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Tetra-μ-acetato-bis{[2-(chloromethyl)pyridine]copper(II)}

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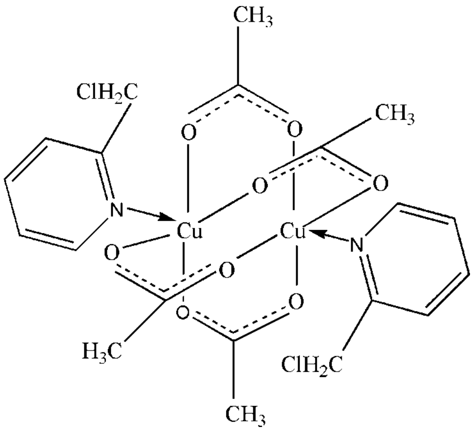
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.041; wR factor = 0.101; data-to-parameter ratio = 15.1.

The molecule of the title compound, $[Cu_2(C_2H_3O_2)_4(C_6H_6ClN)_2]$, lies on an inversion center and the Cu atom has a square-pyramidal CuO_4N geometry. The four acetate groups act as bridging ligands.

Related literature

For the acetate group as a bridging ligand in multinuclear complexes, see: Panagiotopoulos *et al.* (1995); Taft *et al.* (1993); Tangoulis, Raptopolou, Paschalidou *et al.* (1997); Tangoulis, Raptopolou, Terzis *et al.* (1997); Tong *et al.* (2000). For other dinuclear copper compounds, see: Moreland & Doedens (1978).



Experimental

Crystal data

$[Cu_2(C_2H_3O_2)_4(C_6H_6ClN)_2]$
M_r = 618.39
Triclinic, $P\overline{1}$
a = 7.8592 (19) Å
b = 7.959 (2) Å
c = 10.734 (3) Å
α = 100.458 (3)°
β = 110.406 (3)°
γ = 94.199 (3)°
V = 612.0 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.00 mm^{-1}
T = 298 (2) K
0.28 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.604, T_{max} = 0.714
3405 measured reflections
2359 independent reflections
2033 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.102
S = 1.03
2359 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2^i	1.958 (2)	Cu1—O4^i	1.974 (2)
Cu1—O1	1.960 (2)	Cu1—N1	2.243 (3)
Cu1—O3	1.973 (2)		
O2^i—Cu1—O1	168.18 (10)	O2^i—Cu1—N1	98.54 (10)
O2^i—Cu1—O3	90.24 (11)	O1—Cu1—N1	93.27 (10)
O1—Cu1—O3	89.38 (11)	O3—Cu1—N1	89.37 (9)
O1—Cu1—O4^i	89.14 (11)	O4^i—Cu1—N1	102.29 (9)
O3—Cu1—O4^i	168.32 (9)		

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: NG2274).

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supplementary materials

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Tetra-μ-acetato-bis{[2-(chloromethyl)pyridine]copper(II)}

S.-G. Zhang, Q.-S. Liu and J.-M. Shi

Comment

The acetate anion is an useful ligand and a large number of multi-atom bridge complexes have been synthesized with it as a bridging ligand (Panagiotopoulos *et al.* 1995; Taft *et al.* 1993; Tangoulis, Raptopolou, Paschalidou *et al.* 1997; Tangoulis, Raptopolou, Terzis *et al.*, 1997; Tong, *et al.* 2000). We had intended to synthesize a multi-nuclear Cu^{II} complex by using acetate and 2-chloromethylpyridine as ligands, but the title dinuclear complex was obtained.

Two copper atoms are briged by four acetate groups; the copper atoms are also coordinated by the heterocycle so that the geometry at copper is a square pyramid. The bond dimensions are similar to those in other binculear copper systems (Moreland & Doedens, 1978)..

