metal-organic compounds

[1,1′-Diphenyl-3,3′-(propane-1,3-diyldinitrilo)dibut-1-enolato]copper(II)

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The title compound, $[Cu(C_{23}H_{24}N_2O_2)]$ or $[Cu\{(BA)_2pn\}]$, where $(BA)_2pn$ is 1,1′-diphenyl-3,3′-(propane-1,3-diyldinitrilo)dibut-1-enolate, is a mononuclear copper(II) complex, located on a twofold axis. The four-coordinate Cu^{II} atom is in a tetrahedrally distorted square plane defined by the N and O atoms of the Schiff base ligand. In the tetradentate ligand, the two chelate rings are twisted relative to each other, making a dihedral angle of 36.57 (3)°.

Related literature

For general background, see: Bunce *et al.* (1998); Klement *et al.* (1999); Meghdadi *et al.* (2008); Mikuriya *et al.* (2002); Filomeni *et al.* (2007). For a structure determination of the title compound in space group *Cc*, see: Sarkar *et al.* (2008). For the structure of a polymorph, see: Arıcı (2006). For related structures, see: Arıcı *et al.* (2001); Dehghanpour *et al.* (2005).
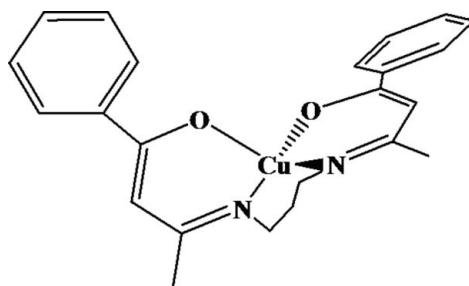
Experimental

Crystal data

$[Cu(C_{23}H_{24}N_2O_2)]$	$V = 1981.3$ (3) Å³
$M_r = 423.98$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 12.2047$ (12) Å	$\mu = 1.12$ mm⁻¹
$b = 20.320$ (2) Å	$T = 100$ (2) K
$c = 8.9992$ (9) Å	$0.50 \times 0.46 \times 0.35$ mm
$\beta = 117.405$ (1)°	

Data collection

Bruker APEXII CCD diffractometer	11028 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	2881 independent reflections
	2780 reflections with $I > 2\sigma(I)$
$T_{min} = 0.57$, $T_{max} = 0.68$	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	129 parameters
$wR(F^2) = 0.063$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.42$ e Å⁻³
2881 reflections	$\Delta\rho_{min} = -0.34$ e Å⁻³

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2424).

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supporting information

[1,1′-Diphenyl-3,3′-(propane-1,3-diyldinitrilo)dibut-1-enolato]copper(II)

Mehdi Salehi, Soraia Meghdadi, Mehdi Amirnasr and Kurt Mereiter

S1. Comment

The chemistry of copper(II) complexes with N_2O_2 Schiff base ligands have been investigated extensively in recent years owing to their interesting physico–chemical properties, and their potential application in catalytic reactions and biological activities (Bunce *et al.*, 1998; Klement *et al.*; 1999, Filomeni *et al.*, 2007). These complexes are also attractive because of their preparative accessibility, diversity and structural variability. Most of the earlier investigations were carried out on the tetradentate Schiff base ligand salen and its derivatives, while *N,N′*–bis(benzoylacetone)–1,3–propylenediimine and its derivatives have rarely been studied [Mikuriya *et al.* 2002]. Two alternative reports on the synthesis and structure of Cu(II) complexes with (BA)$_2$pn ligand under different conditions is already published [Arıcı, 2006; Sarkar *et al.*, 2008]. In this context, we herein report the synthesis and structure of the title compound, [Cu((BA)$_2$pn)], (**I**), and make a brief comparison with the reported structures.

