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Tetra- μ -acetato-bis[(pyridine *N*-oxide)-copper(II)](Cu—Cu)

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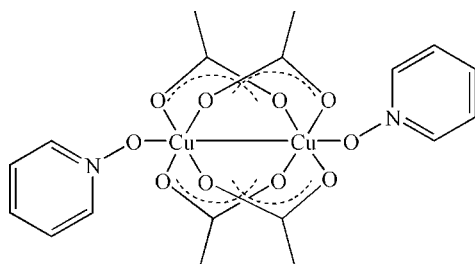
Received 26 May 2009; accepted 24 June 2009

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C—C}) = 0.004$ Å; R factor = 0.025; wR factor = 0.070; data-to-parameter ratio = 13.4.

The molecule of the title binuclear copper(II) complex, $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_5\text{H}_5\text{NO})_2]$, occupies a special position on a crystallographic inversion centre; the coordination environment of the Cu^{II} atom is slightly distorted square-pyramidal and is made up of four O atoms belonging to four acetate groups in the basal plane with the O atom of pyridine *N*-oxide ligand in the apical position. The Cu—Cu distance is 2.6376 (6) Å.

Related literature

For the biological activity of binuclear copper(II) compounds, see: Li *et al.* (2007). For a related structure, see: Zhang (2009).



Experimental

Crystal data

 $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_5\text{H}_5\text{NO})_2]$
 $M_r = 553.46$
Monoclinic, $P2_1/c$ $a = 9.6737$ (11) Å $b = 13.5886$ (16) Å $c = 8.5236$ (10) Å $\beta = 99.970$ (2)° $V = 1103.5$ (2) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 1.98$ mm⁻¹ $T = 296$ K $0.2 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 1998)

 $T_{\text{min}} = 0.673$, $T_{\text{max}} = 0.680$

5445 measured reflections

1936 independent reflections

1713 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.015$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.070$ $S = 1.07$

1936 reflections

145 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.43$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: YA2100).

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supporting information

Acta Cryst. (2009). E65, m850 [doi:10.1107/S1600536809024222]

Tetra- μ -acetato-bis[(pyridine *N*-oxide)copper(II)](*Cu—Cu*)

Yue Cui, Qian Gao, Chao-Yan Zhang and Ya-Bo Xie

S1. Comment

The crystal structures of binuclear copper(II) complexes have been extensively studied because of their possible anticarcinogen properties (Li *et al.*, 2007), and numerous papers dealing with binuclear copper complexes have been published (Zhang, 2009). Herein, we report the synthesis and crystal structure of a new binuclear copper complex.

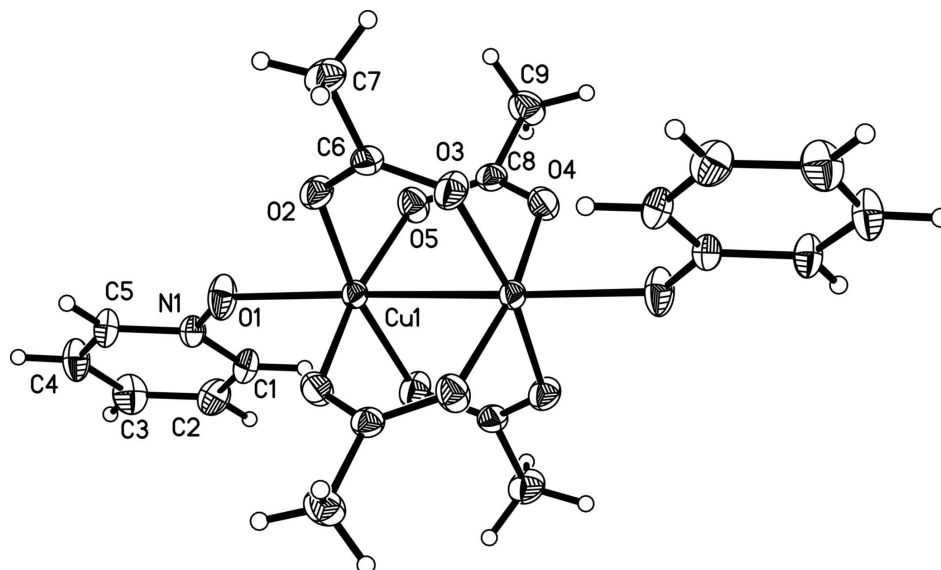
The molecule of the title binuclear copper(II) complex, $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_5\text{H}_5\text{ON})_2]$, occupies a special position in the crystallographic inversion centre; coordination environment of the Cu^{II} atom represents a slightly distorted tetragonal pyramid and is made up of four oxygen atoms belonging to four acetato-group in the basal plane as well as the oxygen atom of pyridine *N*-oxide ligand in the apical position. The Cu—O bond distance between Cu^{II} atom and acetato O atoms vary from 1.9605 (18) Å to 1.9710 (18) Å, while the Cu—O bond distance involving Cu^{II} atom and the O atom of the pyridine *N*-oxide ligand is 2.1507 (18) Å. The Cu1—Cu1^i distance is 2.6376 (6) Å [symmetry code (i): 1 - *x*, -*y*, -*z*].