Experimental

$Cu(OOCCH_3)_2·H_2O$ (0.133 g, 0.664 mmol) and ethanolamine (0.041 g, 0.676 mmol) were dissoved in 8 ml of water; the solution was added into an 8 ml me thanol solution containing 2-chloromethylpyridine (0.170 g, 1.33 mmol). Green crystals were obtained after allowing the mixed solution to stand at room temperature for one week.

Refinement

The H atoms were placed in calculated positions and refined as riding, with C—H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for pyridine ring; C—H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl group, and C—H = 0.97 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for the chloromethyl group.

Figures

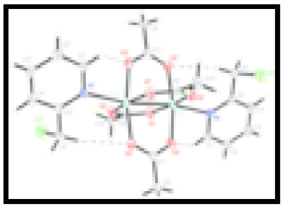


Fig. 1. **Figure 1**. Molecular structure showing the atom numbering scheme with thermal ellipsoids drawn at the 30% probability level; hydrogen bonds (line of dashes). [Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$]

Tetra-μ-acetato-bis{[2-(chloromethyl)pyridine]copper(II)}

Crystal data

$[Cu_2(C_2H_3O_2)_4(C_6H_6ClN)_2]$	$Z = 1$
$M_r = 618.39$	$F_{000} = 314$

Triclinic, $P\overline{1}$

Hall symbol: -P 1

a = 7.8592 (19) Å

b = 7.959 (2) Å

c = 10.734 (3) Å

α = 100.458 (3)°

β = 110.406 (3)°

γ = 94.199 (3)°

V = 612.0 (3) Å^3

D_x = 1.678 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 1146 reflections

θ = 2.6–24.9°

μ = 2.00 mm^{-1}

T = 298 (2) K

Prism, green

0.28 × 0.20 × 0.18 mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298(2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min}$ = 0.604, $T_{\max}$ = 0.714

3405 measured reflections

2359 independent reflections

2033 reflections with $I > 2\sigma(I)$

R_{int} = 0.019

$\theta_{\max}$ = 26.0°

$\theta_{\min}$ = 2.1°

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 8$

$l = -9 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.041

$wR(F^2)$ = 0.102

S = 1.04

2359 reflections

156 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001

$\Delta\rho_{\max}$ = 0.41 e Å^{-3}

$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Extinction correction: none

