

Tetrakis[2-[2-(2,6-dichloroanilino)-phenyl]ethanoato- $\kappa^2O:O'$]bis[(dimethyl sulfoxide- κO)copper(II)]($Cu-Cu$): a binuclear Cu^{II} complex with the non-steroidal anti-inflammatory drug diclofenac

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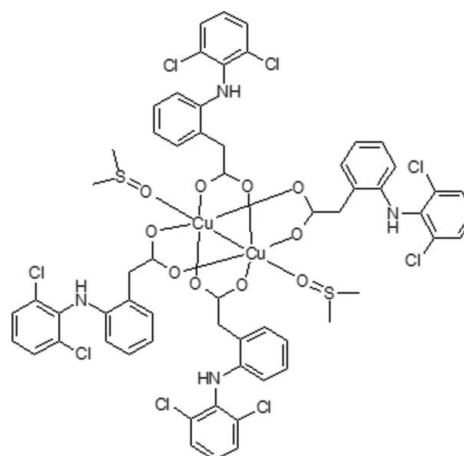
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(C-C) = 0.002$ Å; R factor = 0.031; wR factor = 0.079; data-to-parameter ratio = 27.3.

The title compound, $[Cu_2(C_{14}H_{10}Cl_2NO_2)_4(C_2H_6OS)_2]$, comprises a Cu_2^{II} core that is quadruply bridged by four carboxylate ligands with the dimethyl sulfoxide ligands binding along the $Cu \cdots Cu$ axis. The four carboxylate ligands bind in a bidentate *syn-syn* bridging mode. Molecules reside on crystallographic inversion centres bisecting the mid-point of the $Cu \cdots Cu$ axis. There are no intermolecular interactions of note.

Related literature

Cu^{II} complexes of non-steroidal anti-inflammatory drugs (NSAIDs) show enhanced anti-inflammatory activity and reduced gastrointestinal toxicity compared with their uncomplexed parent drug, see: Weder *et al.* (2002). The structure of the Cu -NSAID is likely to be an important factor for its biological activity. For example, the anti-tumor activity of the monomeric Cu^{II} complex of aspirin $[[Cu(Asp)_2(py)_2]]$ is reportedly more effective than the dimeric $[Cu_2(Asp)_4]$ complex, see: Oberley & Buettner (1979). It has been shown that dinuclear Cu -NSAID complexes exhibit similar biological activity to mononuclear complexes, but with higher stability (Dimiza *et al.*, 2011), making them relevant compounds in the treatment of tumor cell lines (Theodorou *et al.*, 1999). For mono- and binuclear Cu^{II} complexes of diclofenac, see: Sayen *et al.* (2012) for $[Cu(diclofenac)_2(H_2O)_2] \cdot 2H_2O$ and Kovala-Demertzi *et al.* (1997) for $[Cu_2(diclofenac)_4(DMF)_2]$.



Experimental

Crystal data

| | |
|--|-----------------------------------|
| $[Cu_2(C_{14}H_{10}Cl_2NO_2)_4(C_2H_6OS)_2]$ | $\gamma = 68.489$ (5)° |
| $M_r = 1463.90$ | $V = 1539.4$ (11) Å ³ |
| Triclinic, $P\bar{1}$ | $Z = 1$ |
| $a = 10.357$ (5) Å | Mo $K\alpha$ radiation |
| $b = 12.787$ (5) Å | $\mu = 1.17$ mm ⁻¹ |
| $c = 12.925$ (5) Å | $T = 100$ K |
| $\alpha = 81.605$ (5)° | $0.30 \times 0.21 \times 0.18$ mm |
| $\beta = 75.561$ (5)° | |

