

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis{2-methoxy-6-[(3-pyridyl)methyl-aminomethyl]phenolato}copper(II)

Yun Wang,^a Li-Li Zhu^a and Bai-Wang Sun^{b*}

^aDepartment of Chemistry, Key Laboratory of Medicinal Chemistry for Natural Resources, Ministry of Education, Yunnan University, Kunming 650091, People's Republic of China, and ^bOrdered Matter Science Research Center, College of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, People's Republic of China

Correspondence e-mail: chmsunbw@seu.edu.cn

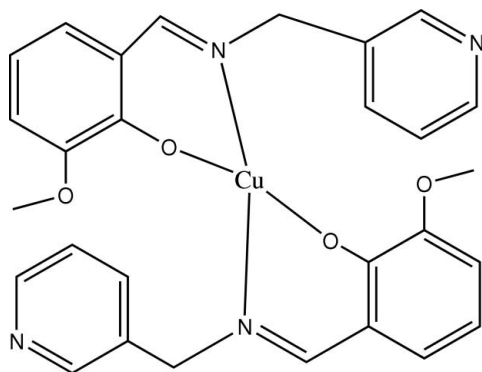
Received 12 July 2009; accepted 24 July 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.035; wR factor = 0.102; data-to-parameter ratio = 15.8.

In the mononuclear title complex, $[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2]$, the Cu^{II} atom lies on an inversion centre and adopts a square-planar coordination geometry. The dihedral angle formed by the pyridine and benzene rings is $74.61(5)^\circ$. Intramolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds are present. The crystal structure is stabilized by weak aromatic $\pi-\pi$ stacking interactions involving neighbouring pyridine rings [centroid-centroid distance = $3.853(2)$ Å].

Related literature

For a related structure, see: Wang *et al.* (2008). For the synthetic procedure, see: Kannappan *et al.* (2005); Zhao *et al.* (2008).



Experimental

Crystal data

$[\text{Cu}(\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}_2)_2]$
 $M_r = 546.07$
 Monoclinic, $P2_1/c$
 $a = 11.455(2)$ Å
 $b = 14.414(3)$ Å
 $c = 7.5491(15)$ Å
 $\beta = 102.55(3)^\circ$

$V = 1216.7(4)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.94$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\text{min}} = 0.824$, $T_{\text{max}} = 0.828$

11771 measured reflections
 2667 independent reflections
 2430 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.102$
 $S = 1.41$
 2667 reflections

169 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.62$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C9}-\text{H9B}\cdots\text{O2}^i$	0.97	2.28	2.862 (2)	118

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

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/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

This work was supported by the National Natural Science Foundation of China (project Nos. 20671019, 20361004) and the Doctoral Fund of the Ministry of Education of China (project No. 20060673015).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2354).

References

- Kannappan, R., Tanase, S., Mutikainen, I., Turpeinen, U. & Reedijk, J. (2005). *Inorg. Chim. Acta*, **358**, 383–388.
 Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Wang, X.-J., Jian, H.-X., Liu, Z.-P., Ni, Q.-L., Gui, L.-C. & Tang, L.-H. (2008). *Polyhedron*, **27**, 2634–2642.
 Zhao, Q.-H., Zhang, L., Du, L. & Fang, R.-B. (2008). *Acta Cryst.* **E64**, m142.

supporting information

Acta Cryst. (2009). E65, m1058 [doi:10.1107/S1600536809029523]

Bis{2-methoxy-6-[(3-pyridyl)methyliminomethyl]phenolato}copper(II)

Yun Wang, Li-Li Zhu and Bai-Wang Sun

S1. Comment

Schiff base metal complexes have been frequently investigated in the past several years, because of their broad range of properties and applications. We herein report the crystal structure of a new complex formed by reaction of $\text{Cu}(\text{CH}_3\text{COO})_2$ and the Schiff base ligand *N*-(3-pyridylmethyl)-3-methoxy-salicylaldiminato.

