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Bis[μ-*N*′-(5-bromo-3-methoxy-2-oxidobenzylidene)-2-hydroxybenzohydrazidato]bis[(*N*,*N*-dimethylformamide)copper(II)]

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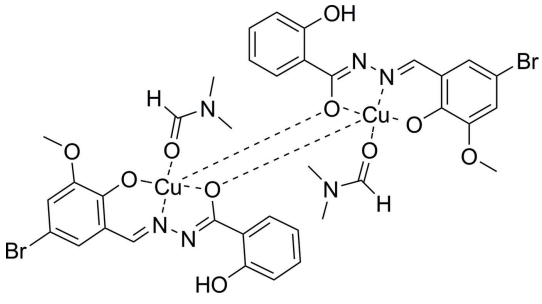
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.040; wR factor = 0.123; data-to-parameter ratio = 17.0.

The title compound, $[Cu_2(C_{15}H_{11}BrN_2O_4)_2(C_3H_7NO)_2]$, is derived from the reaction of *N*′-(5-bromo-2-hydroxy-3-methoxybenzylidene)-2-hydroxybenzohydrazide and copper nitrate in a dimethylformamide solution in the presence of sodium hydroxide. The compound can be regarded as a binuclear centrosymmetric complex. In the crystal, the Cu^{II} atom is fivefold surrounded and adopts a distorted square-pyramidal coordination environment. An intramolecular O—H···N hydrogen bond stabilizes the molecular conformation.

Related literature

For the synthesis of *N*′-(5-bromo-2-hydroxy-3-methoxybenzylidene)-2-hydroxybenzohydrazide and its crystal structure, see: Zhao *et al.* (2012). For the crystal structure of a complex with a similar coordination environment, see: Huang *et al.* (2010).



Experimental

Crystal data

$[Cu_2(C_{15}H_{11}BrN_2O_4)_2(C_3H_7NO)_2]$
M_r = 999.61
Triclinic, $P\overline{1}$
a = 8.3861 (17) Å
b = 9.5795 (19) Å
c = 12.275 (3) Å
α = 90.446 (3)°
β = 97.850 (3)°
γ = 101.688 (3)°
V = 956.0 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 3.27 mm^{-1}
T = 296 K
0.38 × 0.25 × 0.16 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.371, T_{max} = 0.620
5880 measured reflections
4354 independent reflections
2957 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.123
S = 0.99
4354 reflections
256 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4*A*···N2	0.82	1.84	2.566 (3)	146

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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* and local programs.

This project was supported by the National Natural Science Foundation of China (program Nos. 21103135 and 21073139), the Natural Science Basic Research Plan in Shaanxi Province of China (program No. 2011JQ2011), the Foundation of Xi'an University of Science and Technology (program No. 2010QDJ030), the Scientific Research Program funded by Shaanxi Provincial Education Department (program No.12 J K0622) and the Open Foundation of the Laboratory of Space Materials Science and Technology of NWPU.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5995).

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supporting information

Acta Cryst. (2012). E**68**, m1216 [doi:10.1107/S1600536812036100]

Bis[μ-*N*′-(5-bromo-3-methoxy-2-oxidobenzylidene)-2-hydroxybenzohydrazidato]bis[(*N*,*N*-dimethylformamide)copper(II)]

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S1. Comment

Hydrazones attract the interest of researchers due to their various biological activities and their capacity for chelating to most kind of metals. As Fig. 1 shows, the Cu_{II} ion exists in a distorted square-pyramidal coordination geometry and it is located in the center of the coordination basal plane, which is defined by three donor atoms (O2, N1 and O3) of the hydrozone ligand and O5 atom from the DMF molecule with a mean plane deviation of 0.0367 (4) Å. The axial position is occupied by O3 atom from another asymmetric unit. The molecular conformation is stabilized by an intramolecular O—H···N hydrogen bond (Table 1).