Data collection

| | |
|---|--|
| Oxford Diffraction SuperNova Atlas diffractometer | 42084 measured reflections |
| Absorption correction: multi-scan (ABSPACK; Oxford Diffraction, 2010) | 10796 independent reflections |
| $T_{min} = 0.867$, $T_{max} = 1.000$ | 9113 reflections with $I > 2\sigma(I)$ |
| | $R_{int} = 0.030$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.031$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.079$ | $\Delta\rho_{max} = 0.71$ e Å ⁻³ |
| $S = 0.99$ | $\Delta\rho_{min} = -0.51$ e Å ⁻³ |
| 10796 reflections | |
| 396 parameters | |
| 1 restraint | |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-------------|-------------|--------------------------|-------------|
| Cu1—O2 | 1.9647 (11) | Cu1—O1' | 1.9799 (11) |
| Cu1—O1 | 1.9655 (11) | Cu1—O1D | 2.1344 (14) |
| Cu1—O2' | 1.9725 (11) | Cu1—Cu1 ⁱ | 2.6619 (12) |
| O2—Cu1—O1 | 86.92 (5) | O2'—Cu1—O1D | 95.06 (4) |
| O2—Cu1—O2' | 167.83 (4) | O1'—Cu1—O1D | 98.06 (4) |
| O1—Cu1—O2' | 92.47 (6) | O2—Cu1—Cu1 ⁱ | 86.45 (4) |
| O2—Cu1—O1' | 90.59 (5) | O1—Cu1—Cu1 ⁱ | 85.35 (3) |
| O1—Cu1—O1' | 167.60 (4) | O2'—Cu1—Cu1 ⁱ | 81.39 (4) |
| O2'—Cu1—O1' | 87.41 (6) | O1'—Cu1—Cu1 ⁱ | 82.36 (3) |
| O2—Cu1—O1D | 97.11 (5) | O1D—Cu1—Cu1 ⁱ | 176.41 (3) |
| O1—Cu1—O1D | 94.31 (4) | | |

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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: *SHELXL97*.

Dr S. Chevreux and Professor E. Wenger are gratefully acknowledged for the crystal structure determination.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG2076).

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supporting information

Acta Cryst. (2012). E68, m474–m475 [https://doi.org/10.1107/S160053681201152X]

Tetrakis{2-[2-(2,6-dichloroanilino)phenyl]ethanoato- κ^2 O:O'}bis[(dimethyl sulfoxide- κ O)copper(II)](Cu—Cu): a binuclear Cu^{II} complex with the non-steroidal anti-inflammatory drug diclofenac

Stéphanie Sayen and Emmanuel Guillon

S1. Comment

The proposed curative properties of Cu-based non-steroidal anti-inflammatory drugs (NSAIDs) have led to the development of numerous Cu(II) complexes of NSAIDs with enhanced anti-inflammatory activity and reduced gastrointestinal toxicity compared with their uncomplexed parent drug (Weder *et al.*, 2002). Furthermore, little is known of their pharmacokinetic and biodistribution profile in both humans and animals, stability in biological media, or of the relative potency/efficacy of the Cu^{II} monomeric *versus* Cu^{II} dimeric complexes. The structure of the Cu-NSAID is likely to be an important factor for its biological activity. For example, the anti-tumor activity of the monomeric Cu^{II} complex of aspirin ([Cu(Asp)₂(py)₂]) is reportedly more effective than the dimeric [Cu₂(Asp)₄] complex (Oberley & Buettner, 1979). Thus, it appears to be essential to obtain structural information on Cu^(II) complexes of NSAIDs in order to fully understand their biological activity. Being able to act as a ligand through its carboxylate function of the aromatic ring, different diclofenac complexes (Cu-NSAID complex) were described in the literature. It gives rise to a mononuclear [Cu(diclofenac)₂(H₂O)₂].2H₂O complex (Sayen *et al.*, 2012) and a binuclear [Cu₂(diclofenac)₄(DMF)₂] complex without a metal-metal bond (Kovala-Demertzi *et al.*, 1997). The former resulted in a distorted octahedral geometry, whereas the latter resulted in a binuclear copper complex where each metal centre is described as a perfect square bipyramid with a DMF oxygen occupying apical position. In order to favour the metal...metal bond, which stabilizes the complex and thus impact the biological activity, we have tried various coordinating solvents during the recrystallization.

