metal-organic compounds

Di-μ-acetato-κ^4O:O-bis{2-[(2-amino-ethyl)iminomethyl]phenolato-κ^3N,N',O}-copper(II)

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The title complex, $[Cu_2(C_9H_{11}N_2O)_2(C_2H_3O_2)_2]$ or $Cu_2L_2OAc_2$ [L is (salicylideneimino)ethylamine and OAc is acetate], has a centrosymmetric acetate-bridged dinuclear structure with each Cu^{II} ion in a distorted square-pyramidal coordination geometry, the angles at the Cu^{II} ion deviating from ideal values. The basal plane is occupied by two N atoms, one phenoxy O atom and one O atom from an OAc ligand, with an O atom of a bridging OAc ligand in the apical position. The apical Cu—O bond distance is longer than the equatorial Cu—N or Cu—O bond distances. In the crystal structure, intermolecular hydrogen bonds involving the amino N atom and the uncoordinated acetate ligand O atom connect the dinuclear units into a two-dimensional network.

Related literature

For related literature, see: Addison *et al.* (1984); Boyle *et al.* (1998); Chattopadhyay *et al.* (2006); Benelli *et al.* (1990); Dey (1974); Dutta & Das (1988); Gardner *et al.* (1968); Green *et al.* (1973); Mandal & Nag (1984); Mikuriya *et al.* (2001); Nakajima *et al.* (1998); Rettig *et al.* (1999); Saridha *et al.* (2005); Sessler *et al.* (1991); Turner *et al.* (1992); Wang *et al.* (2004).
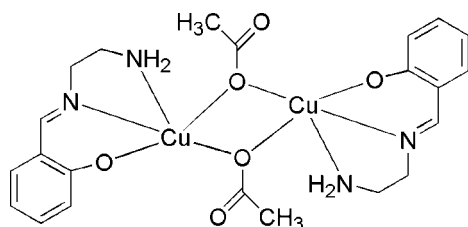
Experimental

Crystal data

$[Cu_2(C_9H_{11}N_2O)_2(C_2H_3O_2)_2]$	V = 1170.4 (4) Å^3
M_r = 571.56	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 11.099 (2) Å	μ = 1.86 mm^{-1}
b = 14.745 (3) Å	T = 293 K
c = 7.4660 (15) Å	$0.28 \times 0.20 \times 0.12$ mm
β = 106.68 (3)°	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	10843 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	2675 independent reflections
	2159 reflections with $I > 2\sigma(I)$
T_{min} = 0.652, T_{max} = 0.795	R_{int} = 0.065

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	154 parameters
$wR(F^2)$ = 0.088	H-atom parameters constrained
S = 1.07	$\Delta\rho_{max}$ = 0.39 e Å^{-3}
2675 reflections	$\Delta\rho_{min}$ = -0.40 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.916 (2)	Cu1—N2	2.011 (2)
Cu1—N1	1.946 (2)	Cu1—O2^i	2.454 (3)
Cu1—O2	1.970 (2)		
O1—Cu1—N1	93.33 (9)	O2—Cu1—N2	93.06 (9)
O1—Cu1—O2	89.89 (8)	O2^i—Cu1—O1	93.10 (8)
N1—Cu1—O2	169.50 (8)	O2—Cu1—O2^i	85.59 (7)
O1—Cu1—N2	174.17 (9)	O2^i—Cu1—N1	104.19 (8)
N1—Cu1—N2	84.65 (10)	O2^i—Cu1—N2	82.12 (8)

Symmetry code: (i) $-x + 1, -y + 2, -z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$B\cdots$O3^{ii}	0.90	2.26	3.009 (6)	140
N2—H2$C\cdots$O1^i	0.90	2.37	3.203 (3)	155

Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $x, -y + \frac{5}{2}, z - \frac{1}{2}$.

Data collection: *CrystalStructure* (Rigaku/MSC, 2004); cell refinement: *CrystalStructure*; data reduction: *CrystalStructure*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2403).

