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# Bis(3,4-dimethoxybenzoato-$\kappa^2O,O'$)-(1,10-phenanthroline-$\kappa^2N,N'$)copper(II)

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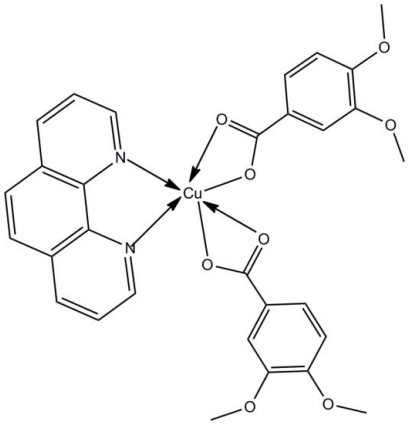
Key indicators: single-crystal X-ray study; $T$ = 273 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.030; $wR$ factor = 0.086; data-to-parameter ratio = 12.6.

The asymmetric unit of the title compound, $[Cu(C_9H_9O_4)_2(C_{12}H_8N_2)]$, contains one half-molecule, the complete molecule being generated by a twofold rotation axis. The $Cu^{II}$ atom exhibits a six-coordinated distorted octahedral geometry with two N atoms from the phenanthroline ligand [Cu—N 2.007 (2) Å] and four O atoms from two 3,4-dimethoxybenzoate ligands [Cu—O 1.950 (1) and 2.524 (1) Å]. The difference in Cu—O bond distances indicates a strong Jahn–Teller effect. In the crystal, C—H$\cdots\pi$ interactions result in chains of molecules along the $c$ axis.

## Related literature

For metal–1,10-phenanthroline complexes with unusual features, see: Ma *et al.* (2004); Bi *et al.* (2004).




## Experimental

### Crystal data

$[Cu(C_9H_9O_4)_2(C_{12}H_8N_2)]$
$M_r$ = 606.07
Monoclinic, $C2/c$
$a$ = 12.1639 (10) Å
$b$ = 11.4296 (9) Å
$c$ = 19.7470 (16) Å
$\beta$ = 104.027 (1)°
$V$ = 2663.5 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.88 mm$^{-1}$
$T$ = 273 K
0.23 × 0.21 × 0.19 mm

### Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.824, $T_{max}$ = 0.851
6857 measured reflections
2351 independent reflections
2136 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.059

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.086
$S$ = 1.01
2351 reflections
187 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 e Å$^{-3}$

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

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C8—H8$B\cdots Cg1$ | 0.96 | 2.98 | 3.642 (3) | 127 |

C1 is the centroid of the C22,C23,C29,C22′,C23′,C29′ ring.

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2194).

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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

*Acta Cryst.* (2010). E**66**, m34 [doi:10.1107/S1600536809052234]

## Bis(3,4-dimethoxybenzoato-$\kappa^2O,O'$)(1,10-phenanthroline-$\kappa^2N,N'$)copper(II)

**Yaru Liu, Junshan Sun and Xiaoli Niu**

### S1. Comment

Metal complexes with carboxylate ligands are among the most investigated complexes in the field of coordination chemistry. In addition, metal–1,10-phenanthroline complexes and their derivatives have attracted much attention during recent decades because of their unusual features (Ma *et al.*, 2004; Bi *et al.*, 2004). In this work, the title compound was obtained from the reaction of 3,4-dimethoxybenzoic acid and cupric acetate in the presence of 1,10-phenanthroline.

The molecular structure of the title complex is shown in Fig. 1. The Cu(II) atom exhibits a six-coordinated distorted octahedral geometry with two N atoms [Cu—N 2.007 (2) Å] from the phenanthroline ligand and four O atoms from the two 3,4-dimethoxybenzoate ligands [Cu—O 1.950 (1), 2.524 (1) Å]. The difference in Cu—O bond distances [Cu—O 1.950 (1), 2.524 (1) Å] indicates a strong Jahn-Teller effect. Two O atoms and two N atoms occupy the equatorial planar position with a slight deviation from the ideal plane of 0.0263 (2)Å, while two O atoms lie in the apical positions with an axis angle of 127.6 (2)° showing a large deviation from the normal 180°. A C8—H8b···$\pi$ interaction results in chains of molecules along the c-axis [H8b···CG1 2.979 (3) Å, where CG1 is the centroid of the C22, C23, C29, C22$^{i}$, C23$^{i}$, C29$^{i}$ ring; symmetry operator, i: -x, y, 0.5 - z].