The structure of the binuclear [bis(2-[2-(2,6-dichlorophenyl)aminophenyl]ethanoate)bis(DMSO)copper(II)] complex (I) has been obtained. It consists of a quadruply bridged neutral molecule lying on a crystallographic centre of inversion (Fig. 1). Indeed, the four carboxylato moieties act as bridging ligands exhibiting a centre of symmetry midway between the two Cu atoms. The solvent used in the synthesis binds in the position *trans* to the Cu—Cu axis. The dimeric structure has a Cu—Cu distance of 2.6619 (12) Å, with an octahedral stereochemistry tetragonally elongated along the Cu—Cu-O_{solvent} axis due to the Jahn-Teller effect (Table 1).

In the binuclear unit, the carboxylic acids are fully deprotonated to balance the charge from the Cu^{II} ions. The stability of the structure is ensured *via* a network of /p.../p interactions involving the phenyl acetate rings of the diclofenac molecules. On the other hand, no intermolecular H-bonding is observed (Fig. 2).

The use of DMSO solvent allowed the formation of a binuclear complex with a Cu₂ metal core, which stabilizes the complex in biological media. It was shown that binuclear Cu-NSAID complexes exhibit similar biological activity as the mononuclear complex, but with a higher stability (Dimiza *et al.*, 2011), making them relevant compounds in the treatment of tumor cell lines (Theodorou *et al.*, 1999).

S2. Experimental

The [bis(2-[2-(2,6-dichlorophenyl)aminophenyl]ethanoate)bis(DMSO)copper(II)] was prepared from a mixture of copper sulfate and diclofenac sodium salt in the molar ratio 1:2 in deionized water. After stirring for 2 hrs at room temperature, the reaction mixture was filtered and the green precipitate was washed with water and dried in air. Crystals suitable for X-ray diffraction measurements were obtained by slow evaporation of a DMSO solution of the complex.

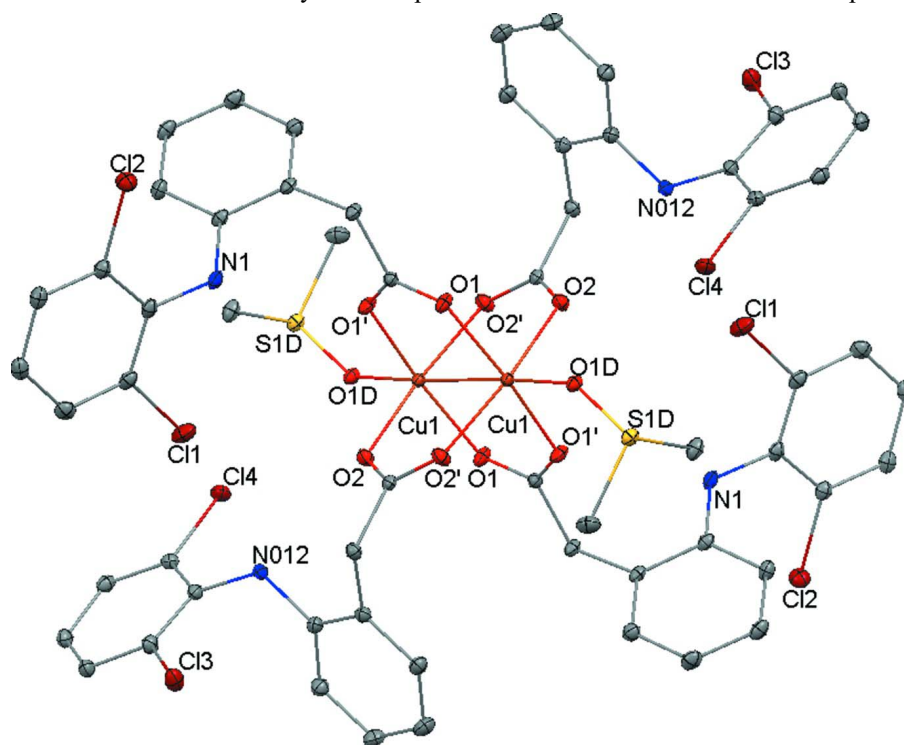


Figure 1

A representation of the title compound (I) with displacement ellipsoids at the 30% probability level.