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supplementary materials

Di-*μ*-acetato-*κ⁴O:O*-bis{2-[(2-aminoethyl)iminomethyl]phenolato-*κ³N,N',O*}copper(II)

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Comment

Schiff bases play a significant role in coordination chemistry as a widely used ligand (Green *et al.*, 1973; Dey, 1974). Not only the nitrogen atoms but also other high electronegativity atoms like oxygen and sulfur exist in the molecular structure lead to various chelation modes (Dutta & Das, 1988; Chattopadhyay *et al.*, 2006; Mikuriya *et al.*, 2001; Nakajima *et al.*, 1998). In this contribution, we report the tridentate Schiff base 2-(Salicylideneimino)ethylamine, which is not saturated and then other donors may be accepted in the coordination environment giving the bridged structures. Several mono- and di-nuclear complexes have been reported (Gardner *et al.*, 1968; Saridha *et al.*, 2005; Mandal & Nag, 1984). Carboxylate is another interesting bridging group because it exhibits several coordination modes (Sessler *et al.*, 1991; Boyle *et al.*, 1998; Turner *et al.*, 1992; Rettig *et al.*, 1999; Wang *et al.*, 2004). We focus our interest in the carboxylate and tridentate Schiff base groups and obtain the title acetate-bridged dinuclear copper(II) complex $Cu_2L_2Ac_2$ (I).

Fig. 1 shows the dimeric structure of (I). The two Cu(II) atoms are inversion-center related and are doubly bridged by two oxygen atoms of two acetate ligands. The Cu(1) atom reveals a CuN_2O_3 coordination environment with the two nitrogen atoms and one oxygen atom of the L^- ligand and one oxygen atom of the acetate occupying the basal plane [Cu(1)—O(1) 1.916 (2) Å, Cu(1)—N(1) 1.946 (2) Å, Cu(1)—N(2) 2.011 (2) Å]. Each acetate group bridges two copper(II) ions through O(2) and O(2 A) oxygen atoms involving axial and equatorial positions in the copper(II) coordination polyhedra, respectively. The axial Cu—O bond distance [Cu(1)—O(2 A) 2.454 (3) Å] is significantly longer than the equatorial one [Cu(1)—O(2) 1.970 (2) Å]. Since many five-coordinate structures with intermediate geometries between regular trigonal bipyramidal (TBP) and square pyramidal (SP), the τ value has been used to evaluate the distortion (Addison *et al.*, 1984). In the present complex, τ values is calculated to be 0.08 which indicates that it is very close to a SP geometry. The Cu(II) centers and bridged oxygen atoms form a rhombic plane with the angles O(2)—Cu(1)—O(2 A) and Cu(1)—O(2)—Cu(1 A) of 85.60 ° and 94.40 °, respectively.

A supramolecular network through weak intermolecular N—H···O hydrogen bonds was displayed in Fig. 2. The intramolecular hydrogen bonds exist through N—H···O (phenol) with a distance of 3.203 Å (N···O), which help to stabilize each of the dinuclear unit. The intermolecular hydrogen bonds exist through N—H···O (acetate) of the adjacent molecules with the N···O distance of 3.009 Å. As a result, the crystal structure can be described as a two-dimensional network.

Experimental

$Cu_2L_2Ac_2$ was synthesized as previously reported with a slight modification (Cristiano *et al.*, 1990). A solution of salicylaldehyde (2.45 g, 20 mmol) was slowly added to a water-ethanol solution (1: 1, *v/v*) of copper (II) acetate (4.00 g, 20 mmol) of 100 ml. After adding NaOH (0.10 g, 2.5 mmol) and heating for 10 min, we carefully add ethylenediamine (1.25 g, 20 mmol) to the resulting black-green solution, which gradually changed to black-blue. After the addition was completed, the solution was heated for half an hour. After evaporation of the excess solvent and cooling in the refrigerator, a dark blue precipitate was formed and collected by filtration. Yield: 65%.

supplementary materials

A small quantity of the precipitate (50 mg, 0.2 mmol) was dissolved in a water-methanol solution (1: 4, *v/v*) of 15 ml approximately. After slow evaporation for two weeks, single crystals sutiable for X-ray diffraction analysis were obtained as light-blue rhombic slices.