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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Cu1	0.53281 (5)	0.54185 (5)	0.39664 (4)	0.03081 (16)
N1	0.6345 (3)	0.6340 (3)	0.2462 (3)	0.0307 (6)
C1	0.8136 (4)	0.6281 (5)	0.2745 (4)	0.0394 (8)
H1	0.8788	0.5878	0.3509	0.047*
C2	0.9059 (5)	0.6781 (5)	0.1972 (4)	0.0518 (10)
H2	1.0306	0.6720	0.2213	0.062*
C3	0.8126 (6)	0.7373 (6)	0.0839 (4)	0.0562 (11)
H3	0.8720	0.7725	0.0297	0.067*
C4	0.6293 (6)	0.7429 (5)	0.0532 (4)	0.0519 (10)
H4	0.5619	0.7809	−0.0239	0.062*
C5	0.5439 (5)	0.6927 (4)	0.1357 (3)	0.0352 (8)
C6	0.3446 (5)	0.7041 (5)	0.1064 (4)	0.0485 (10)
H6A	0.3019	0.6401	0.1613	0.058*
H6B	0.2739	0.6522	0.0112	0.058*
C7	0.8014 (4)	0.6730 (4)	0.6705 (3)	0.0343 (7)
C8	0.9816 (4)	0.7811 (5)	0.7643 (3)	0.0457 (9)
H8A	1.0788	0.7415	0.7375	0.068*
H8B	1.0041	0.7707	0.8562	0.068*
H8C	0.9766	0.8998	0.7589	0.068*
C9	0.6582 (4)	0.2378 (4)	0.4730 (4)	0.0365 (8)
C10	0.7477 (5)	0.0791 (5)	0.4577 (4)	0.0502 (10)
H10A	0.8771	0.1072	0.5097	0.075*
H10B	0.7279	0.0370	0.3633	0.075*
H10C	0.6954	−0.0083	0.4902	0.075*
O1	0.6491 (3)	0.3325 (3)	0.3890 (3)	0.0450 (6)
O2	0.5984 (3)	0.2664 (3)	0.5675 (3)	0.0442 (6)
O3	0.7596 (3)	0.6660 (3)	0.5456 (2)	0.0411 (6)
O4	0.7053 (3)	0.5988 (3)	0.7225 (2)	0.0427 (6)
Cl1	0.30915 (15)	0.92261 (15)	0.14306 (12)	0.0668 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0349 (2)	0.0329 (3)	0.0310 (2)	0.00724 (17)	0.01565 (17)	0.01476 (17)
N1	0.0333 (14)	0.0323 (15)	0.0305 (14)	0.0048 (12)	0.0140 (11)	0.0119 (11)
C1	0.0367 (18)	0.048 (2)	0.041 (2)	0.0113 (16)	0.0184 (16)	0.0170 (16)
C2	0.042 (2)	0.063 (3)	0.062 (3)	0.0084 (19)	0.0298 (19)	0.021 (2)
C3	0.062 (3)	0.070 (3)	0.058 (3)	0.007 (2)	0.042 (2)	0.027 (2)
C4	0.067 (3)	0.058 (3)	0.041 (2)	0.009 (2)	0.0240 (19)	0.0271 (19)
C5	0.0428 (19)	0.0328 (19)	0.0318 (17)	0.0038 (15)	0.0141 (15)	0.0117 (14)
C6	0.041 (2)	0.053 (2)	0.051 (2)	0.0050 (18)	0.0078 (17)	0.0285 (19)
C7	0.0365 (18)	0.0324 (19)	0.0352 (18)	0.0106 (15)	0.0132 (15)	0.0085 (14)

C8	0.0361 (18)	0.058 (3)	0.037 (2)	0.0024 (17)	0.0081 (15)	0.0076 (17)
C9	0.0309 (17)	0.0303 (19)	0.045 (2)	0.0040 (14)	0.0107 (15)	0.0082 (15)
C10	0.056 (2)	0.037 (2)	0.066 (3)	0.0205 (19)	0.028 (2)	0.0183 (19)
O1	0.0557 (15)	0.0406 (15)	0.0547 (15)	0.0177 (12)	0.0322 (13)	0.0219 (12)
O2	0.0543 (15)	0.0415 (15)	0.0499 (15)	0.0209 (12)	0.0265 (12)	0.0219 (12)
O3	0.0413 (13)	0.0536 (16)	0.0285 (12)	0.0018 (12)	0.0113 (10)	0.0144 (11)
O4	0.0432 (13)	0.0543 (16)	0.0305 (12)	−0.0031 (12)	0.0124 (10)	0.0157 (11)
Cl1	0.0626 (7)	0.0657 (8)	0.0815 (8)	0.0271 (6)	0.0277 (6)	0.0299 (6)

Geometric parameters (Å, °)