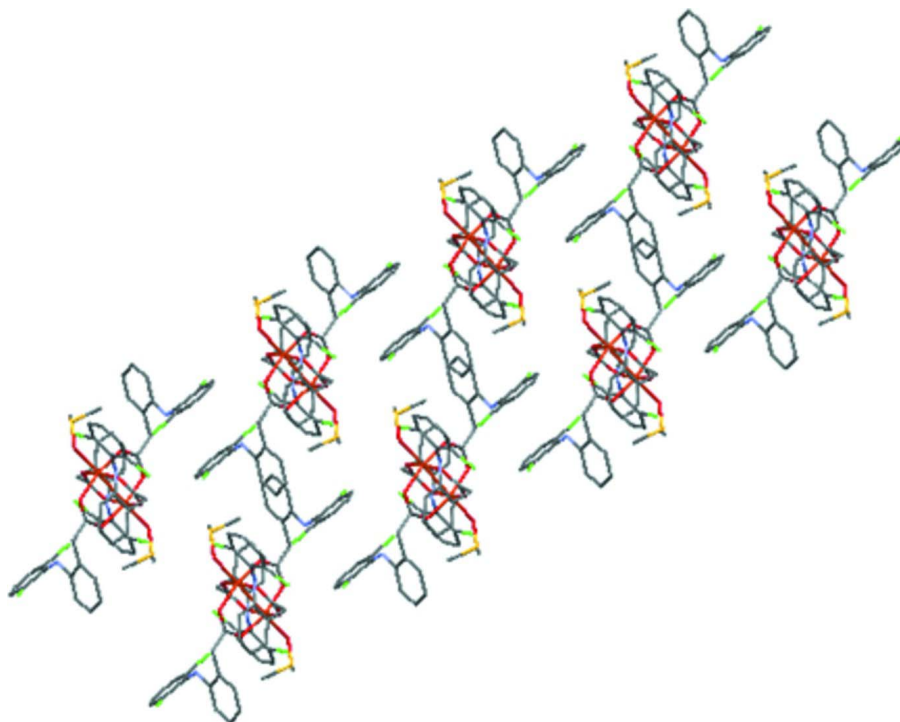


Figure 2

The $\pi \cdots \pi$ stacking interactions in the $[\text{Cu}_2(\text{diclofenac})_4(\text{DMSO})_2]$ complex (H atoms are omitted for clarity).

Tetrakis[2-[2-(2,6-dichloroanilino)phenyl]ethanoato- $\kappa^2\text{O}:\text{O}'$]bis[(dimethyl sulfoxide- κO)copper(II)]($\text{Cu}-\text{Cu}$)

Crystal data

$[\text{Cu}_2(\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NO}_2)_4(\text{C}_2\text{H}_6\text{OS})_2]$

$M_r = 1463.90$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 10.357(5) \text{ \AA}$

$b = 12.787(5) \text{ \AA}$

$c = 12.925(5) \text{ \AA}$

$\alpha = 81.605(5)^\circ$

$\beta = 75.561(5)^\circ$

$\gamma = 68.489(5)^\circ$

$V = 1539.4(11) \text{ \AA}^3$

$Z = 1$

$F(000) = 746$

$D_x = 1.579 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 19895 reflections

$\theta = 3.0\text{--}33.3^\circ$

$\mu = 1.17 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Prismatic, green

$0.30 \times 0.21 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction SuperNova Atlas
diffractometer

Radiation source: SuperNova (Mo) X-ray
Source

Mirror monochromator

Detector resolution: $10.4508 \text{ pixels mm}^{-1}$

CCD scans

Absorption correction: multi-scan

(ABSPACK; Oxford Diffraction, 2010)

$T_{\min} = 0.867$, $T_{\max} = 1.000$

42084 measured reflections

10796 independent reflections

9113 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 33.4^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -15 \rightarrow 15$