S2. Experimental

A solution containing a 1:2:5 molar ratio of picolinic acid *N*-oxide (0.0139 g, 0.1 mmol), CuCO_3 (0.0247 g, 0.2 mmol) and acetic acid (1 ml, 0.5 mmol/ml) in a mixture of ethanol(5 ml) and water (10 ml) was sealed in a 25 ml teflon reactor and kept at 453 K for 3 days, then slowly cooled to 373 K and kept at this temperature for 24 h more. After cooling to room temperature, the mixture was filtered and the filtrate was allowed to stand at room temperature. Block crystals suitable for the X-ray investigation were collected.

S3. Refinement

All H atoms were placed geometrically ($\text{C—H} = 0.93\text{--}0.96$ Å) and included into refinement in the riding motion approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl H atoms].

**Figure 1**

Molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level; hydrogen atoms are shown as small circles of arbitrary radius. The unlabelled atoms are derived by the symmetry transformation $-x + 1, -y, -z$.

Tetra- μ -acetato-bis[(pyridine *N*-oxide)copper(II)](*Cu—Cu*)

Crystal data

$[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_5\text{H}_5\text{NO})_2]$

$M_r = 553.46$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 9.6737$ (11) Å

$b = 13.5886$ (16) Å

$c = 8.5236$ (10) Å

$\beta = 99.970$ (2)°

$V = 1103.5$ (2) Å³

$Z = 2$

$F(000) = 564$

$D_x = 1.666$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3911 reflections

$\theta = 2.6\text{--}27.9^\circ$

$\mu = 1.98$ mm⁻¹

$T = 296$ K

Block, blue

$0.2 \times 0.2 \times 0.2$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1998)