As shown in Fig. 1, the mononuclear title complex is centrosymmetric. The copper atom adopts a square planar coordination geometry provided by two *trans*-arranged phenolate-O and two imine-N atoms from two ligands (Wang *et al.*, 2008). The dihedral angle formed by the pyridine and benzene rings of the same ligand is 74.61 (5)°. An intramolecular C—H···O hydrogen bond (Table 1) stabilizes the molecular conformation. In the crystal structure, weak aromatic π – π stacking interactions involving neighbouring pyridine rings at (x, y, z) and (x, 5/2-y, 1/2+z) are present, with a centroid-to-centroid distance of 3.853 (2) Å.

S2. Experimental

All chemicals were of reagent grade and were used as received with out further purification. 2-Hydroxy-3-methoxy-benzaldehyde (0.152 g, 1 mmol) in ethanol (5 ml) was added to a stirred ethanol solution (5 ml) containing 3-amino-methylpyridine (0.108 g, 1 mmol). The resulting yellow solution was continuously stirred for about 1 h, then $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.100 g, 0.5 mmol) in ethanol (5 ml) was added. The resulting deep green solution was stirred for another 2 h and left to evaporate at room temperature (Kannappan *et al.*, 2005; Zhao *et al.*, 2008). After several days, dark green block crystals suitable for X-ray diffraction analysis were formed.

S3. Refinement

All H atoms were located geometrically and treated as riding atoms, with C—H = 0.93–0.97 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

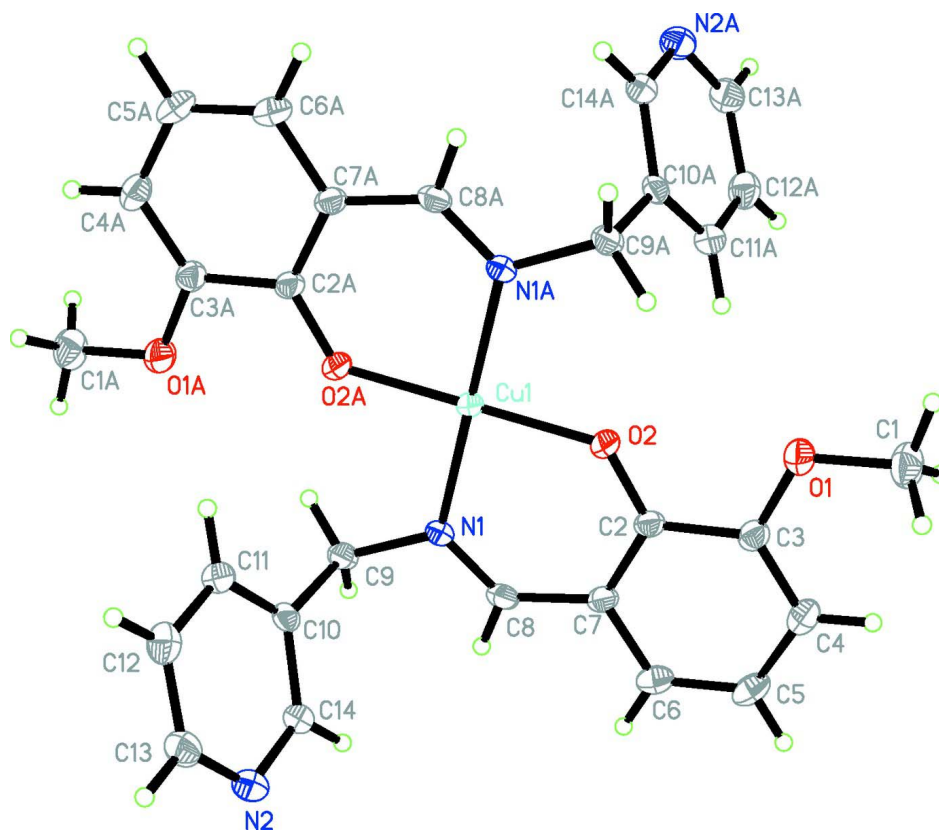


Figure 1

The molecular structure of the title compound with the atom-numbering scheme and all hydrogen atoms. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code A: 2 - x, -y, 1 - z]

Bis[2-methoxy-6-[(3-pyridyl)methyliminomethyl]phenolato]copper(II)

