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## Key indicators

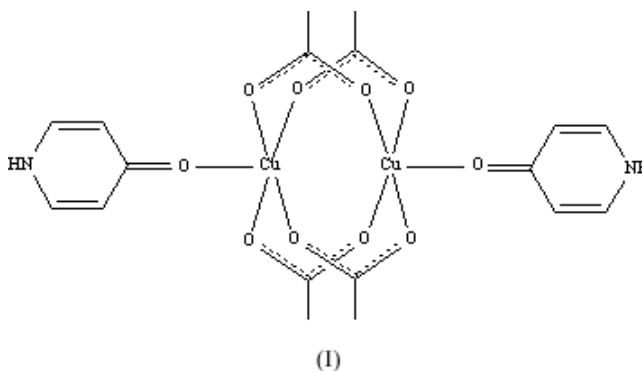
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.028  
 $wR$  factor = 0.079  
Data-to-parameter ratio = 16.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Tetrakis( $\mu$ -acetato- $\kappa^2\text{O}:\text{O}'$ )bis[(4-pyridone- $\kappa\text{O}$ )-  
copper(II)]

In the title centrosymmetric dinuclear complex,  $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_5\text{H}_5\text{NO})_2]$ , the two  $\text{Cu}^{\text{II}}$  atoms are bridged by four acetate groups, the  $\text{Cu}\cdots\text{Cu}$  separation being 2.6468 (7)  $\text{\AA}$ . Each  $\text{Cu}^{\text{II}}$  atom exists in a square-pyramidal coordination environment defined by four carboxyl acetate O atoms and one 4-pyridone O atom. Intermolecular hydrogen bonds give rise to a two-dimensional layer structure.

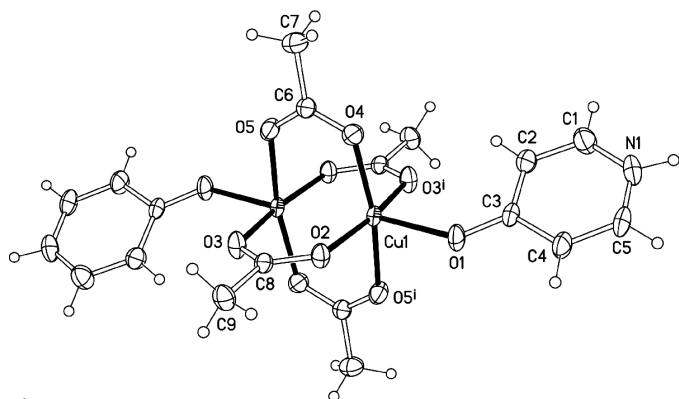
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## Comment

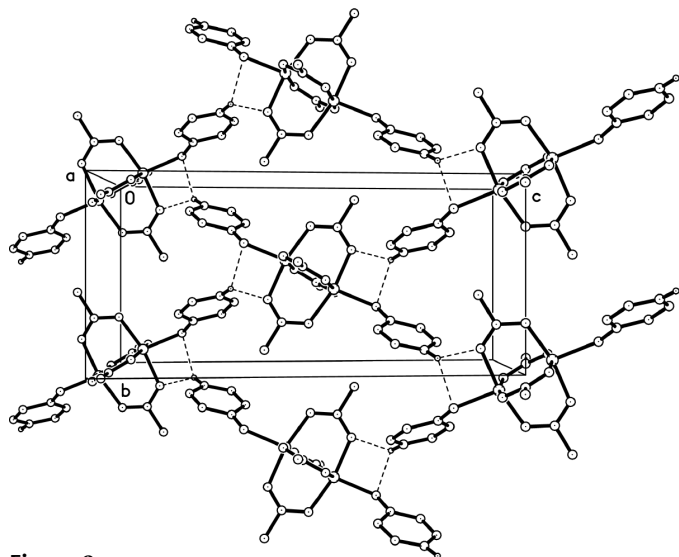
4-Hydroxypyridine has been widely used in pharmaceutical synthesis. However, the reported crystal structures of metal complexes with 4-hydroxypyridine or its tautomer, 4-pyridone, are rare (LaliaKantouri, 1996; Masse & Le Fur, 1998). Recently, we reported the structures of the cobalt complexes  $[\text{CoCl}_2(4\text{-pyridone})_2]$  and  $[\text{Co}(\text{NO}_3)(4\text{-pyridone})_2(\text{H}_2\text{O})_2](\text{NO}_3)$ , in which the Co atoms show a tetrahedral and octahedral geometry, respectively (Gao *et al.*, 2004; Lu *et al.*, 2004). In order to further explore the coordination behavior of the metal with 4-hydroxypyridine or 4-pyridone, we used  $\text{Cu}(\text{acetate})_2\cdot\text{H}_2\text{O}$  instead of cobalt salts in the reaction and synthesized the novel copper complex  $[\text{Cu}_2(\text{acetate})_4(4\text{-pyridone})_2]$ , (I), the crystal structure which is reported here.