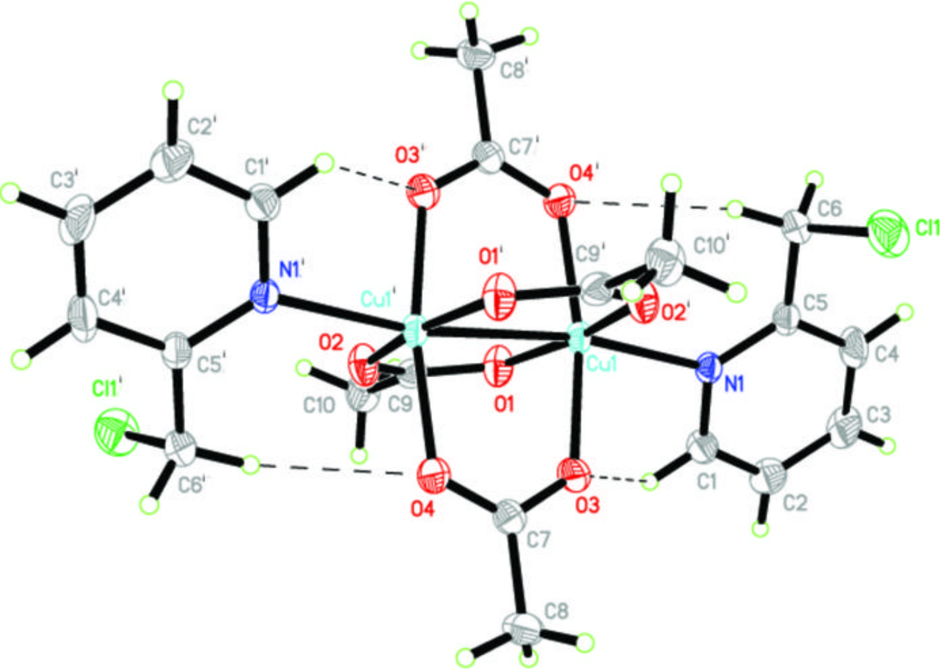
Cu1—O2^{i}	1.958 (2)	C6—Cl1	1.776 (4)
Cu1—O1	1.960 (2)	C6—H6A	0.9700
Cu1—O3	1.973 (2)	C6—H6B	0.9700
Cu1—O4^{i}	1.974 (2)	C7—O3	1.254 (4)
Cu1—N1	2.243 (3)	C7—O4	1.256 (4)
Cu1—Cu1^{i}	2.6302 (9)	C7—C8	1.507 (4)
N1—C1	1.339 (4)	C8—H8A	0.9600
N1—C5	1.339 (4)	C8—H8B	0.9600
C1—C2	1.368 (5)	C8—H8C	0.9600
C1—H1	0.9300	C9—O2	1.252 (4)
C2—C3	1.369 (5)	C9—O1	1.263 (4)
C2—H2	0.9300	C9—C10	1.501 (5)
C3—C4	1.367 (5)	C10—H10A	0.9600
C3—H3	0.9300	C10—H10B	0.9600
C4—C5	1.378 (5)	C10—H10C	0.9600
C4—H4	0.9300	O2—Cu1^{i}	1.958 (2)
C5—C6	1.499 (5)	O4—Cu1^{i}	1.974 (2)
O2^{i}—Cu1—O1	168.18 (10)	N1—C5—C6	116.9 (3)
O2^{i}—Cu1—O3	90.24 (11)	C4—C5—C6	121.1 (3)
O1—Cu1—O3	89.38 (11)	C5—C6—Cl1	110.9 (3)
O2^{i}—Cu1—O4^{i}	88.84 (11)	C5—C6—H6A	109.5
O1—Cu1—O4^{i}	89.14 (11)	Cl1—C6—H6A	109.5
O3—Cu1—O4^{i}	168.32 (9)	C5—C6—H6B	109.5
O2^{i}—Cu1—N1	98.54 (10)	Cl1—C6—H6B	109.5
O1—Cu1—N1	93.27 (10)	H6A—C6—H6B	108.1
O3—Cu1—N1	89.37 (9)	O3—C7—O4	125.4 (3)
O4^{i}—Cu1—N1	102.29 (9)	O3—C7—C8	116.3 (3)
O2^{i}—Cu1—Cu1^{i}	82.46 (7)	O4—C7—C8	118.3 (3)
O1—Cu1—Cu1^{i}	85.80 (7)	C7—C8—H8A	109.5
O3—Cu1—Cu1^{i}	81.15 (7)	C7—C8—H8B	109.5
O4^{i}—Cu1—Cu1^{i}	87.19 (7)	H8A—C8—H8B	109.5
N1—Cu1—Cu1^{i}	170.47 (7)	C7—C8—H8C	109.5
C1—N1—C5	117.0 (3)	H8A—C8—H8C	109.5
C1—N1—Cu1	113.2 (2)	H8B—C8—H8C	109.5