Crystal data

[Cu(C₁₄H₁₃N₂O₂)₂]

M_r = 546.07

Monoclinic, *P*2₁/*c*

Hall symbol: -P 2ybc

a = 11.455 (2) Å

b = 14.414 (3) Å

c = 7.5491 (15) Å

β = 102.55 (3)°

V = 1216.7 (4) Å³

Z = 2

F(000) = 566

D_x = 1.491 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 10382 reflections

θ = 3.2–27.5°

μ = 0.94 mm⁻¹

T = 293 K

Block, dark green

0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2005)

T_{min} = 0.824, *T_{max}* = 0.828

11771 measured reflections

2667 independent reflections

2430 reflections with *I* > 2σ(*I*)

R_{int} = 0.035

θ_{max} = 27.5°, θ_{min} = 3.1°

h = -14→14

k = -18→18

l = -9→9

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.102$
 $S = 1.41$
 2667 reflections
 169 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
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	1.0000	0.0000	0.03101 (13)
N1	0.94828 (11)	1.08186 (9)	-0.22373 (17)	0.0269 (3)
C14	1.04327 (16)	1.27619 (11)	-0.3538 (2)	0.0346 (4)
H14A	0.9670	1.2747	-0.4280	0.041*
C9	1.02998 (15)	1.10214 (10)	-0.3470 (2)	0.0307 (4)
H9A	0.9841	1.1069	-0.4708	0.037*
H9B	1.0867	1.0517	-0.3417	0.037*
C11	1.20928 (16)	1.19482 (12)	-0.1813 (2)	0.0359 (4)
H11A	1.2487	1.1403	-0.1375	0.043*
C7	0.74950 (13)	1.11896 (10)	-0.1721 (2)	0.0294 (4)
O1	0.67391 (12)	1.03058 (10)	0.23920 (19)	0.0457 (3)
C8	0.84437 (15)	1.11952 (11)	-0.2697 (2)	0.0308 (4)
H8A	0.8285	1.1511	-0.3798	0.037*
C10	1.09654 (14)	1.19174 (11)	-0.2930 (2)	0.0284 (3)
N2	1.09381 (14)	1.35872 (10)	-0.3131 (2)	0.0413 (4)
C3	0.65892 (13)	1.07713 (11)	0.0778 (2)	0.0315 (4)
C6	0.64554 (16)	1.17021 (12)	-0.2470 (3)	0.0380 (4)
H6A	0.6412	1.2022	-0.3552	0.046*
C4	0.55774 (15)	1.12611 (12)	0.0004 (3)	0.0379 (4)
H4A	0.4931	1.1278	0.0566	0.045*
C13	1.20181 (17)	1.35935 (13)	-0.2044 (3)	0.0416 (4)
H13A	1.2384	1.4164	-0.1730	0.050*
C5	0.55195 (16)	1.17370 (13)	-0.1642 (3)	0.0424 (5)
H5A	0.4839	1.2075	-0.2160	0.051*
C1	0.58255 (19)	1.03860 (17)	0.3375 (3)	0.0501 (5)

