

Bis(4-ammonio-4-methylpentan-2-one- κ O)dioxalato- κ^4 O¹,O²-copper(II)

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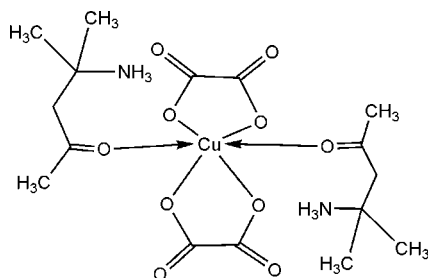
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Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.075; data-to-parameter ratio = 16.8.

The title compound, $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_{14}\text{NO})_2]$, was synthesized by mixing diacetoneamine hydrogen oxalate and copper sulfate in ethanol/water. The molecule is centrosymmetric, so two pairs of equivalent ligands lie *trans* to each other. The Cu^{II} center, located on a position with $2/m$ site symmetry, is six-coordinated by four O atoms from two oxalate ligands at short distances and the carbonyl O atoms from the 4-amino-4-methylpentan-2-one ligands at longer distances. Molecules are linked through intermolecular N—H...O hydrogen bonds between the amino groups and carbonyl O atoms; no intramolecular hydrogen bonds are formed.

Related literature

For the preparation of diacetoneamine, see: Haeseler (1925).



Experimental

Crystal data

$[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_{14}\text{NO})_2]$
 $M_r = 471.94$
 Monoclinic, $C2/m$
 $a = 13.639$ (3) Å
 $b = 7.9749$ (16) Å
 $c = 10.958$ (2) Å
 $\beta = 113.27$ (3)°
 $V = 1094.9$ (4) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.05$ mm⁻¹

$T = 113$ (2) K
 $0.16 \times 0.14 \times 0.14$ mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.850$, $T_{\max} = 0.867$
 4513 measured reflections
 1394 independent reflections
 1247 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.075$
 $S = 1.11$
 1394 reflections
 83 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.31$ e Å⁻³
 $\Delta\rho_{\min} = -0.45$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.9383 (11)	Cu1—O3	2.663 (2)
O1—Cu1—O1 ⁱ	179.999 (2)	O1 ⁱ —Cu1—O1 ⁱⁱ	85.10 (6)
O1—Cu1—O1 ⁱⁱ	94.90 (6)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A...O2 ⁱⁱⁱ	0.86 (3)	2.23 (2)	2.950 (2)	141.8 (5)
N1—H1A...O2 ^{iv}	0.86 (3)	2.23 (2)	2.950 (2)	141.8 (5)
N1—H1B...O2 ^v	0.883 (18)	2.014 (19)	2.8651 (14)	161.5 (16)

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *CrystalStructure* (Rigaku, 2005).

The authors thank Dr Qingmin Wang for assistance with the X-ray structure determination.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JH2070).

References

- Haeseler (1925). *J. Am. Chem. Soc.* **47**, 1195y.
 Rigaku (2005). *CrystalStructure* and *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2009). E65, m182 [doi:10.1107/S1600536808042396]

Bis(4-ammonio-4-methylpentan-2-one- κO)dioxalato- $\kappa^4 O^1, O^2$ -copper(II)

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Comment

In the screening of novel antibiotics, diacetoneamine was obtained in the procedure of isolating active ingredients by the silica gel chromatography. Diacetoneamine exhibits moderately antimicrobial activities against many species of plant-pathogenic fungus. To enhance the bio-activity, a complex was designed and prepared by the mixture of diacetoneamine hydrogen oxalate and copper sulfate. Compared with diacetoneamine, the antimicrobial activities of copper complex was increased dramatically. Diacetoneamine could be prepared from a mixture of mesityl oxide with aqueous ammonia or liquid ammonia (Haeseler, 1925). In this paper, $[\text{Cu}(\text{C}_6\text{H}_{13}\text{NO})_2(\text{C}_2\text{H}_2\text{O}_4)_2]$ was synthesized by the reaction of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and diacetoneamine hydrogen oxalate in ethanol/water and the structure of the resulting complex is presented herein.

