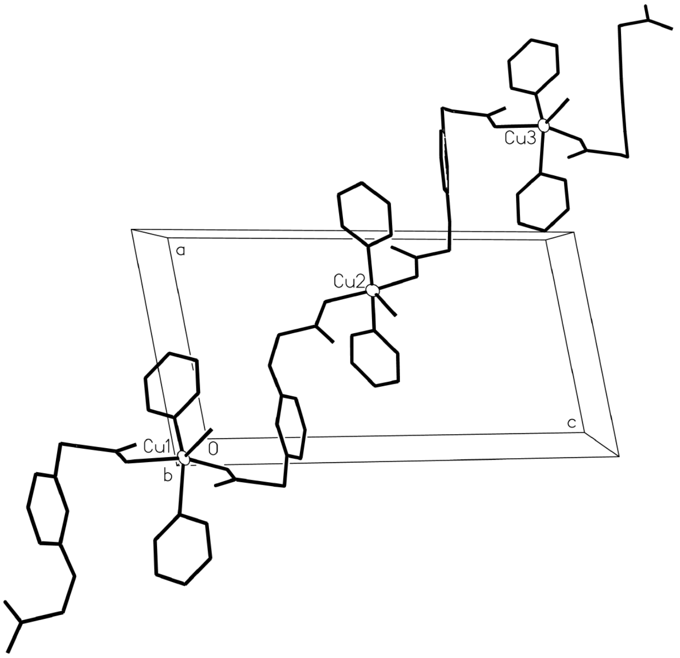


Figure 2
Schematic representation of the chain motif (O4*w*, O5*w* and O6*w* water molecules are not included), in which the Cu1 and Cu3 atoms are each coordinated by a water molecule.

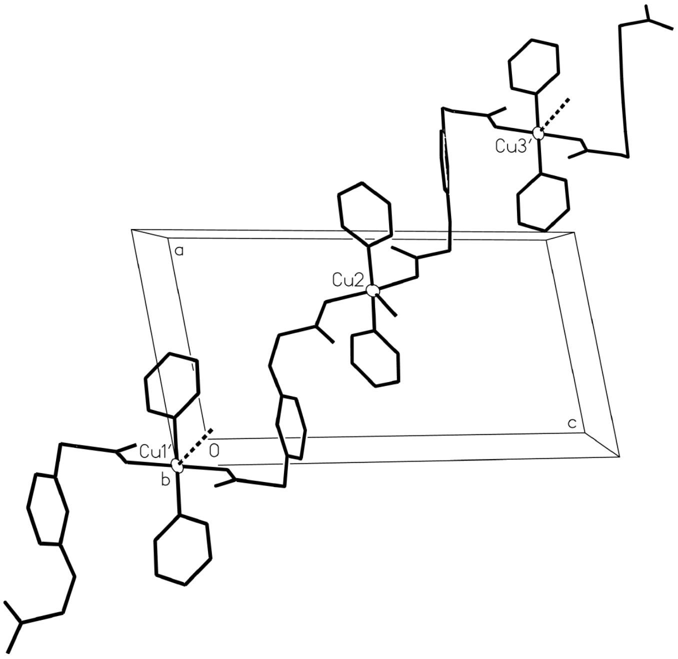


Figure 3
Schematic representation of the chain motif (O4*w*, O5*w* and O6*w* water molecules are not included), in which the Cu1′ and Cu3′ atoms are each more than 3 Å from the water molecules.

adopts a chain motif (Fig. 1) and the uncoordinated water molecules form hydrogen bonds to the chains (Table 2). However, arising from the disordered nature of two of the three Cu atoms that comprise the asymmetric unit, both square-planar and square-pyramidal geometries are shown by the disordered metal atoms (Figs. 2 and 3). The compound is formally a 1.5/0.5 co-crystal, namely *catena*-poly[[[aquabis(pyridine-κN)copper(II)]-μ-1,3-phenylenedioxydiacetato-κ^2-O:O'] dihydrate]–*catena*-poly[[[bis(pyridine-κN)copper(II)]-μ-1,3-phenylenedioxydiacetato-κ^2-O:O'] trihydrate] (1.5/0.5).