H1A	0.6037	1.0030	0.4473	0.075*
H1B	0.5088	1.0157	0.2651	0.075*
H1C	0.5731	1.1026	0.3670	0.075*
C12	1.26288 (17)	1.28035 (13)	-0.1354 (3)	0.0426 (4)
H12A	1.3385	1.2843	-0.0595	0.051*
O2	0.85152 (11)	1.02297 (9)	0.07153 (19)	0.0383 (3)
C2	0.75880 (13)	1.07128 (10)	-0.0065 (2)	0.0287 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02621 (19)	0.03057 (19)	0.0384 (2)	0.00818 (10)	0.01174 (14)	0.01467 (11)
N1	0.0288 (7)	0.0212 (6)	0.0311 (7)	-0.0008 (5)	0.0075 (6)	0.0041 (5)
C14	0.0332 (9)	0.0296 (8)	0.0420 (9)	0.0005 (7)	0.0106 (7)	0.0065 (7)
C9	0.0374 (8)	0.0259 (8)	0.0310 (8)	0.0015 (7)	0.0123 (7)	0.0027 (6)
C11	0.0352 (9)	0.0339 (9)	0.0398 (10)	0.0047 (7)	0.0110 (8)	0.0057 (7)
C7	0.0267 (8)	0.0229 (7)	0.0368 (9)	0.0024 (6)	0.0028 (7)	0.0022 (6)
O1	0.0404 (8)	0.0547 (8)	0.0475 (8)	0.0114 (7)	0.0217 (7)	0.0147 (7)
C8	0.0350 (9)	0.0236 (8)	0.0326 (8)	-0.0014 (6)	0.0045 (7)	0.0069 (6)
C10	0.0329 (8)	0.0273 (8)	0.0290 (8)	0.0006 (6)	0.0155 (7)	0.0042 (6)
N2	0.0434 (9)	0.0280 (7)	0.0529 (10)	-0.0011 (6)	0.0119 (8)	0.0028 (7)
C3	0.0287 (8)	0.0272 (8)	0.0388 (9)	0.0008 (6)	0.0076 (7)	-0.0020 (7)
C6	0.0384 (9)	0.0342 (9)	0.0377 (9)	0.0084 (7)	0.0001 (8)	0.0054 (7)
C4	0.0291 (9)	0.0381 (9)	0.0466 (10)	0.0035 (7)	0.0085 (8)	-0.0074 (8)
C13	0.0438 (11)	0.0318 (9)	0.0498 (11)	-0.0056 (8)	0.0116 (9)	-0.0027 (8)
C5	0.0311 (9)	0.0437 (10)	0.0480 (11)	0.0134 (8)	-0.0014 (8)	0.0001 (8)
C1	0.0476 (12)	0.0642 (13)	0.0443 (11)	0.0038 (10)	0.0229 (10)	-0.0025 (10)
C12	0.0336 (9)	0.0505 (11)	0.0433 (10)	-0.0040 (8)	0.0074 (8)	-0.0022 (8)
O2	0.0295 (7)	0.0430 (6)	0.0452 (7)	0.0136 (5)	0.0144 (6)	0.0194 (6)
C2	0.0264 (8)	0.0213 (7)	0.0375 (9)	0.0016 (6)	0.0051 (7)	0.0017 (6)

Geometric parameters (Å, °)

Cu1—O2 ⁱ	1.9218 (13)	O1—C3	1.369 (2)
Cu1—O2	1.9218 (13)	O1—C1	1.413 (2)
Cu1—N1	2.0399 (13)	C8—H8A	0.9300
Cu1—N1 ⁱ	2.0399 (13)	N2—C13	1.328 (2)
N1—C8	1.285 (2)	C3—C4	1.374 (2)
N1—C9	1.485 (2)	C3—C2	1.427 (2)
C14—N2	1.329 (2)	C6—C5	1.354 (3)
C14—C10	1.394 (2)	C6—H6A	0.9300
C14—H14A	0.9300	C4—C5	1.408 (3)
C9—C10	1.510 (2)	C4—H4A	0.9300
C9—H9A	0.9700	C13—C12	1.378 (3)
C9—H9B	0.9700	C13—H13A	0.9300
C11—C10	1.381 (2)	C5—H5A	0.9300
C11—C12	1.387 (2)	C1—H1A	0.9600
C11—H11A	0.9300	C1—H1B	0.9600