  The structure of [Cu((BA)$_2$pn)], (**I**), is shown in Fig. 1. The complex has symmetry C_2 with Cu(1) and C(12) on a C_2 axis. The coordination geometry around Cu(II) center may be described as distorted square planar. This is indicated by the chelate angles which deviate from 90° (90.19 (4)° (O(1)–Cu(1)–O(1)^i) to 94.56 (3)° (O(1)–Cu(1)–N(1))) and 180° (154.41 (4)° for O(1)–Cu(1)–N(1)^i = O(1)^i–Cu(1)–N(1)). The dihedral angle between the two Cu–O,N chelate rings is 36.57 (3)°. The Cu–O and Cu–N distances of the coordinated (BA)$_2$pn in the equatorial plane, Cu(1)–O(1) = Cu(1)–O(1)^i = 1.9145 (7) Å, Cu(1)–N(1) = Cu(1)–N(1)^i = 1.9394 (9) Å, compare well with the Cu–O and Cu–N distances found in the related complex [Cu((BA)$_2$en)] [Cu–O$_{av}$ = 1.913 (2) Å, Cu–N$_{av}$ = 1.930 (3) Å; Dehghanpour *et al.*, (2005)]. The crystal structure is, in principle, identical to that reported by Sarkar *et al.*, 2008. The space group was determined by these authors as *Cc*, however, it was overlooked that the structure has C_2 axes parallel to *b* and therefore adopts space group symmetry *C*2/*c*. Due to this overlooked space group symmetry (*Cc* instead of *C*2/*c*), chemically equivalent bond lengths and angles in the reported structure vary widely (bond length differences of chemically equivalent bonds up to 0.17 Å (C19–C20 and C8–C9)). In another report (Arıcı, 2006), a polymorphic form of this compound with space group *C*2/*c* and a molecular conformation which differs most significantly from Sarkar's and the present work is presented. Among other features, this complex shows a more planar coordination of Cu with *transoid* O–Cu–N angles of about 170° and a half-chair conformation for the Cu–N,N chelate ring, whereas (**I**) exhibits a twist-boat conformation similar to the di-methyl-substituted homologue (at C(12) of (**I**)) described by Arıcı *et al.* (2001).

S2. Experimental

H$_2$(BA)$_2$pn, *N,N′*–bis(benzoylacetone)–1,3–propylenediimine was prepared according to the literature [Meghdadi *et al.* 2008] by the condensation of of benzoylacetone (0.324 g, 2 mmol) with 1,3–propylenediamine (0.074 g, 1 mmol) in methanol at room temperature. To a solution of H$_2$(BA)$_2$pn (0.362 g, 1 mmol) in methanol (30 ml) was added with stirring copper(II) acetate monohydrate (0.200 g, 1 mmol). The mixture was stirred at room temperature for about 30 min and then filtered. The filtrate was kept undisturbed in air and black oval–shaped crystals of (I) were formed upon slow

evaporation of the solvent after two days. The crystals were filtered off, washed with cold methanol and dried under vacuum.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.95Å (aromatic), 0.99Å (methylene) and 0.98Å (methyl) with $U_{iso}(H) = 1.2\ U_{eq}$(aromatic, methylene) or $U_{iso}(H) = 1.5\ U_{eq}$(methyl).
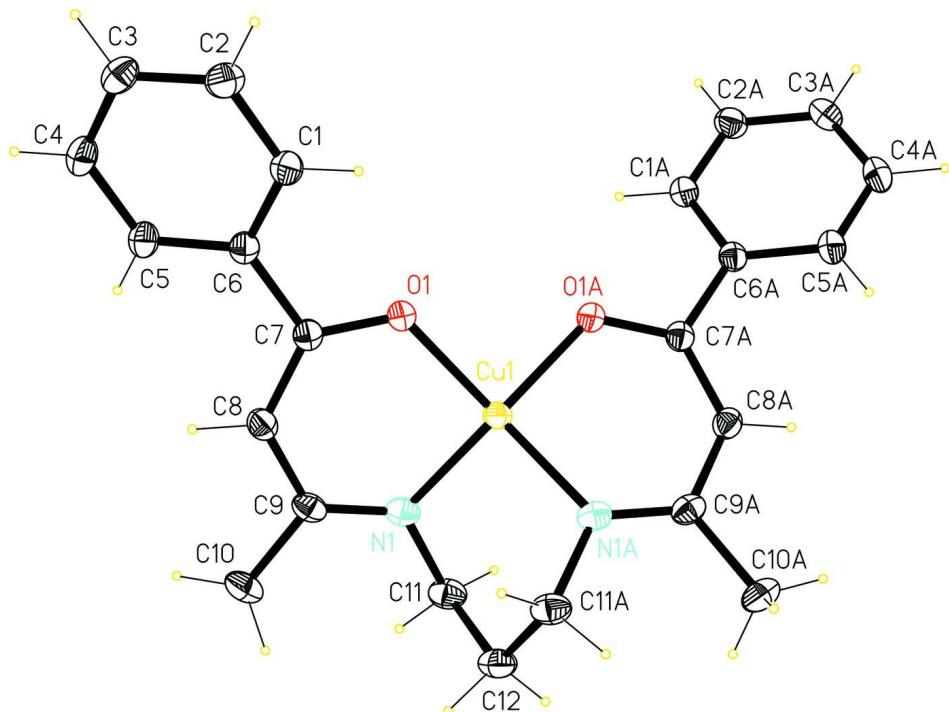