$k = -18 \rightarrow 19$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.079$
 $S = 0.99$
 10796 reflections
 396 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.9652P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.012$
 $\Delta\rho_{\max} = 0.71 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$

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 | 0.120933 (16) | 0.021416 (13) | 0.473791 (12) | 0.01201 (4) |
| Cl3 | -0.08018 (4) | 0.53916 (3) | 0.12807 (3) | 0.02570 (8) |
| Cl2 | -0.24985 (4) | 0.22114 (3) | 1.09549 (3) | 0.02408 (7) |
| S1D | 0.46463 (3) | -0.01303 (3) | 0.37338 (3) | 0.01652 (7) |
| Cl4 | 0.36720 (4) | 0.26927 (3) | 0.29584 (3) | 0.02399 (8) |
| Cl1 | -0.13597 (4) | -0.16032 (3) | 0.90149 (3) | 0.02907 (9) |
| O2 | 0.02500 (10) | 0.14887 (8) | 0.38286 (8) | 0.01807 (19) |
| O1D | 0.31958 (10) | 0.04789 (8) | 0.43929 (8) | 0.01638 (18) |
| O1 | 0.03591 (10) | 0.12257 (9) | 0.59225 (8) | 0.0190 (2) |
| O1' | 0.16521 (11) | -0.08291 (9) | 0.36053 (8) | 0.0197 (2) |
| O2' | 0.17899 (11) | -0.11273 (9) | 0.57158 (9) | 0.0205 (2) |
| N012 | 0.05900 (13) | 0.35894 (10) | 0.27795 (10) | 0.0178 (2) |
| H012 | 0.097 (2) | 0.2948 (17) | 0.2976 (15) | 0.021* |
| C14 | -0.21991 (14) | 0.07801 (12) | 1.10092 (11) | 0.0177 (2) |
| C28 | -0.06437 (14) | 0.42098 (11) | 0.35062 (11) | 0.0169 (2) |
| C8 | -0.31758 (14) | 0.17788 (12) | 0.88170 (10) | 0.0159 (2) |
| N1 | -0.19748 (13) | 0.08795 (11) | 0.90651 (10) | 0.0205 (2) |
| H1 | -0.153 (2) | 0.0471 (17) | 0.8576 (16) | 0.025* |
| C31 | 0.17566 (15) | 0.56327 (12) | 0.07734 (12) | 0.0199 (3) |
| H31 | 0.1352 | 0.6248 | 0.0308 | 0.024* |
| C13 | -0.21504 (15) | 0.01805 (13) | 1.19914 (11) | 0.0199 (3) |
| H13 | -0.2323 | 0.0557 | 1.2620 | 0.024* |
| C27 | -0.07237 (16) | 0.51895 (12) | 0.39113 (12) | 0.0205 (3) |
| H27 | 0.0052 | 0.5456 | 0.3691 | 0.025* |