The dimeric structure of (I) is illustrated in Fig. 1. The two  $\text{Cu}^{\text{II}}$  atoms are bridged by four different acetate groups, and the center of the dimer corresponds to a crystallographic center of symmetry. Each Cu atom shows an approximate square-pyramidal geometry with four carboxyl O atoms in the basal plane [mean  $\text{Cu}-\text{O}(\text{carboxyl}) = 1.972(1)\text{ \AA}$ ] and the O atoms of the 4-pyridone ligands in the axial positions, with a significantly longer  $\text{Cu}-\text{O}$  distance [2.117(1)  $\text{\AA}$ ]. A large number of copper(II) carboxylates of this type, *viz.*  $[\text{Cu}_2(\text{RCO}_2)_4L_2]$  ( $L$  denotes the axial ligand and the  $R$  groups include a variety of small and bulky organic groups), have been structurally characterized (Chen *et al.*, 1998; Blake *et al.*, 1991; Sun *et al.*, 1994). In these complexes, the intramolecular



**Figure 1**  
ORTEP (Johnson, 1976) plot of (I), with 30% probability displacement ellipsoids. Symmetry code (i) as in Table 1.



**Figure 2**  
Crystal packing of (I), with the N—H...O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Cu...Cu distance can vary from 2.563 (4) Å in [Cu<sub>2</sub>(EtCO<sub>2</sub>)<sub>4</sub>(dioxane)<sub>2</sub>] (Borel & Leclare, 1976) to the longest distance of 2.886 (2) Å in [Cu<sub>2</sub>(F<sub>3</sub>CCO<sub>2</sub>)<sub>4</sub>(quinoline)<sub>2</sub>] (Moreland & Doedens, 1975). In (I), the Cu...Cu separation is 2.6468 (7) Å, which is nearly identical with that in [Cu<sub>2</sub>(acetate)<sub>4</sub>(4-pymet)<sub>2</sub>], 2.647 (1) Å (4-pymet = 4-pyridylmethanol; Hoang *et al.*, 1993). The differences in the Cu...Cu separation can be explained by the influence of the donor ability of the axial ligand (Melník, 1982). In the title complex, the bond lengths C1—C2, C4—C5 and C3—O1 in the 4-pyridone ligand are 1.354 (3), 1.349 (3) and 1.271 (2) Å, respectively (Table 1). The protonated 4-pyridone N atoms do not engage in coordination owing to their weak coordination ability, but form hydrogen bonds with the 4-pyridone O atoms and the carboxyl O atoms of neighbouring molecules (Table 2), giving rise to a layer structure parallel to the *bc* plane (Fig. 2)

## Experimental

The title complex, (I), was synthesized by the addition of Cu(acetate)<sub>2</sub>·H<sub>2</sub>O (1 mmol) to an ethanol solution of 4-hydroxypyridine

(3 mmol). The solution was allowed to evaporate at room temperature, and blue prismatic crystals were obtained after about seven days. Analysis calculated for C<sub>18</sub>H<sub>22</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>10</sub>: C 39.06, H 4.01, N 5.06%; found: C 38.87, H 4.12, N 5.21%.