### S2. Experimental

The reaction was carried out by the solvothermal method. 3,4-dimythoxybenzoic acid (0.121 g, 2 mmol), cupric acetate (0.199 g, 1 mmol) and 1,10-phenanthroline (0.180 g, 1 mmol) were added to the airtight vessel with a 1:2 ratio of ethanol to water. The resulting blue solution was filtered. The filtrate was left for several days at room temperature to yield blue, block-shaped crystals.

The yield was 78% and elemental analysis: calc. for $C_{30}H_{26}CuN_2O_8$: C 59.45, H 4.32, N 4.62; found: C 59.31, H 4.49, N 4.53. The elemental analyses were performed with a PERKIN ELMER MODEL 2400 SERIES II.

### S3. Refinement

The $U_{iso}$(H) values were set at 1.2$U_{eq}$(C—H) for the H atoms in the phenanthroline and aromatic ring, and 1.5$U_{eq}$(C—H) for the methyl moiety. As the diffraction intensities were of high quality, the The H atoms could be located in difference Fourier maps.

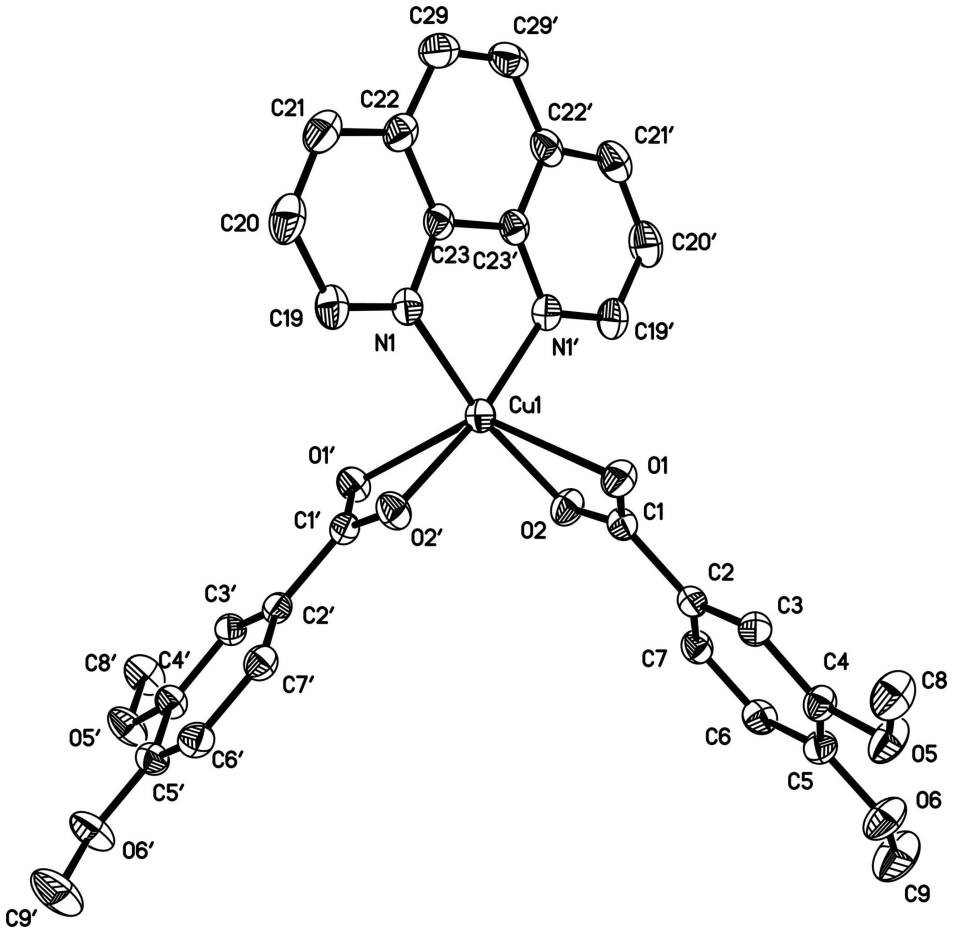


**Figure 1**

The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms. (Symmetry code: -*x*, *y*, 0.5 - *z*)