Refinement

H atoms bound to C and N atoms were placed in caculated positions with C—H = 0.93–0.77Å and N—H = 0.90Å and included in the refinement with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(C)$ for methyl H atoms.

Figures

Fig. 1. A view of complex (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. [symmetry code: (A) $-x + 1$, $-y + 2$, $-z$]
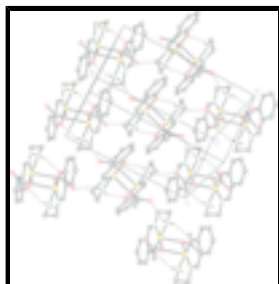

Fig. 2. A hydrogen bonded (dashed lines) layer within the crystal structure of the title compound.

Di-μ-acetato-κ⁴*O*:*O*-bis{2-[(2-\ aminoethyl)iminomethyl]phenolato-\ κ³*N*,*N*',*O*}copper(II)

Crystal data

$[Cu_2(C_9H_{11}N_2O)_2(C_2H_3O_2)_2]$	$F_{000} = 588$
$M_r = 571.56$	$D_x = 1.622$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2675 reflections
$a = 11.099$ (2) Å	$\theta = 3.2–27.5°$
$b = 14.745$ (3) Å	$\mu = 1.86$ mm^{-1}
$c = 7.4660$ (15) Å	$T = 293$ K
$\beta = 106.68$ (3)°	Rhomb, blue
$V = 1170.4$ (4) Å^3	$0.28 \times 0.20 \times 0.12$ mm
$Z = 2$	

Data collection

Rigaku R-AXIS RAPID IP diffractometer	2675 independent reflections
Radiation source: fine-focus sealed tube	2159 reflections with $I > 2\sigma(I)$

Monochromator: graphite	$R_{int} = 0.065$
Detector resolution: 100x100 microns pixels mm^{-1}	$\theta_{max} = 27.5°$
$T = 293$ K	$\theta_{min} = 3.2°$
ω scans	$h = -14 \rightarrow 14$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$k = -19 \rightarrow 19$
$T_{min} = 0.652$, $T_{max} = 0.795$	$l = -8 \rightarrow 9$
10843 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.010P)^2 + 1.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.007$
2675 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.40$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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_{iso}*/U_{eq}
Cu1	0.42654 (3)	1.09572 (2)	−0.06380 (4)	0.03275 (12)
O1	0.31409 (19)	1.07381 (13)	0.0841 (3)	0.0416 (5)
O2	0.57032 (18)	1.06438 (13)	0.1520 (3)	0.0380 (4)
N1	0.2959 (2)	1.14930 (14)	−0.2682 (3)	0.0363 (5)
N2	0.5350 (2)	1.10879 (15)	−0.2366 (3)	0.0383 (5)
H2B	0.5828	1.1590	−0.2081	0.046*
H2C	0.5860	1.0604	−0.2263	0.046*
C1	0.1953 (3)	1.09581 (18)	0.0429 (4)	0.0373 (6)
C7	0.1813 (3)	1.16371 (18)	−0.2704 (4)	0.0392 (7)
H7A	0.1292	1.1917	−0.3762	0.047*