## Crystal data

[Cu<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>NO)<sub>2</sub>]  
*M<sub>r</sub>* = 553.48  
 Monoclinic, *C*2/*c*  
*a* = 13.445 (3) Å  
*b* = 8.6747 (17) Å  
*c* = 18.821 (4) Å  
 $\beta$  = 98.04 (3)°  
*V* = 2173.5 (8) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.691 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 8497 reflections  
 $\theta$  = 3.1–27.5°  
 $\mu$  = 2.01 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, blue  
 0.37 × 0.26 × 0.19 mm

## Data collection

Rigaku R-Axis RAPID diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  
*T<sub>min</sub>* = 0.522, *T<sub>max</sub>* = 0.701  
 10015 measured reflections

2493 independent reflections  
 2275 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.022  
 $\theta_{max}$  = 27.5°  
*h* = -17 → 17  
*k* = -11 → 9  
*l* = -24 → 24

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.028  
*wR*(*F*<sup>2</sup>) = 0.079  
*S* = 1.04  
 2493 reflections  
 150 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 1.7434P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.70 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.34 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Cu1—Cu1 <sup>i</sup>	2.6468 (7)	Cu1—O1	2.117 (1)
Cu1—O2	1.964 (1)	O1—C3	1.271 (2)
Cu1—O3 <sup>i</sup>	1.9694 (15)	C1—C2	1.354 (3)
Cu1—O4	1.974 (2)	C4—C5	1.349 (3)
Cu1—O5 <sup>i</sup>	1.998 (2)		
O2—Cu1—O3 <sup>i</sup>	167.81 (6)	O3 <sup>i</sup> —Cu1—O5 <sup>i</sup>	89.21 (7)
O2—Cu1—O4	90.92 (7)	O3 <sup>i</sup> —Cu1—O4	89.30 (7)
O2—Cu1—O5 <sup>i</sup>	88.01 (7)	O4—Cu1—O5 <sup>i</sup>	167.82 (6)
O2—Cu1—O1	93.90 (6)	O4—Cu1—O1	103.04 (7)
O3 <sup>i</sup> —Cu1—O1	97.93 (6)	O5 <sup>i</sup> —Cu1—O1	89.14 (7)

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H10...O5 <sup>ii</sup>	0.90 (3)	2.22 (2)	2.981 (3)	142 (2)
N1—H10...O1 <sup>iii</sup>	0.90 (3)	2.36 (2)	3.080 (3)	137 (2)

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

C-bound H atoms were placed in calculated positions [C—H = 0.93 (aromatic) and 0.96 Å (methyl), and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C)] in the riding-model approximation. H atoms on nitrogen were located in difference Fourier synthesis maps and refined with an N—H distance restraint of 0.90 (1) Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick,

1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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## References

- Blake, A. J., Gould, R. O. & Winpenny, R. E. P. (1991). *Acta Cryst.* **C47**, 1077–1079.
- Borel, M. M. & Leclaire, A. (1976). *Acta Cryst.* **A32**, 1275–1280.
- Chen, X.-M., Feng, X.-L., Xu, Z.-T., Zhang, X.-H., Xue, F. & Thomas, C. W. (1998). *Polyhedron*, **17**, 2639–2646.
- Gao, S., Lu, Z.-Z., Huo, L.-H., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst.* **E60**, m609–m610.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Hoang, N. N., Valach, F. & Melník, M. (1993). *Acta Cryst.* **C49**, 467–469.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
- LaliaKantouri, M. (1996). *Transition Met. Chem.* **21**, 491–493.
- Lu, Z.-Z., Gao, S., Huo, L.-H., Zhang, X., Zhao, H. & Zhao, J.-G. (2004). *Acta Cryst.* **E60**, m811–m813.
- Masse, R. & Le Fur, Y. (1998). *Z. Kristallogr. New Cryst. Struct.* **213**, 114.
- Melník, M. (1982). *Coord. Chem. Rev.* **42**, 259–293.
- Moreland, J. A. & Doedens, R. J. (1975). *J. Am. Chem. Soc.* **97**, 508–514.
- Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MSO (2002). *CrystalStructure*. Rigaku/MSO Inc., 9009 New Trails Drive, The Woodlands, TX 77381, USA.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sun, H.-Y., Zhang, M.-J., Huang, C.-H. & Xu, G.-X. (1994). *Acta Sci. Nat. Univ. Pekin.* **30**, 177–180. (In Chinese.)