S2. Experimental

A solution of copper nitrate (186.2 mg, 1.0 mmol) in DMF (2 ml) was added to a solution of *N*′-(5-bromo-2-hydroxy-3-methoxybenzylidene)-2-hydroxybenzohydrazide (361.5 mg, 1.0 mmol) in DMF (10 ml) and stirred at room temperature for 2 h before being filtered. The dark green filtrate was allow to evaperate slowly in the air for several days. Green crystals was collected by filtration and dried under vacumn, yield 59.3%.

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with C—H = 0.95–0.99 Å, O—H = 0.82 Å and with U_{iso}(H) = 1.2 U_{eq}(C,O) (1.5 for methyl groups and the hydroxyl group). The methyl groups bonded to N and the hydroxyl group were allowed to rotate but not to tip.

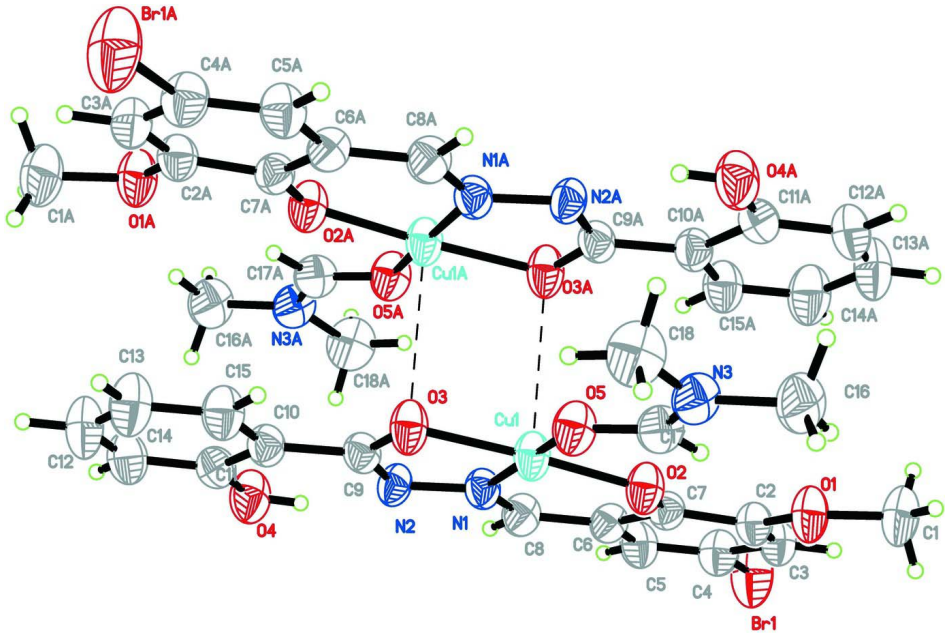

Figure 1

The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

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Crystal data

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β = 97.850 (3)°
γ = 101.688 (3)°
V = 956.0 (3) Å^3
Z = 1
F(000) = 502
D_x = 1.736 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3650 reflections
θ = 1.8–26.5°
μ = 3.27 mm^{-1}
T = 296 K
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Data collection