**Bis(3,4-dimethoxybenzoato-$\kappa^2O,O'$)(1,10-phenanthroline-$\kappa^2N,N'$)copper(II)**

*Crystal data*

$[Cu(C_9H_9O_4)_2(C_{12}H_8N_2)]$
$M_r$ = 606.07
Monoclinic, *C*2/*c*
*a* = 12.1639 (10) Å
*b* = 11.4296 (9) Å
*c* = 19.7470 (16) Å
$\beta$ = 104.027 (1)°
*V* = 2663.5 (4) Å$^3$
*Z* = 4
*F*(000) = 1252
$D_x$ = 1.511 Mg m$^{-3}$
Mo *K*$\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4483 reflections
$\theta$ = 2.5–28.3°
$\mu$ = 0.88 mm$^{-1}$
*T* = 273 K
Block, blue
0.23 × 0.21 × 0.19 mm

*Data collection*

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.824, $T_{max}$ = 0.851
6857 measured reflections
2351 independent reflections
2136 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.059
$\theta_{max}$ = 25.1°, $\theta_{min}$ = 2.1°
$h$ = −14→14
$k$ = −10→13
$l$ = −23→22

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.086
$S$ = 1.01
2351 reflections
187 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
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 1.2527P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 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 | 0.0000 | 0.96118 (3) | 0.2500 | 0.03588 (14) |
| O1 | 0.00052 (11) | 0.87873 (12) | 0.36863 (7) | 0.0437 (3) |
| O2 | 0.10961 (12) | 0.84452 (12) | 0.29637 (7) | 0.0445 (3) |
| O5 | 0.11674 (13) | 0.56453 (14) | 0.55593 (8) | 0.0539 (4) |
| O6 | 0.27611 (14) | 0.44980 (13) | 0.52542 (9) | 0.0592 (4) |
| N1 | −0.10829 (13) | 1.09400 (15) | 0.21869 (8) | 0.0389 (4) |
| C1 | 0.07772 (15) | 0.82281 (16) | 0.35206 (9) | 0.0364 (4) |
| C2 | 0.13570 (15) | 0.72454 (16) | 0.39696 (9) | 0.0341 (4) |
| C3 | 0.09898 (15) | 0.69411 (16) | 0.45613 (10) | 0.0365 (4) |
| H3 | 0.0407 | 0.7364 | 0.4676 | 0.044* |
| C4 | 0.14771 (16) | 0.60242 (17) | 0.49769 (10) | 0.0385 (4) |
| C5 | 0.23698 (17) | 0.53957 (16) | 0.48098 (11) | 0.0406 (5) |
| C6 | 0.27502 (16) | 0.57054 (18) | 0.42332 (11) | 0.0418 (5) |
| H6 | 0.3349 | 0.5300 | 0.4126 | 0.050* |
| C7 | 0.22402 (16) | 0.66243 (17) | 0.38092 (10) | 0.0389 (4) |
| H7 | 0.2493 | 0.6823 | 0.3416 | 0.047* |
| C8 | 0.0266 (2) | 0.6253 (2) | 0.57448 (12) | 0.0583 (6) |
| H8A | 0.0494 | 0.7045 | 0.5868 | 0.087* |
| H8B | 0.0079 | 0.5872 | 0.6135 | 0.087* |
| H8C | −0.0385 | 0.6255 | 0.5356 | 0.087* |
| C9 | 0.3730 (2) | 0.3888 (3) | 0.51835 (16) | 0.0801 (9) |
| H9A | 0.3578 | 0.3514 | 0.4735 | 0.120* |