C7—C6	1.411 (2)	C1—H1C	0.9600
C7—C2	1.411 (2)	C12—H12A	0.9300
C7—C8	1.439 (2)	O2—C2	1.2993 (18)
O2 ⁱ —Cu1—O2	180.0	C14—C10—C9	119.92 (15)
O2 ⁱ —Cu1—N1	89.00 (6)	C13—N2—C14	116.70 (16)
O2—Cu1—N1	91.00 (6)	O1—C3—C4	124.16 (16)
O2 ⁱ —Cu1—N1 ⁱ	91.00 (6)	O1—C3—C2	114.21 (14)
O2—Cu1—N1 ⁱ	89.00 (6)	C4—C3—C2	121.63 (16)
N1—Cu1—N1 ⁱ	180.00 (6)	C5—C6—C7	121.24 (17)
C8—N1—C9	114.85 (13)	C5—C6—H6A	119.4
C8—N1—Cu1	123.58 (12)	C7—C6—H6A	119.4
C9—N1—Cu1	121.57 (10)	C3—C4—C5	119.95 (17)
N2—C14—C10	124.60 (17)	C3—C4—H4A	120.0
N2—C14—H14A	117.7	C5—C4—H4A	120.0
C10—C14—H14A	117.7	N2—C13—C12	123.81 (17)
N1—C9—C10	110.44 (12)	N2—C13—H13A	118.1
N1—C9—H9A	109.6	C12—C13—H13A	118.1
C10—C9—H9A	109.6	C6—C5—C4	119.92 (16)
N1—C9—H9B	109.6	C6—C5—H5A	120.0
C10—C9—H9B	109.6	C4—C5—H5A	120.0
H9A—C9—H9B	108.1	O1—C1—H1A	109.5
C10—C11—C12	119.04 (16)	O1—C1—H1B	109.5
C10—C11—H11A	120.5	H1A—C1—H1B	109.5
C12—C11—H11A	120.5	O1—C1—H1C	109.5
C6—C7—C2	120.31 (16)	H1A—C1—H1C	109.5
C6—C7—C8	117.23 (15)	H1B—C1—H1C	109.5
C2—C7—C8	122.44 (14)	C13—C12—C11	118.62 (17)
C3—O1—C1	117.61 (15)	C13—C12—H12A	120.7
N1—C8—C7	128.12 (15)	C11—C12—H12A	120.7
N1—C8—H8A	115.9	C2—O2—Cu1	130.63 (12)
C7—C8—H8A	115.9	O2—C2—C7	124.05 (15)
C11—C10—C14	117.21 (15)	O2—C2—C3	119.02 (15)
C11—C10—C9	122.86 (14)	C7—C2—C3	116.93 (14)
O2 ⁱ —Cu1—N1—C8	175.74 (14)	C8—C7—C6—C5	-179.88 (16)
O2—Cu1—N1—C8	-4.26 (14)	O1—C3—C4—C5	178.43 (17)
O2 ⁱ —Cu1—N1—C9	-4.15 (11)	C2—C3—C4—C5	-1.4 (3)
O2—Cu1—N1—C9	175.85 (11)	C14—N2—C13—C12	0.8 (3)
C8—N1—C9—C10	86.53 (17)	C7—C6—C5—C4	0.4 (3)
Cu1—N1—C9—C10	-93.57 (13)	C3—C4—C5—C6	0.8 (3)
C9—N1—C8—C7	-174.86 (15)	N2—C13—C12—C11	0.0 (3)
Cu1—N1—C8—C7	5.3 (2)	C10—C11—C12—C13	-0.5 (3)
C6—C7—C8—N1	176.48 (16)	N1—Cu1—O2—C2	1.65 (16)
C2—C7—C8—N1	-2.3 (3)	N1 ⁱ —Cu1—O2—C2	-178.35 (16)
C12—C11—C10—C14	0.2 (3)	Cu1—O2—C2—C7	0.5 (3)
C12—C11—C10—C9	-178.60 (16)	Cu1—O2—C2—C3	-179.78 (12)
N2—C14—C10—C11	0.7 (3)	C6—C7—C2—O2	-179.72 (16)

N2—C14—C10—C9	179.51 (16)	C8—C7—C2—O2	-1.0 (3)
N1—C9—C10—C11	94.88 (18)	C6—C7—C2—C3	0.5 (2)
N1—C9—C10—C14	-83.88 (18)	C8—C7—C2—C3	179.25 (14)
C10—C14—N2—C13	-1.1 (3)	O1—C3—C2—O2	1.1 (2)
C1—O1—C3—C4	-4.3 (3)	C4—C3—C2—O2	-179.07 (16)
C1—O1—C3—C2	175.52 (16)	O1—C3—C2—C7	-179.13 (14)
C2—C7—C6—C5	-1.1 (3)	C4—C3—C2—C7	0.7 (2)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C9—H9B \cdots O2 ⁱ	0.97	2.28	2.862 (2)	118

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