$T_{\min} = 0.673$, $T_{\max} = 0.680$

5445 measured reflections

1936 independent reflections

1713 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -10 \rightarrow 11$

$k = -16 \rightarrow 9$

$l = -10 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.070$

$S = 1.07$

1936 reflections

145 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.7718P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	0.55087 (19)	-0.15687 (13)	-0.0542 (2)	0.0457 (5)
O4	0.69513 (18)	-0.02840 (14)	0.1692 (2)	0.0411 (4)
Cu1	0.38549 (3)	0.01927 (2)	0.05882 (3)	0.02846 (12)
O5	0.50246 (19)	0.00354 (14)	0.2694 (2)	0.0424 (4)
O2	0.35940 (18)	-0.12383 (13)	0.0480 (2)	0.0408 (4)
N1	0.11758 (19)	0.11134 (15)	0.1808 (2)	0.0330 (4)
C8	0.6302 (3)	-0.01859 (17)	0.2828 (3)	0.0335 (5)
O1	0.18110 (19)	0.03795 (15)	0.1215 (3)	0.0520 (5)
C6	0.4409 (3)	-0.18155 (18)	-0.0051 (3)	0.0349 (5)
C1	0.1856 (3)	0.1945 (2)	0.2326 (3)	0.0409 (6)
H1A	0.2801	0.2014	0.2261	0.049*
C5	-0.0186 (2)	0.1004 (2)	0.1894 (3)	0.0406 (6)
H5A	-0.0653	0.0428	0.1529	0.049*
C9	0.7115 (3)	-0.0358 (2)	0.4475 (3)	0.0506 (7)
H9A	0.8070	-0.0518	0.4408	0.076*
H9B	0.6700	-0.0892	0.4966	0.076*
H9C	0.7096	0.0228	0.5102	0.076*
C2	0.1170 (3)	0.2692 (2)	0.2948 (3)	0.0499 (7)
H2A	0.1650	0.3265	0.3302	0.060*
C4	-0.0892 (3)	0.1741 (2)	0.2519 (4)	0.0509 (7)
H4A	-0.1835	0.1658	0.2581	0.061*
C3	-0.0225 (3)	0.2599 (2)	0.3054 (4)	0.0545 (8)
H3A	-0.0702	0.3102	0.3474	0.065*
C7	0.4047 (3)	-0.2887 (2)	-0.0104 (4)	0.0530 (7)
H7A	0.3190	-0.2983	0.0300	0.080*
H7B	0.4789	-0.3249	0.0539	0.080*
H7C	0.3930	-0.3117	-0.1184	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0419 (10)	0.0288 (9)	0.0715 (13)	-0.0013 (8)	0.0238 (9)	-0.0027 (9)
O4	0.0337 (9)	0.0532 (12)	0.0363 (9)	0.0075 (8)	0.0062 (7)	0.0057 (8)
Cu1	0.02487 (17)	0.02651 (18)	0.03512 (19)	0.00156 (11)	0.00833 (12)	0.00071 (11)
O5	0.0362 (10)	0.0558 (12)	0.0356 (9)	0.0061 (8)	0.0071 (7)	-0.0015 (8)
O2	0.0409 (10)	0.0286 (9)	0.0557 (11)	-0.0019 (7)	0.0158 (8)	0.0008 (8)
N1	0.0279 (10)	0.0374 (11)	0.0350 (10)	-0.0006 (9)	0.0088 (8)	-0.0034 (9)
C8	0.0374 (13)	0.0264 (12)	0.0364 (13)	-0.0007 (10)	0.0055 (10)	0.0015 (10)
O1	0.0339 (10)	0.0484 (12)	0.0788 (14)	-0.0019 (8)	0.0237 (9)	-0.0203 (10)
C6	0.0356 (13)	0.0277 (12)	0.0402 (13)	-0.0017 (10)	0.0034 (10)	0.0044 (10)
C1	0.0319 (13)	0.0444 (15)	0.0470 (15)	-0.0119 (11)	0.0089 (11)	-0.0035 (12)
C5	0.0275 (12)	0.0444 (15)	0.0512 (15)	-0.0077 (11)	0.0106 (11)	-0.0127 (12)
C9	0.0508 (16)	0.0627 (19)	0.0368 (15)	0.0086 (14)	0.0031 (12)	0.0055 (13)
C2	0.0540 (17)	0.0408 (15)	0.0554 (18)	-0.0122 (13)	0.0108 (13)	-0.0108 (13)
C4	0.0308 (14)	0.0589 (18)	0.0654 (18)	-0.0008 (12)	0.0146 (12)	-0.0178 (15)
C3	0.0526 (17)	0.0506 (18)	0.0626 (19)	0.0068 (14)	0.0162 (14)	-0.0180 (15)
C7	0.0568 (18)	0.0282 (14)	0.077 (2)	-0.0029 (12)	0.0187 (15)	0.0036 (14)

Geometric parameters (\AA , $^\circ$)

O3—C6	1.254 (3)	C1—C2	1.369 (4)
O4—C8	1.250 (3)	C1—H1A	0.9300
Cu1—O5	1.9605 (18)	C5—C4	1.370 (4)
Cu1—O2	1.9610 (18)	C5—H5A	0.9300
Cu1—O4 ⁱ	1.9685 (17)	C9—H9A	0.9600
Cu1—O3 ⁱ	1.9710 (18)	C9—H9B	0.9600
Cu1—O1	2.1507 (18)	C9—H9C	0.9600
Cu1—Cu1 ⁱ	2.6376 (6)	C2—C3	1.373 (4)
O5—C8	1.257 (3)	C2—H2A	0.9300
O2—C6	1.251 (3)	C4—C3	1.372 (4)
N1—O1	1.317 (3)	C4—H4A	0.9300
N1—C5	1.340 (3)	C3—H3A	0.9300
N1—C1	1.344 (3)	C7—H7A	0.9600
C8—C9	1.504 (3)	C7—H7B	0.9600
C6—C7	1.496 (3)	C7—H7C	0.9600
C6—O3—Cu1 ⁱ	123.11 (16)	O3—C6—C7	117.3 (2)
C8—O4—Cu1 ⁱ	126.30 (16)	N1—C1—C2	120.5 (2)
O5—Cu1—O2	89.09 (8)	N1—C1—H1A	119.7
O5—Cu1—O4 ⁱ	167.89 (7)	C2—C1—H1A	119.7
O2—Cu1—O4 ⁱ	89.45 (8)	N1—C5—C4	120.1 (2)
O5—Cu1—O3 ⁱ	89.38 (8)	N1—C5—H5A	120.0
O2—Cu1—O3 ⁱ	167.91 (7)	C4—C5—H5A	120.0
O4 ⁱ —Cu1—O3 ⁱ	89.55 (8)	C8—C9—H9A	109.5
O5—Cu1—O1	101.25 (8)	C8—C9—H9B	109.5
O2—Cu1—O1	90.70 (7)	H9A—C9—H9B	109.5

