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Tetra-μ-acetato-κ^8O:O'-bis[(3-hydroxypyridine-κN)copper(II)]

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In the title dimeric complex, $[Cu_2(Ac)_4(3\text{-PyOH})_2]$ or $[Cu_2(C_2H_3O_2)_4(C_5H_5NO)_2]$ (Ac^- is acetate and PyOH is hydroxypyridine), each Cu^{II} atom exists in a square pyramidal coordination environment, defined by four different acetate O atoms and one 3-hydroxypyridine N atom. Two Cu^{II} atoms are bridged by four acetate groups, and the center of the dimer corresponds to a crystallographic center of symmetry, the Cu$\cdots$Cu separation being 2.6598 (8) Å. These dimeric units are linked *via* O—H$\cdots$O hydrogen bonds into a two-dimensional layer supramolecular network.

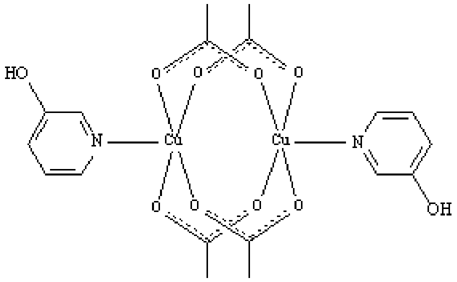
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.095
Data-to-parameter ratio = 17.1

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

Comment

Many promising supramolecular architectures based on covalent linkages and hydrogen-bonding interactions have been reported in recent years. The selection of an appropriate ligand is crucial to determining the structure of the coordination framework and its properties. Fortunately, 3-PyOH (3-hydroxypyridine) is a good candidate for the construction of supramolecular complexes, in which not only is it capable of binding to metal centers but also it can form regular hydrogen bonds by functioning as both hydrogen donor and acceptor (Breeze & Wang, 1993). However, hydrogen-bonding supramolecular complexes based on 3-PyOH are relatively rare (Castillo *et al.*, 2000; Kawata *et al.*, 1997). Recently, we have reported the $[Co(Ac)_4(3\text{-PyOH})_2]$ (Gao, Zhang *et al.*, 2004), $[Ni(Ac)_4(3\text{-PyOH})_2]$ (Zhang *et al.*, 2004) and $[Cu(Ac)_4(3\text{-PyOH})_2]$ (Gao, Lu *et al.*, 2004) complexes (Ac^- is acetate), in which the Co^{II} and Ni^{II} complexes exhibit hydrogen-bonded layer architectures and the Cu^{II} complex is a hydrogen-bonding chain structure constructed by 3-PyOH ligands. In order to further explore the coordination behavior of the metal with 3-hydroxypyridine, we synthesized and characterized a novel dimeric copper complex, $[Cu_2(Ac)_4(3\text{-PyOH})_2]$, (I), by the reaction of $Cu(Ac)_2\cdot H_2O$ and 3-PyOH in ethanol solution.



(I)

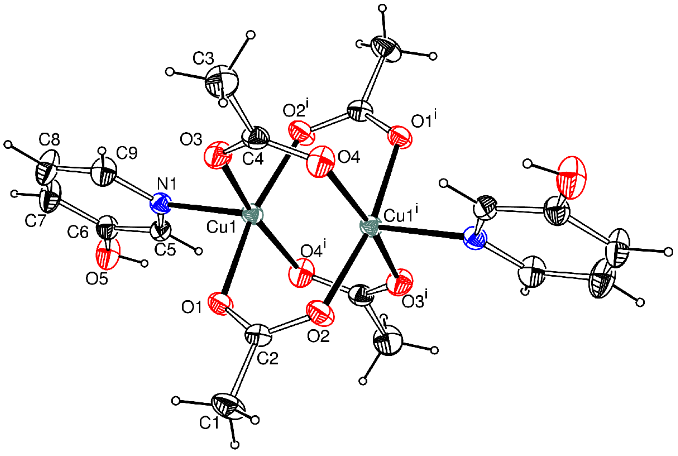


Figure 1

Molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

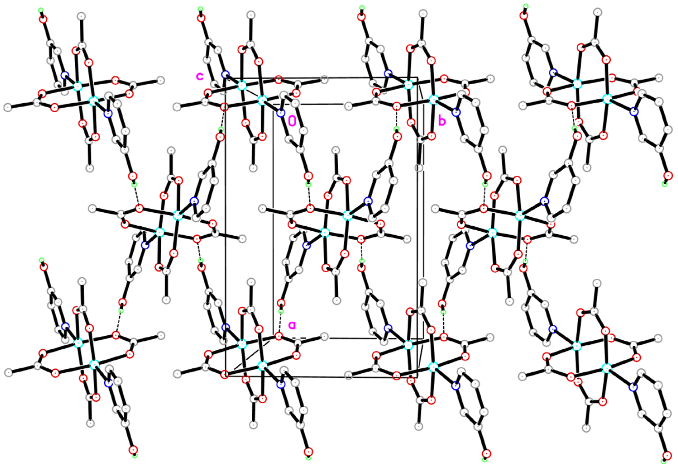


Figure 2

The packing of (I), with the O—H$\cdots$O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