Experimental

Diacetoneamine hydrogen oxalate (0.6 mmol 123 mg) was dissolved in ethanol/water (2/1, volume ratio, 10 ml) and the solution was heated to boiling. Copper sulfate (0.3 mmol 75 mg) was dissolved in deionized water (10 ml), and was added dropwise to the solution and stirred for 10 minutes. The mother liquor was placed at room temperature, and single crystals were obtained on standing.

Figures

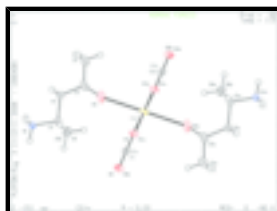


Fig. 1. Molecular structure of the title compound, showing the coordination geometry. Displacement ellipsoids are drawn at the 50% probability level.

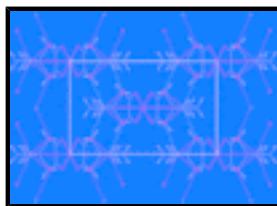


Fig. 2. Packing diagram viewed down the *c*-axis, showing hydrogen bonds.

Bis(4-ammonio-4-methylpentan-2-one- κO)dioxalato- $\kappa^4 O^1, O^2$)copper(II)

Crystal data

$[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{C}_6\text{H}_{14}\text{NO})_2]$

$F_{000} = 494$

$M_r = 471.94$

$D_x = 1.432 \text{ Mg m}^{-3}$

supplementary materials

Monoclinic, $C2/m$

$a = 13.639 (3) \text{ \AA}$

$b = 7.9749 (16) \text{ \AA}$

$c = 10.958 (2) \text{ \AA}$

$\beta = 113.27 (3)^\circ$

$V = 1094.9 (4) \text{ \AA}^3$

$Z = 2$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2107 reflections

$\theta = 3.3\text{--}27.9^\circ$

$\mu = 1.05 \text{ mm}^{-1}$

$T = 113 (2) \text{ K}$

Prism, colorless

$0.16 \times 0.14 \times 0.14 \text{ mm}$

Data collection

Rigaku Saturn CCD area-detector diffractometer

Radiation source: rotating anode

Monochromator: confocal

Detector resolution: $7.31 \text{ pixels mm}^{-1}$

$T = 113(2) \text{ K}$

ω and φ scans

Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)

$T_{\min} = 0.850$, $T_{\max} = 0.867$

4513 measured reflections

1394 independent reflections

1247 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.9^\circ$

$\theta_{\min} = 3.3^\circ$

$h = -17 \rightarrow 17$

$k = -10 \rightarrow 9$

$l = -12 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.075$

$S = 1.11$

1394 reflections

83 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.4743P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.45 \text{ e \AA}^{-3}$