Figure 1

The *ORTEP* drawing of (I), with atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) 1-x, y, 1/2-z].

[1,1′-Diphenyl-3,3′-(propane-1,3-diyldinitrilo)dibut-1-enolato]copper(II)

Crystal data
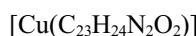
[Cu(C₂₃H₂₄N₂O₂)]	$F(000) = 884$
$M_r = 423.98$	$D_x = 1.421$ Mg m⁻³
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 8926 reflections
$a = 12.2047\ (12)$ Å	$\theta = 2.1–30.0°$
$b = 20.320\ (2)$ Å	$\mu = 1.12$ mm⁻¹
$c = 8.9992\ (9)$ Å	$T = 100$ K
$\beta = 117.405\ (1)°$	Oval, black
$V = 1981.3\ (3)$ Å³	$0.50 \times 0.46 \times 0.35$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	φ and ω scans
Radiation source: fine-focus sealed tube	Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
Graphite monochromator	$T_{min} = 0.57$, $T_{max} = 0.68$

11028 measured reflections

2881 independent reflections

2780 reflections with $I > 2\sigma(I)$

$R_{int} = 0.019$

$\theta_{max} = 30.0°$, $\theta_{min} = 2.6°$

$h = -17 \rightarrow 17$

$k = -28 \rightarrow 28$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.063$

$S = 1.05$

2881 reflections

129 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

$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 1.3062P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.42$ e Å^{-3}

$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Experimental. Dark crystals from methanol. Bruker Kappa *APEX*II CCD diffractometer, full sphere data collection.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.5000	0.285854 (8)	0.2500	0.01604 (6)	
O1	0.58573 (7)	0.35237 (3)	0.19375 (9)	0.01910 (14)	
N1	0.62650 (9)	0.21952 (4)	0.30042 (11)	0.01918 (16)	
C1	0.62862 (9)	0.44403 (5)	−0.00488 (13)	0.02073 (18)	
H1A	0.5465	0.4414	−0.0198	0.025*	
C2	0.66276 (10)	0.49606 (5)	−0.07553 (14)	0.0239 (2)	
H2A	0.6036	0.5284	−0.1396	0.029*	
C3	0.78315 (10)	0.50085 (5)	−0.05262 (13)	0.0227 (2)	
H3A	0.8060	0.5360	−0.1023	0.027*	
C4	0.87007 (10)	0.45401 (5)	0.04322 (13)	0.02263 (19)	
H4A	0.9529	0.4578	0.0615	0.027*	
C5	0.83576 (9)	0.40168 (5)	0.11223 (13)	0.02040 (18)	
H5A	0.8954	0.3696	0.1767	0.024*	
C6	0.71452 (9)	0.39567 (5)	0.08789 (12)	0.01713 (17)	
C7	0.67614 (9)	0.33962 (5)	0.16071 (11)	0.01684 (17)	
C8	0.73853 (9)	0.28017 (5)	0.18784 (13)	0.01919 (18)	
H8A	0.8005	0.2772	0.1522	0.023*	
C9	0.71826 (10)	0.22321 (5)	0.26408 (12)	0.01902 (18)	
C10	0.81019 (10)	0.16754 (5)	0.30347 (14)	0.0251 (2)	
H10A	0.7658	0.1263	0.2580	0.038*	