| | | | | |
|------|---------------|---------------|--------------|------------|
| C2 | -0.15089 (14) | 0.23216 (12) | 0.72217 (11) | 0.0162 (2) |
| H2A | -0.0860 | 0.2187 | 0.7713 | 0.019* |
| H2B | -0.1537 | 0.3038 | 0.6800 | 0.019* |
| C9 | -0.19799 (14) | 0.02709 (12) | 1.00581 (11) | 0.0176 (3) |
| C1 | -0.08847 (14) | 0.13770 (11) | 0.64569 (10) | 0.0136 (2) |
| C30 | 0.09412 (15) | 0.50313 (12) | 0.14053 (11) | 0.0187 (3) |
| C1D | 0.44047 (16) | -0.01951 (14) | 0.24247 (11) | 0.0219 (3) |
| H02A | 0.3665 | -0.0520 | 0.2481 | 0.033* |
| H02B | 0.5298 | -0.0667 | 0.1995 | 0.033* |
| H02C | 0.4118 | 0.0566 | 0.2080 | 0.033* |
| C5 | -0.55113 (15) | 0.35002 (13) | 0.82325 (12) | 0.0232 (3) |
| H5 | -0.6306 | 0.4077 | 0.8023 | 0.028* |
| C12 | -0.18466 (15) | -0.09755 (14) | 1.20482 (12) | 0.0221 (3) |
| H12 | -0.1810 | -0.1394 | 1.2718 | 0.026* |
| C11 | -0.15969 (15) | -0.15203 (13) | 1.11267 (13) | 0.0223 (3) |
| H11 | -0.1375 | -0.2313 | 1.1161 | 0.027* |
| C7 | -0.45321 (15) | 0.19793 (13) | 0.94636 (11) | 0.0190 (3) |
| H7 | -0.4663 | 0.1523 | 1.0103 | 0.023* |
| C6 | -0.56910 (15) | 0.28436 (13) | 0.91755 (12) | 0.0216 (3) |
| H6 | -0.6609 | 0.2986 | 0.9625 | 0.026* |
| C2D | 0.50562 (18) | -0.15937 (13) | 0.41473 (14) | 0.0281 (3) |
| H03A | 0.5213 | -0.1717 | 0.4879 | 0.042* |
| H03B | 0.5917 | -0.2037 | 0.3665 | 0.042* |
| H03C | 0.4263 | -0.1828 | 0.4124 | 0.042* |
| C4 | -0.41565 (15) | 0.33051 (12) | 0.75986 (12) | 0.0198 (3) |
| H4 | -0.4034 | 0.3757 | 0.6955 | 0.024* |
| C26 | -0.19259 (16) | 0.57789 (13) | 0.46336 (12) | 0.0227 (3) |
| H26 | -0.1974 | 0.6449 | 0.4900 | 0.027* |
| C22 | -0.17896 (14) | 0.28408 (11) | 0.32842 (11) | 0.0162 (2) |
| H22A | -0.1299 | 0.2857 | 0.2522 | 0.019* |
| H22B | -0.2780 | 0.2907 | 0.3311 | 0.019* |
| C32 | 0.31703 (15) | 0.53252 (12) | 0.08282 (12) | 0.0205 (3) |
| H32 | 0.3734 | 0.5742 | 0.0412 | 0.025* |
| C10 | -0.16740 (15) | -0.09000 (13) | 1.01577 (11) | 0.0196 (3) |
| C21 | -0.10505 (14) | 0.17246 (11) | 0.38384 (10) | 0.0142 (2) |
| C23 | -0.17988 (14) | 0.38320 (11) | 0.37996 (11) | 0.0159 (2) |
| C3 | -0.29740 (14) | 0.24632 (11) | 0.78848 (10) | 0.0151 (2) |
| C24 | -0.29898 (15) | 0.44231 (12) | 0.45452 (12) | 0.0201 (3) |
| H24 | -0.3769 | 0.4160 | 0.4769 | 0.024* |
| C25 | -0.30575 (16) | 0.53873 (13) | 0.49652 (13) | 0.0243 (3) |
| H25 | -0.3872 | 0.5775 | 0.5475 | 0.029* |
| C33 | 0.37580 (15) | 0.44104 (12) | 0.14897 (12) | 0.0196 (3) |
| H33 | 0.4735 | 0.4179 | 0.1507 | 0.024* |
| C34 | 0.29167 (14) | 0.38323 (11) | 0.21269 (11) | 0.0167 (2) |
| C29 | 0.14713 (14) | 0.41375 (11) | 0.21268 (11) | 0.0163 (2) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|--------------|--------------|--------------|---------------|---------------|---------------|
| Cu1 | 0.01134 (7) | 0.01206 (8) | 0.01214 (7) | -0.00424 (6) | -0.00065 (5) | -0.00190 (5) |
| Cl3 | 0.01649 (15) | 0.03093 (19) | 0.02816 (18) | -0.00870 (14) | -0.00621 (13) | 0.00686 (14) |
| Cl2 | 0.02819 (18) | 0.02315 (17) | 0.02436 (16) | -0.01136 (14) | -0.00732 (14) | -0.00237 (13) |
| S1D | 0.01188 (14) | 0.01976 (16) | 0.01874 (15) | -0.00561 (12) | -0.00296 (11) | -0.00384 (12) |
| Cl4 | 0.02377 (17) | 0.01794 (16) | 0.02430 (16) | -0.00113 (13) | -0.00500 (13) | 0.00066 (12) |