Extinction correction: none

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ is used only for calculat-

ing 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.01576 (13)
O1	0.44732 (8)	0.33564 (13)	0.35854 (10)	0.0177 (2)
O2	0.36121 (9)	0.32743 (14)	0.13800 (10)	0.0200 (2)
N1	0.76865 (14)	0.5000	0.11200 (17)	0.0153 (4)
H1A	0.727 (2)	0.5000	0.029 (3)	0.023*
H1B	0.8108 (14)	0.412 (2)	0.1262 (17)	0.023*
O3	0.67707 (15)	0.5000	0.45267 (19)	0.0361 (4)
C1	0.40342 (10)	0.40251 (18)	0.24483 (13)	0.0142 (3)
C2	0.8619 (2)	0.5000	0.5942 (2)	0.0320 (6)
H2A	0.8364	0.5000	0.6642	0.048*
H2B	0.9045	0.4017	0.6013	0.048*
C3	0.76883 (19)	0.5000	0.4625 (2)	0.0216 (5)
C4	0.80035 (16)	0.5000	0.3451 (2)	0.0170 (4)
H4A	0.8441	0.4031	0.3524	0.020*
C5	0.71136 (16)	0.5000	0.2061 (2)	0.0168 (4)
C6	0.64379 (13)	0.6585 (2)	0.17734 (17)	0.0274 (4)
H6A	0.5934	0.6585	0.0841	0.041*
H6B	0.6903	0.7570	0.1944	0.041*
H6C	0.6042	0.6620	0.2349	0.041*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0216 (2)	0.00972 (19)	0.01316 (19)	0.000	0.00386 (14)	0.000
O1	0.0239 (6)	0.0113 (5)	0.0155 (5)	−0.0008 (4)	0.0053 (4)	0.0002 (4)
O2	0.0245 (6)	0.0152 (6)	0.0166 (5)	−0.0027 (4)	0.0042 (4)	−0.0028 (4)
N1	0.0160 (9)	0.0143 (9)	0.0147 (8)	0.000	0.0052 (7)	0.000
O3	0.0348 (10)	0.0458 (12)	0.0400 (10)	0.000	0.0280 (9)	0.000
C1	0.0133 (7)	0.0114 (7)	0.0189 (7)	−0.0013 (5)	0.0074 (6)	−0.0009 (5)
C2	0.0452 (15)	0.0325 (14)	0.0208 (11)	0.000	0.0156 (11)	0.000
C3	0.0303 (12)	0.0149 (10)	0.0248 (11)	0.000	0.0165 (9)	0.000
C4	0.0168 (10)	0.0172 (10)	0.0189 (10)	0.000	0.0089 (8)	0.000
C5	0.0152 (10)	0.0172 (11)	0.0200 (10)	0.000	0.0092 (8)	0.000
C6	0.0222 (8)	0.0298 (10)	0.0326 (9)	0.0100 (7)	0.0133 (7)	0.0059 (7)

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

Cu1—O1 ⁱ	1.9383 (11)	C1—C1 ⁱ	1.555 (3)
Cu1—O1	1.9383 (11)	C2—C3	1.499 (3)
Cu1—O1 ⁱⁱ	1.9383 (11)	C2—H2A	0.9601
Cu1—O1 ⁱⁱⁱ	1.9383 (11)	C2—H2B	0.9600
Cu1—O3	2.663 (2)	C3—C4	1.508 (3)

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Cu1—O3	2.663 (2)	C4—C5	1.528 (3)
O1—C1	1.2672 (17)	C4—H4A	0.9601
O2—C1	1.2361 (17)	C5—C6	1.522 (2)
N1—C5	1.520 (3)	C5—C6 ⁱ	1.522 (2)
N1—H1A	0.86 (3)	C6—H6A	0.9800
N1—H1B	0.883 (18)	C6—H6B	0.9800
O3—C3	1.213 (3)	C6—H6C	0.9800
O1 ⁱ —Cu1—O1	85.10 (6)	O3—C3—C4	123.8 (2)
O1 ⁱ —Cu1—O1 ⁱⁱ	94.90 (6)	C2—C3—C4	113.71 (19)
O1—Cu1—O1 ⁱⁱ	179.999 (2)	C3—C4—C5	117.95 (18)
O1 ⁱ —Cu1—O1 ⁱⁱⁱ	180	C3—C4—H4A	107.8
O1—Cu1—O1 ⁱⁱⁱ	94.90 (6)	C5—C4—H4A	107.8
O1 ⁱⁱ —Cu1—O1 ⁱⁱⁱ	85.10 (6)	N1—C5—C6	106.94 (11)
C1—O1—Cu1	112.56 (10)	N1—C5—C6 ⁱ	106.94 (11)
C5—N1—H1A	114.0 (17)	C6—C5—C6 ⁱ	112.28 (19)
C5—N1—H1B	110.8 (11)	N1—C5—C4	104.95 (16)
H1A—N1—H1B	107.6 (14)	C6—C5—C4	112.57 (11)
O2—C1—O1	126.13 (14)	C6 ⁱ —C5—C4	112.57 (11)
O2—C1—C1 ⁱ	118.98 (8)	C5—C6—H6A	109.5
O1—C1—C1 ⁱ	114.89 (8)	C5—C6—H6B	109.5
C3—C2—H2A	109.5	H6A—C6—H6B	109.5
C3—C2—H2B	109.5	C5—C6—H6C	109.5
H2A—C2—H2B	109.5	H6A—C6—H6C	109.5
O3—C3—C2	122.5 (2)	H6B—C6—H6C	109.5
O1 ⁱ —Cu1—O1—C1	-1.03 (11)	O3—C3—C4—C5	0.0
O1 ⁱⁱ —Cu1—O1—C1	-71 (11)	C2—C3—C4—C5	180.0
O1 ⁱⁱⁱ —Cu1—O1—C1	178.97 (11)	C3—C4—C5—N1	180.0
Cu1—O1—C1—O2	-178.41 (11)	C3—C4—C5—C6	64.06 (12)
Cu1—O1—C1—C1 ⁱ	0.84 (9)	C3—C4—C5—C6 ⁱ	-64.06 (12)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O2 ^{iv}	0.86 (3)	2.23 (2)	2.950 (2)	141.8 (5)
N1—H1A \cdots O2 ^v	0.86 (3)	2.23 (2)	2.950 (2)	141.8 (5)
N1—H1B \cdots O2 ^{vi}	0.883 (18)	2.014 (19)	2.8651 (14)	161.5 (16)