| | | | | |
|---|---|---|---|---|
| H9B | 0.3926 | 0.3307 | 0.5544 | 0.120* |
| H9C | 0.4349 | 0.4426 | 0.5223 | 0.120* |
| C19 | −0.21817 (17) | 1.0896 (2) | 0.18725 (11) | 0.0482 (5) |
| H19 | −0.2525 | 1.0172 | 0.1756 | 0.058* |
| C20 | −0.28296 (19) | 1.1910 (2) | 0.17132 (12) | 0.0588 (6) |
| H20 | −0.3597 | 1.1854 | 0.1497 | 0.071* |
| C21 | −0.23515 (19) | 1.2974 (2) | 0.18712 (11) | 0.0547 (6) |
| H21 | −0.2793 | 1.3646 | 0.1774 | 0.066* |
| C22 | −0.11811 (18) | 1.30632 (18) | 0.21845 (10) | 0.0454 (5) |
| C23 | −0.05979 (16) | 1.20062 (17) | 0.23347 (9) | 0.0375 (4) |
| C29 | −0.0562 (2) | 1.41293 (19) | 0.23526 (11) | 0.0541 (6) |
| H29 | −0.0942 | 1.4839 | 0.2257 | 0.065* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0365 (2) | 0.0395 (2) | 0.0311 (2) | 0.000 | 0.00731 (14) | 0.000 |
| O1 | 0.0448 (7) | 0.0459 (8) | 0.0407 (7) | 0.0081 (6) | 0.0110 (6) | 0.0047 (6) |
| O2 | 0.0497 (8) | 0.0496 (8) | 0.0357 (7) | 0.0074 (6) | 0.0134 (6) | 0.0075 (6) |
| O5 | 0.0605 (9) | 0.0624 (9) | 0.0452 (8) | 0.0236 (7) | 0.0253 (7) | 0.0197 (7) |
| O6 | 0.0618 (10) | 0.0582 (10) | 0.0624 (10) | 0.0301 (8) | 0.0244 (8) | 0.0214 (8) |
| N1 | 0.0365 (8) | 0.0467 (9) | 0.0323 (8) | 0.0016 (7) | 0.0060 (7) | −0.0015 (7) |
| C1 | 0.0377 (9) | 0.0363 (10) | 0.0330 (9) | −0.0037 (8) | 0.0044 (8) | −0.0019 (8) |
| C2 | 0.0369 (9) | 0.0339 (9) | 0.0304 (9) | −0.0024 (8) | 0.0062 (7) | −0.0038 (8) |
| C3 | 0.0359 (9) | 0.0377 (10) | 0.0362 (10) | 0.0059 (8) | 0.0093 (8) | −0.0022 (8) |
| C4 | 0.0400 (10) | 0.0423 (11) | 0.0345 (10) | 0.0049 (8) | 0.0115 (8) | 0.0023 (8) |
| C5 | 0.0415 (10) | 0.0381 (11) | 0.0410 (11) | 0.0074 (8) | 0.0077 (9) | 0.0009 (8) |
| C6 | 0.0391 (10) | 0.0430 (10) | 0.0449 (11) | 0.0061 (8) | 0.0133 (9) | −0.0075 (9) |
| C7 | 0.0426 (10) | 0.0421 (10) | 0.0336 (9) | −0.0013 (8) | 0.0125 (8) | −0.0040 (8) |
| C8 | 0.0647 (14) | 0.0700 (15) | 0.0497 (12) | 0.0195 (12) | 0.0321 (11) | 0.0105 (11) |
| C9 | 0.0833 (19) | 0.0836 (19) | 0.0792 (18) | 0.0514 (16) | 0.0313 (15) | 0.0234 (15) |
| C19 | 0.0376 (10) | 0.0640 (13) | 0.0404 (11) | 0.0020 (10) | 0.0042 (9) | −0.0029 (10) |
| C20 | 0.0405 (11) | 0.0834 (18) | 0.0493 (13) | 0.0151 (12) | 0.0046 (10) | 0.0050 (12) |
| C21 | 0.0580 (13) | 0.0639 (15) | 0.0431 (12) | 0.0226 (12) | 0.0139 (10) | 0.0087 (11) |
| C22 | 0.0599 (12) | 0.0508 (12) | 0.0290 (9) | 0.0124 (10) | 0.0173 (9) | 0.0053 (9) |
| C23 | 0.0435 (10) | 0.0451 (11) | 0.0255 (9) | 0.0019 (8) | 0.0116 (8) | 0.0001 (8) |
| C29 | 0.0834 (15) | 0.0426 (11) | 0.0415 (12) | 0.0092 (11) | 0.0251 (11) | 0.0036 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—O2$^{i}$ | 1.950 (1) | C6—C7 | 1.392 (3) |
| Cu1—O2 | 1.950 (1) | C6—H6 | 0.9300 |
| Cu1—N1$^{i}$ | 2.007 (2) | C7—H7 | 0.9300 |
| Cu1—N1 | 2.007 (2) | C8—H8A | 0.9600 |
| Cu1—O1 | 2.524 (1) | C8—H8B | 0.9600 |
| O1—C1 | 1.244 (2) | C8—H8C | 0.9600 |
| O2—C1 | 1.276 (2) | C9—H9A | 0.9600 |
| O5—C4 | 1.365 (2) | C9—H9B | 0.9600 |