| Cl1 | 0.02692 (18) | 0.02932 (19) | 0.02732 (18) | -0.00156 (15) | -0.00549 (14) | -0.01270 (15) |
| O2 | 0.0154 (4) | 0.0174 (5) | 0.0202 (5) | -0.0061 (4) | -0.0037 (4) | 0.0033 (4) |
| O1D | 0.0130 (4) | 0.0179 (5) | 0.0176 (4) | -0.0055 (4) | -0.0002 (3) | -0.0039 (4) |
| O1 | 0.0154 (4) | 0.0255 (5) | 0.0171 (4) | -0.0091 (4) | 0.0031 (4) | -0.0097 (4) |
| O1' | 0.0168 (5) | 0.0198 (5) | 0.0232 (5) | -0.0089 (4) | 0.0040 (4) | -0.0112 (4) |
| O2' | 0.0176 (5) | 0.0186 (5) | 0.0256 (5) | -0.0086 (4) | -0.0057 (4) | 0.0057 (4) |
| N012 | 0.0174 (5) | 0.0128 (5) | 0.0200 (5) | -0.0058 (4) | 0.0018 (4) | 0.0003 (4) |
| C14 | 0.0140 (6) | 0.0215 (7) | 0.0176 (6) | -0.0060 (5) | -0.0030 (5) | -0.0018 (5) |
| C28 | 0.0164 (6) | 0.0154 (6) | 0.0163 (6) | -0.0046 (5) | -0.0010 (5) | -0.0003 (5) |
| C8 | 0.0138 (6) | 0.0196 (6) | 0.0139 (5) | -0.0041 (5) | -0.0031 (4) | -0.0048 (5) |
| N1 | 0.0152 (5) | 0.0249 (6) | 0.0139 (5) | -0.0001 (5) | 0.0005 (4) | -0.0023 (4) |
| C31 | 0.0186 (6) | 0.0176 (6) | 0.0207 (6) | -0.0060 (5) | -0.0012 (5) | 0.0019 (5) |
| C13 | 0.0152 (6) | 0.0294 (7) | 0.0163 (6) | -0.0087 (5) | -0.0040 (5) | -0.0014 (5) |
| C27 | 0.0205 (6) | 0.0192 (7) | 0.0220 (6) | -0.0080 (5) | -0.0023 (5) | -0.0026 (5) |
| C2 | 0.0149 (6) | 0.0175 (6) | 0.0167 (6) | -0.0064 (5) | -0.0002 (5) | -0.0062 (5) |
| C9 | 0.0116 (5) | 0.0231 (7) | 0.0159 (6) | -0.0038 (5) | -0.0016 (5) | -0.0019 (5) |
| C1 | 0.0139 (5) | 0.0135 (6) | 0.0123 (5) | -0.0031 (4) | -0.0028 (4) | -0.0013 (4) |
| C30 | 0.0150 (6) | 0.0198 (6) | 0.0206 (6) | -0.0070 (5) | -0.0021 (5) | 0.0000 (5) |
| C1D | 0.0190 (6) | 0.0308 (8) | 0.0181 (6) | -0.0108 (6) | -0.0015 (5) | -0.0066 (5) |
| C5 | 0.0145 (6) | 0.0254 (7) | 0.0257 (7) | -0.0015 (5) | -0.0044 (5) | -0.0035 (6) |
| C12 | 0.0150 (6) | 0.0296 (8) | 0.0202 (6) | -0.0072 (5) | -0.0059 (5) | 0.0051 (6) |
| C11 | 0.0152 (6) | 0.0213 (7) | 0.0279 (7) | -0.0035 (5) | -0.0062 (5) | 0.0012 (6) |
| C7 | 0.0157 (6) | 0.0244 (7) | 0.0157 (6) | -0.0066 (5) | -0.0005 (5) | -0.0033 (5) |
| C6 | 0.0124 (6) | 0.0288 (8) | 0.0220 (6) | -0.0053 (5) | -0.0005 (5) | -0.0074 (6) |
| C2D | 0.0259 (8) | 0.0193 (7) | 0.0342 (8) | -0.0007 (6) | -0.0085 (6) | -0.0017 (6) |
| C4 | 0.0181 (6) | 0.0197 (6) | 0.0196 (6) | -0.0043 (5) | -0.0032 (5) | -0.0025 (5) |
| C26 | 0.0226 (7) | 0.0181 (7) | 0.0260 (7) | -0.0040 (5) | -0.0040 (6) | -0.0069 (5) |
| C22 | 0.0162 (6) | 0.0161 (6) | 0.0163 (6) | -0.0055 (5) | -0.0050 (5) | 0.0013 (5) |
| C32 | 0.0190 (6) | 0.0197 (7) | 0.0217 (6) | -0.0091 (5) | 0.0017 (5) | -0.0015 (5) |
| C10 | 0.0141 (6) | 0.0226 (7) | 0.0196 (6) | -0.0023 (5) | -0.0032 (5) | -0.0052 (5) |
| C21 | 0.0156 (6) | 0.0143 (6) | 0.0116 (5) | -0.0044 (5) | -0.0015 (4) | -0.0024 (4) |
| C23 | 0.0157 (6) | 0.0142 (6) | 0.0168 (6) | -0.0041 (5) | -0.0037 (5) | 0.0002 (4) |
| C3 | 0.0132 (5) | 0.0170 (6) | 0.0153 (5) | -0.0049 (5) | -0.0006 (4) | -0.0068 (4) |
| C24 | 0.0148 (6) | 0.0210 (7) | 0.0220 (6) | -0.0043 (5) | -0.0015 (5) | -0.0022 (5) |
| C25 | 0.0183 (7) | 0.0240 (7) | 0.0259 (7) | -0.0025 (5) | 0.0000 (5) | -0.0084 (6) |
| C33 | 0.0147 (6) | 0.0199 (7) | 0.0233 (6) | -0.0056 (5) | -0.0004 (5) | -0.0056 (5) |
| C34 | 0.0168 (6) | 0.0135 (6) | 0.0177 (6) | -0.0033 (5) | -0.0025 (5) | -0.0020 (5) |
| C29 | 0.0164 (6) | 0.0140 (6) | 0.0175 (6) | -0.0062 (5) | 0.0005 (5) | -0.0024 (5) |