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Radiation source: fine-focus sealed tube
Graphite monochromator
thin–slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.371, T_{max} = 0.620
5880 measured reflections
4354 independent reflections
2957 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 29.5°, θ_{min} = 2.7°
h = −10→9
k = −13→9
l = −15→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.123$
$S = 0.99$
4354 reflections
256 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
$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.08579 (5)	0.69096 (4)	1.00600 (3)	0.04176 (15)
Br1	−0.38768 (6)	1.16095 (5)	1.23139 (4)	0.0821 (2)
O2	0.1023 (3)	0.8271 (2)	1.11968 (18)	0.0456 (6)
O3	0.0529 (3)	0.5575 (2)	0.88176 (17)	0.0472 (6)
N1	−0.1145 (3)	0.7314 (3)	0.9327 (2)	0.0383 (6)
C8	−0.1977 (4)	0.8182 (4)	0.9650 (3)	0.0435 (8)
H8A	−0.2920	0.8293	0.9194	0.052*
N2	−0.1691 (3)	0.6616 (3)	0.8310 (2)	0.0397 (6)
O4	−0.3540 (3)	0.5853 (3)	0.6472 (2)	0.0592 (7)
H4A	−0.3231	0.6295	0.7064	0.089*
O1	0.1737 (3)	0.9882 (3)	1.29675 (19)	0.0532 (6)
C7	−0.0064 (4)	0.8995 (3)	1.1382 (2)	0.0373 (7)
C5	−0.2652 (4)	0.9817 (4)	1.0956 (3)	0.0473 (8)
H5A	−0.3618	0.9825	1.0485	0.057*
C2	0.0244 (4)	0.9885 (4)	1.2357 (3)	0.0427 (8)
C15	−0.0090 (4)	0.4028 (4)	0.6826 (3)	0.0503 (9)
H15A	0.0814	0.3948	0.7334	0.060*
C9	−0.0709 (4)	0.5740 (3)	0.8131 (2)	0.0378 (7)
C10	−0.1099 (4)	0.4926 (3)	0.7074 (3)	0.0404 (7)
C3	−0.0851 (4)	1.0652 (4)	1.2625 (3)	0.0463 (8)
H3A	−0.0634	1.1207	1.3274	0.056*
C13	−0.1735 (5)	0.3340 (5)	0.5115 (3)	0.0665 (11)
H13A	−0.1945	0.2805	0.4456	0.080*
C11	−0.2471 (4)	0.5005 (4)	0.6306 (3)	0.0442 (8)
C4	−0.2312 (5)	1.0593 (4)	1.1908 (3)	0.0501 (9)

C12	−0.2778 (5)	0.4198 (4)	0.5330 (3)	0.0595 (10)
H12A	−0.3695	0.4240	0.4822	0.071*
C6	−0.1546 (4)	0.8990 (3)	1.0669 (3)	0.0396 (7)
C14	−0.0388 (5)	0.3255 (5)	0.5852 (3)	0.0641 (11)
H14A	0.0322	0.2676	0.5694	0.077*
O5	0.2998 (3)	0.6509 (2)	1.06249 (19)	0.0480 (6)
N3	0.5109 (3)	0.6665 (3)	1.1985 (2)	0.0469 (7)
C17	0.3796 (4)	0.7041 (4)	1.1530 (3)	0.0456 (8)
H17A	0.3414	0.7742	1.1886	0.055*
C16	0.6002 (5)	0.7336 (5)	1.3018 (3)	0.0617 (11)
H16A	0.5433	0.8023	1.3272	0.093*
H16B	0.7090	0.7806	1.2907	0.093*
H16C	0.6073	0.6622	1.3557	0.093*
C1	0.2101 (6)	1.0583 (5)	1.4017 (3)	0.0672 (11)
H1A	0.3178	1.0496	1.4351	0.101*
H1B	0.1304	1.0154	1.4472	0.101*
H1C	0.2066	1.1573	1.3941	0.101*
C18	0.5749 (5)	0.5542 (5)	1.1512 (4)	0.0654 (11)
H18A	0.4883	0.4937	1.1028	0.098*
H18B	0.6171	0.4988	1.2089	0.098*
H18C	0.6616	0.5955	1.1104	0.098*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0362 (2)	0.0507 (3)	0.0374 (2)	0.01501 (18)	−0.00696 (16)	−0.00787 (17)
Br1	0.0733 (3)	0.1088 (4)	0.0734 (3)	0.0549 (3)	−0.0096 (2)	−0.0330 (3)
O2	0.0385 (13)	0.0546 (14)	0.0435 (12)	0.0180 (11)	−0.0066 (10)	−0.0112 (10)
O3	0.0419 (13)	0.0591 (15)	0.0408 (12)	0.0209 (11)	−0.0079 (10)	−0.0123 (10)
N1	0.0389 (15)	0.0411 (15)	0.0336 (13)	0.0104 (12)	−0.0023 (11)	−0.0008 (11)
C8	0.0374 (17)	0.046 (2)	0.0449 (18)	0.0123 (15)	−0.0077 (14)	−0.0012 (15)
N2	0.0387 (15)	0.0393 (15)	0.0375 (14)	0.0080 (12)	−0.0067 (11)	−0.0072 (11)
O4	0.0599 (16)	0.0672 (18)	0.0486 (15)	0.0250 (14)	−0.0163 (12)	−0.0091 (12)
O1	0.0450 (14)	0.0676 (17)	0.0441 (13)	0.0160 (12)	−0.0094 (11)	−0.0157 (12)
C7	0.0384 (17)	0.0368 (17)	0.0360 (16)	0.0086 (14)	0.0018 (13)	−0.0004 (13)
C5	0.0402 (19)	0.059 (2)	0.0440 (19)	0.0185 (16)	−0.0023 (15)	−0.0039 (16)
C2	0.0405 (18)	0.048 (2)	0.0374 (17)	0.0088 (15)	−0.0014 (14)	−0.0027 (14)
C15	0.043 (2)	0.061 (2)	0.047 (2)	0.0170 (17)	−0.0022 (15)	−0.0081 (16)
C9	0.0331 (16)	0.0435 (19)	0.0334 (16)	0.0037 (14)	−0.0015 (13)	0.0015 (13)
C10	0.0389 (18)	0.0436 (19)	0.0354 (16)	0.0040 (15)	0.0006 (13)	−0.0007 (14)
C3	0.050 (2)	0.049 (2)	0.0398 (18)	0.0120 (16)	0.0042 (15)	−0.0070 (15)
C13	0.071 (3)	0.083 (3)	0.045 (2)	0.020 (2)	−0.0027 (19)	−0.022 (2)
C11	0.046 (2)	0.046 (2)	0.0379 (17)	0.0096 (16)	−0.0007 (15)	0.0021 (14)
C4	0.048 (2)	0.054 (2)	0.051 (2)	0.0195 (17)	0.0041 (16)	−0.0053 (16)
C12	0.062 (3)	0.069 (3)	0.040 (2)	0.009 (2)	−0.0111 (17)	−0.0053 (18)
C6	0.0348 (17)	0.0389 (18)	0.0440 (18)	0.0088 (14)	0.0004 (13)	−0.0017 (14)
C14	0.063 (3)	0.076 (3)	0.056 (2)	0.024 (2)	0.0040 (19)	−0.019 (2)
O5	0.0379 (13)	0.0562 (15)	0.0488 (13)	0.0164 (11)	−0.0074 (10)	−0.0079 (11)