C6	0.1268 (3)	1.14059 (18)	−0.1248 (4)	0.0388 (6)
C8	0.3441 (3)	1.17848 (19)	−0.4217 (4)	0.0439 (7)
H8A	0.3751	1.2402	−0.4010	0.053*
H8B	0.2777	1.1764	−0.5390	0.053*
C3	0.0044 (3)	1.0980 (2)	0.1428 (5)	0.0578 (9)
H3A	−0.0363	1.0827	0.2314	0.069*
C5	−0.0006 (3)	1.1638 (2)	−0.1492 (5)	0.0509 (8)
H5A	−0.0447	1.1935	−0.2581	0.061*
C2	0.1283 (3)	1.0751 (2)	0.1724 (5)	0.0492 (8)
H2A	0.1697	1.0448	0.2820	0.059*
C4	−0.0610 (3)	1.1440 (3)	−0.0189 (6)	0.0620 (10)
H4A	−0.1445	1.1608	−0.0375	0.074*
C9	0.4492 (3)	1.1152 (2)	−0.4288 (4)	0.0444 (7)
H9A	0.4159	1.0559	−0.4727	0.053*
H9B	0.4938	1.1387	−0.5132	0.053*
O3	0.6197 (3)	1.20989 (15)	0.1595 (3)	0.0636 (7)
C10	0.6400 (3)	1.13237 (19)	0.2222 (4)	0.0364 (6)
C11	0.7492 (3)	1.1133 (3)	0.3916 (5)	0.0594 (9)
H11A	0.7948	1.1684	0.4325	0.089*
H11B	0.8039	1.0696	0.3601	0.089*
H11C	0.7185	1.0898	0.4901	0.089*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0409 (2)	0.02722 (18)	0.02902 (19)	0.00513 (14)	0.00822 (13)	0.00394 (12)
O1	0.0430 (12)	0.0456 (12)	0.0369 (11)	0.0091 (9)	0.0123 (9)	0.0104 (8)
O2	0.0418 (11)	0.0312 (10)	0.0364 (10)	0.0011 (9)	0.0040 (8)	0.0037 (8)
N1	0.0495 (15)	0.0265 (11)	0.0302 (12)	0.0032 (10)	0.0071 (10)	0.0011 (8)
N2	0.0458 (14)	0.0304 (12)	0.0388 (13)	0.0013 (10)	0.0122 (10)	0.0022 (9)
C1	0.0442 (16)	0.0276 (13)	0.0391 (15)	−0.0010 (12)	0.0104 (12)	−0.0035 (10)
C7	0.0451 (17)	0.0274 (14)	0.0354 (15)	0.0030 (12)	−0.0038 (12)	−0.0002 (10)
C6	0.0402 (16)	0.0273 (14)	0.0455 (16)	0.0009 (12)	0.0069 (12)	−0.0044 (11)
C8	0.064 (2)	0.0328 (15)	0.0321 (15)	0.0041 (14)	0.0101 (13)	0.0082 (11)
C3	0.054 (2)	0.055 (2)	0.075 (3)	−0.0083 (17)	0.0350 (19)	−0.0121 (17)
C5	0.0393 (17)	0.0391 (17)	0.067 (2)	−0.0020 (14)	0.0038 (15)	−0.0044 (14)
C2	0.055 (2)	0.0421 (17)	0.0540 (19)	−0.0056 (15)	0.0211 (15)	−0.0042 (14)
C4	0.0373 (18)	0.051 (2)	0.097 (3)	−0.0039 (16)	0.0182 (19)	−0.0133 (19)
C9	0.064 (2)	0.0398 (16)	0.0321 (15)	0.0013 (15)	0.0176 (14)	0.0010 (11)
O3	0.0890 (19)	0.0327 (12)	0.0596 (15)	0.0009 (12)	0.0063 (13)	−0.0027 (10)
C10	0.0409 (16)	0.0351 (15)	0.0350 (14)	0.0035 (13)	0.0137 (12)	−0.0014 (11)
C11	0.0465 (19)	0.071 (2)	0.054 (2)	−0.0057 (17)	0.0034 (15)	0.0008 (16)

Geometric parameters ($Å$, °)

Cu1—O1	1.916 (2)	C8—C9	1.506 (4)
Cu1—N1	1.946 (2)	C8—H8A	0.9700
Cu1—O2	1.970 (2)	C8—H8B	0.9700
Cu1—N2	2.011 (2)	C3—C2	1.370 (5)