H10B	0.8598	0.1635	0.4250	0.038*	
H10C	0.8645	0.1768	0.2528	0.038*	
C11	0.60558 (11)	0.16066 (5)	0.37870 (13)	0.02317 (19)	
H11A	0.5853	0.1741	0.4689	0.028*	
H11B	0.6821	0.1341	0.4297	0.028*	
C12	0.5000	0.11873 (7)	0.2500	0.0241 (3)	
H12A	0.4673	0.0900	0.3093	0.029*	0.50
H12B	0.5327	0.0900	0.1907	0.029*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01768 (9)	0.01421 (9)	0.01729 (9)	0.000	0.00895 (7)	0.000
O1	0.0193 (3)	0.0171 (3)	0.0243 (3)	0.0005 (2)	0.0130 (3)	0.0002 (2)
N1	0.0227 (4)	0.0162 (4)	0.0171 (4)	0.0019 (3)	0.0078 (3)	0.0007 (3)
C1	0.0175 (4)	0.0200 (4)	0.0242 (5)	−0.0008 (3)	0.0093 (4)	−0.0006 (3)
C2	0.0222 (5)	0.0208 (4)	0.0254 (5)	−0.0008 (4)	0.0083 (4)	0.0019 (4)
C3	0.0244 (5)	0.0227 (5)	0.0208 (4)	−0.0068 (4)	0.0103 (4)	−0.0020 (3)
C4	0.0192 (4)	0.0275 (5)	0.0225 (4)	−0.0055 (4)	0.0108 (4)	−0.0029 (4)
C5	0.0159 (4)	0.0240 (5)	0.0207 (4)	−0.0014 (3)	0.0079 (4)	−0.0008 (3)
C6	0.0164 (4)	0.0185 (4)	0.0164 (4)	−0.0019 (3)	0.0075 (3)	−0.0028 (3)
C7	0.0156 (4)	0.0184 (4)	0.0156 (4)	−0.0014 (3)	0.0064 (3)	−0.0026 (3)
C8	0.0174 (4)	0.0194 (4)	0.0205 (4)	0.0005 (3)	0.0085 (4)	−0.0031 (3)
C9	0.0193 (4)	0.0175 (4)	0.0161 (4)	0.0020 (3)	0.0046 (4)	−0.0033 (3)
C10	0.0238 (5)	0.0208 (5)	0.0260 (5)	0.0065 (4)	0.0075 (4)	−0.0027 (4)
C11	0.0308 (5)	0.0183 (4)	0.0199 (4)	0.0031 (4)	0.0113 (4)	0.0039 (3)
C12	0.0327 (8)	0.0159 (6)	0.0260 (7)	0.000	0.0154 (6)	0.000

Geometric parameters (Å, º)

Cu1—O1	1.9145 (7)	C5—C6	1.3978 (13)
Cu1—O1^i	1.9145 (7)	C5—H5A	0.9500
Cu1—N1	1.9394 (9)	C6—C7	1.4928 (13)
Cu1—N1^i	1.9395 (9)	C7—C8	1.3882 (13)
O1—C7	1.2943 (11)	C8—C9	1.4241 (14)
N1—C9	1.3054 (14)	C8—H8A	0.9500
N1—C11	1.4688 (13)	C9—C10	1.5158 (14)
C1—C2	1.3925 (14)	C10—H10A	0.9800
C1—C6	1.3986 (14)	C10—H10B	0.9800
C1—H1A	0.9500	C10—H10C	0.9800
C2—C3	1.3900 (15)	C11—C12	1.5342 (14)
C2—H2A	0.9500	C11—H11A	0.9900
C3—C4	1.3903 (16)	C11—H11B	0.9900
C3—H3A	0.9500	C12—C11^i	1.5342 (14)
C4—C5	1.3896 (14)	C12—H12A	0.9900
C4—H4A	0.9500	C12—H12B	0.9900
O1—Cu1—O1^i	90.19 (4)	O1—C7—C8	126.18 (9)