O4 ⁱ —Cu1—O1	90.79 (8)	C8—C9—H9C	109.5
O3 ⁱ —Cu1—O1	101.35 (7)	H9A—C9—H9C	109.5
O5—Cu1—Cu1 ⁱ	86.37 (6)	H9B—C9—H9C	109.5
O2—Cu1—Cu1 ⁱ	83.97 (5)	C1—C2—C3	120.3 (3)
O4 ⁱ —Cu1—Cu1 ⁱ	81.52 (5)	C1—C2—H2A	119.8
O3 ⁱ —Cu1—Cu1 ⁱ	83.97 (5)	C3—C2—H2A	119.8
O1—Cu1—Cu1 ⁱ	170.66 (6)	C5—C4—C3	120.9 (3)
C8—O5—Cu1	120.79 (16)	C5—C4—H4A	119.6
C6—O2—Cu1	123.67 (16)	C3—C4—H4A	119.6
O1—N1—C5	117.7 (2)	C4—C3—C2	117.8 (3)
O1—N1—C1	121.9 (2)	C4—C3—H3A	121.1
C5—N1—C1	120.3 (2)	C2—C3—H3A	121.1
O4—C8—O5	124.9 (2)	C6—C7—H7A	109.5
O4—C8—C9	117.0 (2)	C6—C7—H7B	109.5
O5—C8—C9	118.0 (2)	H7A—C7—H7B	109.5
N1—O1—Cu1	134.01 (15)	C6—C7—H7C	109.5
O2—C6—O3	125.2 (2)	H7A—C7—H7C	109.5
O2—C6—C7	117.5 (2)	H7B—C7—H7C	109.5
O2—Cu1—O5—C8	82.77 (19)	O5—Cu1—O1—N1	76.0 (2)
O4 ⁱ —Cu1—O5—C8	-0.3 (5)	O2—Cu1—O1—N1	165.2 (2)
O3 ⁱ —Cu1—O5—C8	-85.24 (19)	O4 ⁱ —Cu1—O1—N1	-105.3 (2)
O1—Cu1—O5—C8	173.30 (19)	O3 ⁱ —Cu1—O1—N1	-15.6 (3)
Cu1 ⁱ —Cu1—O5—C8	-1.25 (18)	Cu1—O2—C6—O3	1.9 (4)
O5—Cu1—O2—C6	-88.0 (2)	Cu1—O2—C6—C7	-178.14 (19)
O4 ⁱ —Cu1—O2—C6	79.9 (2)	Cu1 ⁱ —O3—C6—O2	-0.8 (4)
O3 ⁱ —Cu1—O2—C6	-5.3 (5)	Cu1 ⁱ —O3—C6—C7	179.25 (19)
O1—Cu1—O2—C6	170.7 (2)	O1—N1—C1—C2	-179.5 (2)
Cu1 ⁱ —Cu1—O2—C6	-1.59 (19)	C5—N1—C1—C2	0.0 (4)
Cu1 ⁱ —O4—C8—O5	-3.5 (4)	O1—N1—C5—C4	179.2 (3)
Cu1 ⁱ —O4—C8—C9	175.76 (18)	C1—N1—C5—C4	-0.3 (4)
Cu1—O5—C8—O4	3.1 (3)	N1—C1—C2—C3	0.1 (4)
Cu1—O5—C8—C9	-176.22 (18)	N1—C5—C4—C3	0.5 (5)
C5—N1—O1—Cu1	172.94 (19)	C5—C4—C3—C2	-0.3 (5)
C1—N1—O1—Cu1	-7.5 (4)	C1—C2—C3—C4	0.0 (5)

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