Experimental

Copper diacetate monohydrate (4.00 g, 20 mmol) and sodium hydroxide (1.60 g, 40 mmol) were dissolved in water and the solution added to an aqueous solution of 1,3-phenylenedi(oxyacetic acid) (4.52 g, 20 mmol). The mixture was warmed, and to the warm solution was added excess pyridine (3 ml). Blue crystals deposited from the filtered solution after several days. Analysis calculated for $C_{40}H_{48}Cu_2N_4O_{18}$: C 48.05, H 4.84, N 5.60%; found: C 48.21, H 4.79, N 5.56%.

Crystal data

$[Cu_2(C_{10}H_8O_6)_2(C_5H_5N)_4(H_2O)_2]\cdot4H_2O$
$M_r = 999.90$
Triclinic, $P\overline{1}$
$a = 9.046$ (2) Å
$b = 14.626$ (3) Å
$c = 17.588$ (4) Å
$\alpha = 104.40$ (2)°
$\beta = 100.20$ (2)°
$\gamma = 92.47$ (2)°
$V = 2209.1$ (8) Å^3
$Z = 2$
$D_x = 1.503$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20300 reflections
$\theta = 3.2$–27.4°
$\mu = 1.04$ mm^{-1}
$T = 295$ (2) K
Prism, blue
0.38 × 0.25 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.432$, $T_{\max} = 0.827$
21663 measured reflections
10073 independent reflections
6123 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 18$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.135$
$S = 1.01$
10073 reflections
624 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.67$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.905 (4)	Cu2—N3	2.006 (3)
Cu1—O1^{i}	2.143 (4)	Cu2—O2*w*	2.251 (2)
Cu1—N1	2.001 (4)	Cu3—O11	2.100 (9)
Cu1—N1^{i}	2.156 (4)	Cu3—O11^{ii}	1.931 (9)
Cu1—O1*w*	2.509 (4)	Cu3—N4	1.966 (9)
Cu1′—O1	1.951 (3)	Cu3—N4^{ii}	2.173 (9)
Cu1′—O1^{i}	1.951 (3)	Cu3—O3*w*	2.293 (7)
Cu1′—N1	2.006 (3)	Cu3′—O11	1.951 (2)
Cu1′—N1^{i}	2.006 (3)	Cu3′—O11^{ii}	1.951 (2)
Cu2—O5	1.985 (2)	Cu3′—N4	2.008 (3)
Cu2—O7	1.993 (2)	Cu3′—N4^{ii}	2.008 (3)
Cu2—N2	2.001 (3)		
O1—Cu1—O1^{i}	149.2 (1)	O7—Cu2—N3	89.8 (1)
O1—Cu1—O1*w*	96.6 (2)	O7—Cu2—O2*w*	92.2 (1)
O1—Cu1—N1	92.6 (2)	O2*w*—Cu2—N2	92.7 (1)
O1—Cu1—N1^{i}	85.9 (2)	O2*w*—Cu2—N3	95.5 (1)
O1^{i}—Cu1—N1	83.9 (1)	N2—Cu2—N3	171.8 (1)
O1^{i}—Cu1—N1^{i}	82.1 (1)	O11—Cu3—O11^{ii}	150.9 (3)
O1^{i}—Cu1—O1*w*	114.0 (2)	O11—Cu3—O3*w*	110.1 (4)
O1*w*—Cu1—N1	105.4 (2)	O11—Cu3—N4	86.3 (3)
O1*w*—Cu1—N1^{i}	105.0 (2)	O11—Cu3—N4^{ii}	82.4 (3)
N1—Cu1—N1^{i}	149.6 (1)	O11^{ii}—Cu3—N4	92.5 (4)
O1—Cu1′—O1^{i}	180	O11^{ii}—Cu3—N4^{ii}	85.2 (4)
O1—Cu1′—N1	91.1 (1)	O11^{ii}—Cu3—O3*w*	98.3 (3)
O1—Cu1′—N1^{i}	88.9 (1)	O3*w*—Cu3—N4	105.1 (3)
O1^{i}—Cu1′—N1	88.9 (1)	O3*w*—Cu3—N4^{ii}	103.0 (3)
O1^{i}—Cu1′—N1^{i}	91.1 (1)	N4—Cu3—N4^{ii}	151.9 (3)
N1—Cu1′—N1^{i}	180	O11—Cu3′—O11^{ii}	180
O5—Cu2—O7	170.4 (1)	O11—Cu3′—N4	89.3 (1)
O5—Cu2—N2	91.5 (1)	O11—Cu3′—N4^{ii}	90.7 (1)
O5—Cu2—N3	87.5 (1)	O11^{ii}—Cu3′—N4	90.7 (1)
O5—Cu2—O2*w*	97.3 (1)	O11^{ii}—Cu3′—N4^{ii}	89.3 (1)
O7—Cu2—N2	89.9 (1)	N4—Cu3′—N4^{ii}	180