C5—N1—Cu1	129.8 (2)	O2—C9—O1	125.0 (3)
N1—C1—C2	123.6 (3)	O2—C9—C10	117.8 (3)
N1—C1—H1	118.2	O1—C9—C10	117.2 (3)
C2—C1—H1	118.2	C9—C10—H10A	109.5
C1—C2—C3	119.3 (3)	C9—C10—H10B	109.5
C1—C2—H2	120.4	H10A—C10—H10B	109.5
C3—C2—H2	120.4	C9—C10—H10C	109.5
C4—C3—C2	117.8 (3)	H10A—C10—H10C	109.5
C4—C3—H3	121.1	H10B—C10—H10C	109.5
C2—C3—H3	121.1	C9—O1—Cu1	121.2 (2)
C3—C4—C5	120.4 (3)	C9—O2—Cu1^{i}	125.5 (2)
C3—C4—H4	119.8	C7—O3—Cu1	126.7 (2)
C5—C4—H4	119.8	C7—O4—Cu1^{i}	119.5 (2)
N1—C5—C4	121.9 (3)		

O2^{i}—Cu1—N1—C1	131.3 (2)	C4—C5—C6—Cl1	−71.9 (4)
O1—Cu1—N1—C1	−48.1 (2)	O2—C9—O1—Cu1	−0.8 (5)
O3—Cu1—N1—C1	41.2 (2)	C10—C9—O1—Cu1	179.3 (2)
O4^{i}—Cu1—N1—C1	−138.0 (2)	O2^{i}—Cu1—O1—C9	−7.9 (7)
O2^{i}—Cu1—N1—C5	−48.5 (3)	O3—Cu1—O1—C9	80.3 (3)
O1—Cu1—N1—C5	132.0 (3)	O4^{i}—Cu1—O1—C9	−88.1 (3)
O3—Cu1—N1—C5	−138.6 (3)	N1—Cu1—O1—C9	169.6 (3)
O4^{i}—Cu1—N1—C5	42.2 (3)	Cu1^{i}—Cu1—O1—C9	−0.9 (3)
C5—N1—C1—C2	−0.1 (5)	O1—C9—O2—Cu1^{i}	2.9 (5)
Cu1—N1—C1—C2	−179.9 (3)	C10—C9—O2—Cu1^{i}	−177.1 (2)
N1—C1—C2—C3	−0.2 (6)	O4—C7—O3—Cu1	1.1 (5)
C1—C2—C3—C4	−0.2 (6)	C8—C7—O3—Cu1	−178.4 (2)
C2—C3—C4—C5	1.0 (6)	O2^{i}—Cu1—O3—C7	81.3 (3)
C1—N1—C5—C4	0.8 (5)	O1—Cu1—O3—C7	−86.9 (3)
Cu1—N1—C5—C4	−179.4 (3)	O4^{i}—Cu1—O3—C7	−4.2 (6)
C1—N1—C5—C6	−178.3 (3)	N1—Cu1—O3—C7	179.8 (3)
Cu1—N1—C5—C6	1.6 (4)	Cu1^{i}—Cu1—O3—C7	−1.1 (3)
C3—C4—C5—N1	−1.3 (6)	O3—C7—O4—Cu1^{i}	−0.2 (5)
C3—C4—C5—C6	177.7 (4)	C8—C7—O4—Cu1^{i}	179.3 (2)
N1—C5—C6—Cl1	107.1 (3)		

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

Fig. 1


C8'
C2'
O3'
C7'
C1'
O4'
C6
Cl1
C3'
C9'
C10'
O1'
N1'
Cu1'
C5
O2'
C4'
O2
Cu1
C4
N1
Cl1'
C5'
C10
C9
O1
C3
C6'
C1
O4
O3
C2
C7
C8