| | | | |
|---|---|---|---|
| O5—C8 | 1.419 (2) | C9—H9C | 0.9600 |
| O6—C5 | 1.359 (2) | C19—C20 | 1.394 (3) |
| O6—C9 | 1.406 (3) | C19—H19 | 0.9300 |
| N1—C19 | 1.331 (2) | C20—C21 | 1.351 (3) |
| N1—C23 | 1.355 (2) | C20—H20 | 0.9300 |
| C1—C2 | 1.497 (3) | C21—C22 | 1.412 (3) |
| C2—C7 | 1.387 (3) | C21—H21 | 0.9300 |
| C2—C3 | 1.392 (3) | C22—C23 | 1.396 (3) |
| C3—C4 | 1.374 (3) | C22—C29 | 1.429 (3) |
| C3—H3 | 0.9300 | C23—C23$^{i}$ | 1.443 (4) |
| C4—C5 | 1.406 (3) | C29—C29$^{i}$ | 1.350 (5) |
| C5—C6 | 1.375 (3) | C29—H29 | 0.9300 |

| | | | |
|---|---|---|---|
| O2$^{i}$—Cu1—O2 | 93.72 (9) | C7—C6—H6 | 119.9 |
| O2$^{i}$—Cu1—N1$^{i}$ | 170.07 (6) | C2—C7—C6 | 120.39 (18) |
| O2—Cu1—N1$^{i}$ | 92.84 (6) | C2—C7—H7 | 119.8 |
| O2$^{i}$—Cu1—N1 | 92.84 (6) | C6—C7—H7 | 119.8 |
| O2—Cu1—N1 | 170.07 (6) | O5—C8—H8A | 109.5 |
| N1$^{i}$—Cu1—N1 | 81.69 (9) | O5—C8—H8B | 109.5 |
| O2$^{i}$—Cu1—O1 | 91.61 (5) | H8A—C8—H8B | 109.5 |
| O2—Cu1—O1 | 57.40 (5) | O5—C8—H8C | 109.5 |
| N1$^{i}$—Cu1—O1 | 98.20 (5) | H8A—C8—H8C | 109.5 |
| N1—Cu1—O1 | 114.98 (5) | H8B—C8—H8C | 109.5 |
| C1—O1—Cu1 | 77.28 (11) | O6—C9—H9A | 109.5 |
| C1—O2—Cu1 | 102.80 (12) | O6—C9—H9B | 109.5 |
| C4—O5—C8 | 116.78 (15) | H9A—C9—H9B | 109.5 |
| C5—O6—C9 | 118.78 (19) | O6—C9—H9C | 109.5 |
| C19—N1—C23 | 118.06 (18) | H9A—C9—H9C | 109.5 |
| C19—N1—Cu1 | 128.66 (15) | H9B—C9—H9C | 109.5 |
| C23—N1—Cu1 | 113.28 (12) | N1—C19—C20 | 121.5 (2) |
| O1—C1—O2 | 122.24 (17) | N1—C19—H19 | 119.3 |
| O1—C1—C2 | 120.47 (17) | C20—C19—H19 | 119.3 |
| O2—C1—C2 | 117.28 (16) | C21—C20—C19 | 120.5 (2) |
| C7—C2—C3 | 119.18 (17) | C21—C20—H20 | 119.7 |
| C7—C2—C1 | 121.90 (17) | C19—C20—H20 | 119.7 |
| C3—C2—C1 | 118.91 (16) | C20—C21—C22 | 119.9 (2) |
| C4—C3—C2 | 120.81 (17) | C20—C21—H21 | 120.1 |
| C4—C3—H3 | 119.6 | C22—C21—H21 | 120.1 |
| C2—C3—H3 | 119.6 | C23—C22—C21 | 115.9 (2) |
| O5—C4—C3 | 125.33 (17) | C23—C22—C29 | 118.47 (19) |
| O5—C4—C5 | 114.98 (16) | C21—C22—C29 | 125.62 (19) |
| C3—C4—C5 | 119.69 (18) | N1—C23—C22 | 124.09 (17) |
| O6—C5—C6 | 126.41 (18) | N1—C23—C23$^{i}$ | 115.86 (10) |
| O6—C5—C4 | 113.81 (18) | C22—C23—C23$^{i}$ | 120.05 (12) |
| C6—C5—C4 | 119.77 (18) | C29$^{i}$—C29—C22 | 121.46 (12) |

| | | | |
|---|---|---|---|
| C5—C6—C7 | 120.13 (18) | C29$^{i}$—C29—H29 | 119.3 |
| C5—C6—H6 | 119.9 | C22—C29—H29 | 119.3 |

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

*Hydrogen-bond geometry (Å, º)*

C1 is the centroid of the C22,C23,C29,C22′,C23′,C29′ ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C8—H8*B*···*Cg*1 | 0.96 | 2.98 | 3.642 (3) | 127 |