Cu1—O2[i]	2.454 (3)	C3—C4	1.393 (5)
O1—C1	1.306 (3)	C3—H3A	0.9300
O2—C10	1.283 (3)	C5—C4	1.362 (5)
N1—C7	1.285 (4)	C5—H5A	0.9300
N1—C8	1.462 (4)	C2—H2A	0.9300
N2—C9	1.480 (4)	C4—H4A	0.9300
N2—H2B	0.9000	C9—H9A	0.9700
N2—H2C	0.9000	C9—H9B	0.9700
C1—C2	1.413 (4)	O3—C10	1.231 (3)
C1—C6	1.426 (4)	C10—C11	1.506 (4)
C7—C6	1.429 (4)	C11—H11A	0.9600
C7—H7A	0.9300	C11—H11B	0.9600
C6—C5	1.415 (4)	C11—H11C	0.9600
O1—Cu1—N1	93.33 (9)	C9—C8—H8A	110.1
O1—Cu1—O2	89.89 (8)	N1—C8—H8B	110.1
N1—Cu1—O2	169.50 (8)	C9—C8—H8B	110.1
O1—Cu1—N2	174.17 (9)	H8A—C8—H8B	108.4
N1—Cu1—N2	84.65 (10)	C2—C3—C4	120.6 (3)
O2—Cu1—N2	93.06 (9)	C2—C3—H3A	119.7
O2[i]—Cu1—O1	93.10 (8)	C4—C3—H3A	119.7
O2—Cu1—O2[i]	85.59 (7)	C4—C5—C6	122.3 (3)
O2[i]—Cu1—N1	104.19 (8)	C4—C5—H5A	118.8
O2[i]—Cu1—N2	82.12 (8)	C6—C5—H5A	118.8
C1—O1—Cu1	127.10 (17)	C3—C2—C1	122.5 (3)
C10—O2—Cu1	113.76 (17)	C3—C2—H2A	118.8
C7—N1—C8	121.7 (2)	C1—C2—H2A	118.8
C7—N1—Cu1	126.14 (19)	C5—C4—C3	118.8 (3)
C8—N1—Cu1	112.09 (19)	C5—C4—H4A	120.6
C9—N2—Cu1	106.92 (18)	C3—C4—H4A	120.6
C9—N2—H2B	110.3	N2—C9—C8	107.2 (2)
Cu1—N2—H2B	110.3	N2—C9—H9A	110.3
C9—N2—H2C	110.3	C8—C9—H9A	110.3
Cu1—N2—H2C	110.3	N2—C9—H9B	110.3
H2B—N2—H2C	108.6	C8—C9—H9B	110.3
O1—C1—C2	118.7 (3)	H9A—C9—H9B	108.5
O1—C1—C6	124.7 (3)	O3—C10—O2	123.2 (3)
C2—C1—C6	116.6 (3)	O3—C10—C11	120.5 (3)
N1—C7—C6	125.7 (2)	O2—C10—C11	116.3 (3)
N1—C7—H7A	117.1	C10—C11—H11A	109.5
C6—C7—H7A	117.1	C10—C11—H11B	109.5
C5—C6—C1	119.1 (3)	H11A—C11—H11B	109.5
C5—C6—C7	118.0 (3)	C10—C11—H11C	109.5
C1—C6—C7	122.9 (3)	H11A—C11—H11C	109.5
N1—C8—C9	107.9 (2)	H11B—C11—H11C	109.5
N1—C8—H8A	110.1		

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2B···O3[ii]	0.90	2.26	3.009 (6)	140
N2—H2C···O1[i]	0.90	2.37	3.203 (3)	155

Symmetry codes: (ii) *x*, −*y*+5/2, *z*−1/2; (i) −*x*+1, −*y*+2, −*z*.

Fig. 1

Fig. 2