N3	0.0310 (14)	0.0506 (18)	0.0537 (17)	0.0044 (12)	−0.0062 (12)	−0.0006 (13)
C17	0.0346 (18)	0.049 (2)	0.050 (2)	0.0069 (15)	−0.0017 (15)	0.0024 (16)
C16	0.047 (2)	0.070 (3)	0.060 (2)	0.0083 (19)	−0.0155 (18)	−0.0032 (19)
C1	0.061 (3)	0.077 (3)	0.055 (2)	0.010 (2)	−0.014 (2)	−0.022 (2)
C18	0.045 (2)	0.076 (3)	0.077 (3)	0.026 (2)	−0.003 (2)	−0.005 (2)

Geometric parameters (Å, º)

Cu1—O2	1.874 (2)	C9—C10	1.470 (4)
Cu1—N1	1.907 (3)	C10—C11	1.399 (4)
Cu1—O3	1.936 (2)	C3—C4	1.398 (5)
Cu1—O5	1.948 (2)	C3—H3A	0.9300
Br1—C4	1.899 (4)	C13—C14	1.364 (6)
O2—C7	1.294 (4)	C13—C12	1.365 (6)
O3—C9	1.282 (4)	C13—H13A	0.9300
N1—C8	1.281 (4)	C11—C12	1.385 (5)
N1—N2	1.386 (3)	C12—H12A	0.9300
C8—C6	1.429 (4)	C14—H14A	0.9300
C8—H8A	0.9300	O5—C17	1.262 (4)
N2—C9	1.326 (4)	N3—C17	1.284 (4)
O4—C11	1.359 (4)	N3—C18	1.446 (5)
O4—H4A	0.8200	N3—C16	1.454 (5)
O1—C2	1.369 (4)	C17—H17A	0.9300
O1—C1	1.414 (4)	C16—H16A	0.9600
C7—C6	1.418 (4)	C16—H16B	0.9600
C7—C2	1.426 (4)	C16—H16C	0.9600
C5—C4	1.345 (5)	C1—H1A	0.9600
C5—C6	1.412 (5)	C1—H1B	0.9600
C5—H5A	0.9300	C1—H1C	0.9600
C2—C3	1.358 (5)	C18—H18A	0.9600
C15—C14	1.367 (5)	C18—H18B	0.9600
C15—C10	1.382 (5)	C18—H18C	0.9600
C15—H15A	0.9300		