As shown in Fig. 1, the two Cu^{II} atoms of complex (I) are bridged by four different acetate groups, and the center of the dimer corresponds to a crystallographic center of symmetry. Each Cu^{II} atom has a distorted square pyramidal geometry defined by four carboxyl O atoms and one N atom of a 3-PyOH ligand in the axial position. The four O atoms coordinated to each Cu^{II} atom are coplanar (r.m.s. 0.0002 Å), and the Cu atom deviates 0.2196 (11) Å from the plane. The Cu—O(carboxyl) bond distances [1.967 (2)–2.002 (2) Å] are shorter than the Cu—N distance [2.163 (2) Å]. The Cu$\cdots$Cu separation [2.6598 (8) Å] is slightly longer than the corresponding distance in [Cu(Ac)$_2$(4-pyridone)]$_2$ [2.6468 (7) Å; Lu *et al.*, 2004], in which 4-hydroxypyridine is coordinated as its tautomer 4-pyridone and the protonated 4-pyridone N atoms form N—H$\cdots$O hydrogen bonds. By contrast, in (I) these dimeric units are linked *via* O—H$\cdots$O hydrogen bonds between the uncoordinated hydroxy O atoms of the 3-PyOH ligands and the O atoms of acetate groups to give a two-dimensional layer structure (Fig. 2 and Table 2).

Experimental

The title complex was prepared by the addition of Cu(Ac)$_2$·H$_2$O (5 mmol) to an ethanol solution of 3-hydroxypyridine (5 mmol). The mixed solution was allowed to evaporate at room temperature, and green single crystals were isolated from the solution after eight days. Analysis calculated for $C_{18}H_{22}Cu_2N_2O_{10}$: C 39.06, H 4.01, N 5.06%; found: C 39.13, H 4.11, N 5.11%.

Crystal data

[Cu$_2$(C$_2$H$_3$O$_2$)$_4$(C$_5$H$_5$NO)$_2$]
M_r = 553.48
Orthorhombic, *Pbca*
a = 13.248 (3) Å
b = 8.5327 (17) Å
c = 19.858 (4) Å
V = 2244.8 (8) Å^3
Z = 4
D_x = 1.638 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 15 896 reflections
θ = 3.0–27.4°
μ = 1.95 mm^{-1}
T = 293 (2) K
Prism, green
0.38 × 0.25 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min}$ = 0.514, $T_{\max}$ = 0.718
19 830 measured reflections
2566 independent reflections
1880 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.068
$\theta_{\max}$ = 27.5°
$h = -17 \rightarrow 17$
$k = -10 \rightarrow 11$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.095
S = 1.04
2566 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.9981P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—Cu1^{i}	2.6598 (8)	Cu1—O2^{i}	1.976 (2)
Cu1—O4^{i}	1.967 (2)	Cu1—O1	2.002 (2)
Cu1—O3	1.973 (2)	Cu1—N1	2.163 (2)
O4^{i}—Cu1—O3	167.17 (9)	O2^{i}—Cu1—O1	167.23 (9)
O4^{i}—Cu1—O2^{i}	89.62 (11)	O4^{i}—Cu1—N1	96.10 (9)
O3—Cu1—O2^{i}	89.92 (11)	O3—Cu1—N1	96.68 (9)
O4^{i}—Cu1—O1	87.58 (10)	O2^{i}—Cu1—N1	97.12 (9)
O3—Cu1—O1	90.05 (9)	O1—Cu1—N1	95.56 (9)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H10$\cdots$O1^{ii}	0.85 (3)	1.90 (3)	2.732 (3)	168 (5)

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

H atoms on C atoms were placed in calculated positions and included in the refinement using the riding model approximation [C—H = 0.93 Å (aromatic) or 0.96 Å (methyl), and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C$_{\rm aromatic}$) and 1.5$U_{\rm eq}$(C$_{\rm methyl}$)]. The H atom of the hydroxy group was located in a difference map and refined with an O—H distance restraint of 0.85 (1) and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

m1406 Shan Gao et al. • [Cu$_2$(C$_2$H$_3$O$_2$)$_4$(C$_5$H$_5$NO)$_2$] Acta Cryst. (2004). E60, m1405–m1407

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku Corporation, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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