Symmetry codes: (iv) $-x+1, y, -z$; (v) $-x+1, -y+1, -z$; (vi) $x+1/2, -y+1/2, z$.

Fig. 1

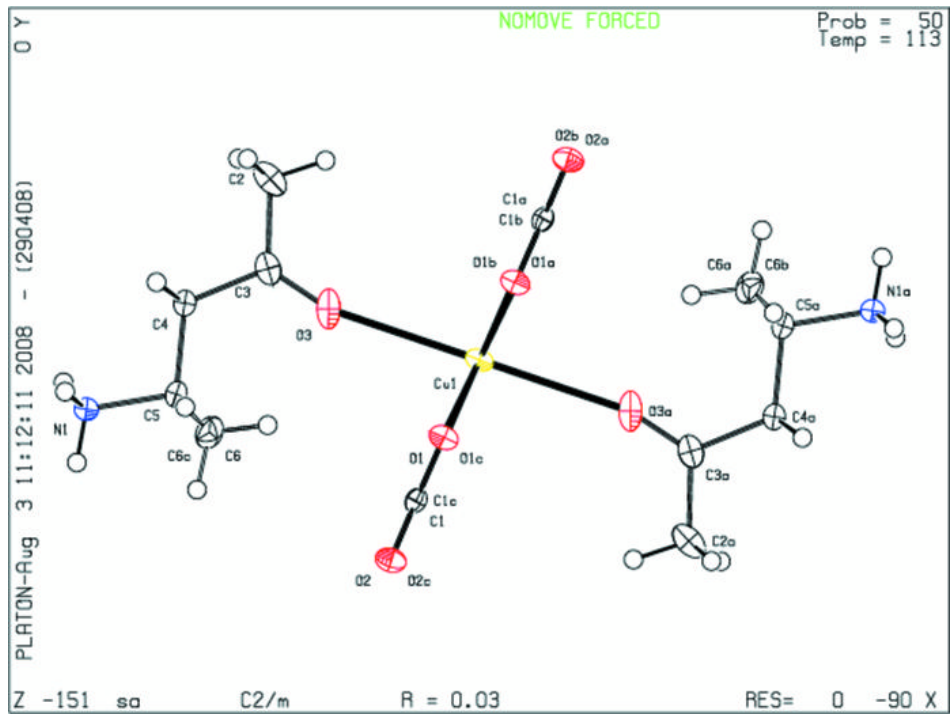


Fig. 2