O2—Cu1—N1	93.33 (10)	O4—C11—C12	117.5 (3)
O2—Cu1—O3	174.87 (9)	O4—C11—C10	122.6 (3)
N1—Cu1—O3	81.62 (10)	C12—C11—C10	119.8 (3)
O2—Cu1—O5	91.67 (10)	C5—C4—C3	122.0 (3)
N1—Cu1—O5	172.69 (11)	C5—C4—Br1	119.4 (3)
O3—Cu1—O5	93.28 (9)	C3—C4—Br1	118.7 (3)
C7—O2—Cu1	127.5 (2)	C13—C12—C11	120.0 (4)
C9—O3—Cu1	110.17 (19)	C13—C12—H12A	120.0
C8—N1—N2	118.0 (3)	C11—C12—H12A	120.0
C8—N1—Cu1	127.4 (2)	C5—C6—C7	119.7 (3)
N2—N1—Cu1	114.56 (19)	C5—C6—C8	117.7 (3)
N1—C8—C6	124.1 (3)	C7—C6—C8	122.6 (3)
N1—C8—H8A	118.0	C13—C14—C15	119.5 (4)
C6—C8—H8A	118.0	C13—C14—H14A	120.2

C9—N2—N1	109.4 (2)	C15—C14—H14A	120.2
C11—O4—H4A	109.5	C17—O5—Cu1	122.1 (2)
C2—O1—C1	118.4 (3)	C17—N3—C18	121.9 (3)
O2—C7—C6	124.4 (3)	C17—N3—C16	121.1 (3)
O2—C7—C2	118.6 (3)	C18—N3—C16	117.0 (3)
C6—C7—C2	117.0 (3)	O5—C17—N3	123.4 (3)
C4—C5—C6	120.2 (3)	O5—C17—H17A	118.3
C4—C5—H5A	119.9	N3—C17—H17A	118.3
C6—C5—H5A	119.9	N3—C16—H16A	109.5
C3—C2—O1	124.7 (3)	N3—C16—H16B	109.5
C3—C2—C7	122.2 (3)	H16A—C16—H16B	109.5
O1—C2—C7	113.1 (3)	N3—C16—H16C	109.5
C14—C15—C10	121.6 (3)	H16A—C16—H16C	109.5
C14—C15—H15A	119.2	H16B—C16—H16C	109.5
C10—C15—H15A	119.2	O1—C1—H1A	109.5
O3—C9—N2	123.8 (3)	O1—C1—H1B	109.5
O3—C9—C10	119.6 (3)	H1A—C1—H1B	109.5
N2—C9—C10	116.5 (3)	O1—C1—H1C	109.5
C15—C10—C11	118.0 (3)	H1A—C1—H1C	109.5
C15—C10—C9	119.2 (3)	H1B—C1—H1C	109.5
C11—C10—C9	122.8 (3)	N3—C18—H18A	109.5
C2—C3—C4	118.9 (3)	N3—C18—H18B	109.5
C2—C3—H3A	120.6	H18A—C18—H18B	109.5
C4—C3—H3A	120.6	N3—C18—H18C	109.5
C14—C13—C12	120.9 (4)	H18A—C18—H18C	109.5
C14—C13—H13A	119.6	H18B—C18—H18C	109.5
C12—C13—H13A	119.6		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···N2	0.82	1.84	2.566 (3)	146