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $3-x, 1-y, 2-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*2···O2^{i}	0.85 (1)	2.02 (3)	2.792 (5)	151 (5)
O2*w*—H2*w*2···O6	0.85 (1)	1.95 (2)	2.663 (4)	140 (3)
O2*w*—H2*w*1···O4*w*	0.85 (1)	1.90 (1)	2.741 (4)	172 (5)
O3*w*—H3*w*1···O12	0.86 (1)	2.04 (3)	2.722 (4)	136 (4)
O4*w*—H4*w*2···O6^{iii}	0.86 (1)	2.17 (2)	2.919 (4)	146 (4)
O4*w*—H4*w*1···O5*w*	0.86 (1)	2.02 (2)	2.812 (4)	154 (5)
O5*w*—H5*w*1···O1^{iii}	0.86 (1)	2.34 (4)	2.982 (5)	132 (4)
O5*w*—H5*w*2···O7	0.86 (1)	1.99 (2)	2.830 (3)	165 (5)
O6*w*—H6*w*1···O8	0.86 (1)	2.05 (2)	2.889 (4)	165 (6)

Symmetry codes: (i) $-x, 2-y, -z$; (iii) $1-x, 2-y, 1-z$.

Of the three independent Cu atoms, two (Cu1 and Cu3) lie on different inversion sites so that their site occupancy should each be 0.5 in the asymmetric unit. However, the two atoms are each disordered over two sites and the occupancies refined to almost 0.25 for each component (Cu1/Cu1′ and Cu3/Cu3′). The disorder is such that the primed atoms lie on the inversion centers whereas the unprimed atoms lie in general positions, at about 0.5 Å from the primed atoms. Arising from the disorder, the Cu1 atom is coordinated by the O1*w* water molecule and is five-coordinate in a quasi-square pyramidal environment [Cu1—O1*w* = 2.509 (4) Å]. On the other hand, this water molecule is more than 3 Å from the companion Cu1′ atom, so that the Cu1′ atom is better regarded as existing in a square-planar geometry only. A similar type of disorder also affects the pair of Cu3/Cu3′ atoms. The H atoms were placed in calculated positions [aromatic C—H = 0.93 Å and aliphatic C—H = 0.96 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The water H atoms were located and refined with distance restraints of O—H = 0.85±0.01 Å and H···H = 1.39±0.01 Å, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). The disorder affected the O1*w* and O3*w* water molecules; the refinement of the H atoms necessitated restraining the Cu1···H1*w*1 and Cu1···H1*w*2 distances to be within ±0.05 Å of each other (as well as the Cu3···H3*w*1 and Cu3···H3*w*2 distances). The O1*w* and O3*w* molecules each form only one hydrogen bond to a neighboring acceptor atom.

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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