O1—Cu1—N1	94.56 (3)	O1—C7—C6	114.90 (8)
O1ⁱ—Cu1—N1	154.41 (4)	C8—C7—C6	118.91 (9)
O1—Cu1—N1ⁱ	154.41 (4)	C7—C8—C9	126.09 (9)
O1ⁱ—Cu1—N1ⁱ	94.56 (3)	C7—C8—H8A	117.0
N1—Cu1—N1ⁱ	91.94 (5)	C9—C8—H8A	117.0
C7—O1—Cu1	123.15 (6)	N1—C9—C8	121.79 (9)
C9—N1—C11	121.70 (9)	N1—C9—C10	121.77 (9)
C9—N1—Cu1	125.72 (7)	C8—C9—C10	116.43 (9)
C11—N1—Cu1	112.51 (7)	C9—C10—H10A	109.5
C2—C1—C6	120.42 (9)	C9—C10—H10B	109.5
C2—C1—H1A	119.8	H10A—C10—H10B	109.5
C6—C1—H1A	119.8	C9—C10—H10C	109.5
C3—C2—C1	120.23 (10)	H10A—C10—H10C	109.5
C3—C2—H2A	119.9	H10B—C10—H10C	109.5
C1—C2—H2A	119.9	N1—C11—C12	111.17 (8)
C2—C3—C4	119.78 (10)	N1—C11—H11A	109.4
C2—C3—H3A	120.1	C12—C11—H11A	109.4
C4—C3—H3A	120.1	N1—C11—H11B	109.4
C5—C4—C3	120.01 (10)	C12—C11—H11B	109.4
C5—C4—H4A	120.0	H11A—C11—H11B	108.0
C3—C4—H4A	120.0	C11—C12—C11ⁱ	112.54 (12)
C4—C5—C6	120.79 (10)	C11—C12—H12A	109.1
C4—C5—H5A	119.6	C11ⁱ—C12—H12A	109.1
C6—C5—H5A	119.6	C11—C12—H12B	109.1
C5—C6—C1	118.73 (9)	C11ⁱ—C12—H12B	109.1
C5—C6—C7	121.42 (9)	H12A—C12—H12B	107.8
C1—C6—C7	119.84 (9)		
O1ⁱ—Cu1—O1—C7	171.40 (9)	Cu1—O1—C7—C8	−11.84 (13)
N1—Cu1—O1—C7	16.58 (8)	Cu1—O1—C7—C6	168.64 (6)
N1ⁱ—Cu1—O1—C7	−87.60 (11)	C5—C6—C7—O1	151.44 (9)
O1—Cu1—N1—C9	−12.71 (9)	C1—C6—C7—O1	−27.61 (13)
O1ⁱ—Cu1—N1—C9	−112.72 (10)	C5—C6—C7—C8	−28.11 (13)
N1ⁱ—Cu1—N1—C9	142.51 (10)	C1—C6—C7—C8	152.83 (9)
O1—Cu1—N1—C11	170.40 (7)	O1—C7—C8—C9	−3.07 (16)
O1ⁱ—Cu1—N1—C11	70.39 (11)	C6—C7—C8—C9	176.44 (9)
N1ⁱ—Cu1—N1—C11	−34.37 (6)	C11—N1—C9—C8	179.86 (9)
C6—C1—C2—C3	−0.83 (16)	Cu1—N1—C9—C8	3.24 (14)
C1—C2—C3—C4	−0.93 (16)	C11—N1—C9—C10	−1.20 (15)
C2—C3—C4—C5	1.64 (16)	Cu1—N1—C9—C10	−177.83 (7)
C3—C4—C5—C6	−0.59 (15)	C7—C8—C9—N1	7.75 (16)
C4—C5—C6—C1	−1.15 (15)	C7—C8—C9—C10	−171.24 (10)
C4—C5—C6—C7	179.79 (9)	C9—N1—C11—C12	−102.55 (11)
C2—C1—C6—C5	1.85 (15)	Cu1—N1—C11—C12	74.48 (9)
C2—C1—C6—C7	−179.07 (9)	N1—C11—C12—C11ⁱ	−37.68 (6)

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