Geometric parameters (Å, °)

| | | | |
|----------------------|-------------|---------------------|-------------|
| Cu1—O2 | 1.9647 (11) | C2—H2B | 0.9900 |
| Cu1—O1 | 1.9655 (11) | C9—C10 | 1.405 (2) |
| Cu1—O2' | 1.9725 (11) | C1—O1 ⁱ | 1.2592 (17) |
| Cu1—O1' | 1.9799 (11) | C30—C29 | 1.400 (2) |
| Cu1—O1D | 2.1344 (14) | C1D—H02A | 0.9800 |
| Cu1—Cu1 ⁱ | 2.6619 (12) | C1D—H02B | 0.9800 |
| Cl3—C30 | 1.7350 (17) | C1D—H02C | 0.9800 |
| Cl2—C14 | 1.7344 (17) | C5—C6 | 1.389 (2) |
| S1D—O1D | 1.5122 (11) | C5—C4 | 1.390 (2) |
| S1D—C1D | 1.7889 (16) | C5—H5 | 0.9500 |
| S1D—C2D | 1.7905 (18) | C12—C11 | 1.388 (2) |
| Cl4—C34 | 1.7368 (15) | C12—H12 | 0.9500 |
| Cl1—C10 | 1.7406 (16) | C11—C10 | 1.385 (2) |
| O2—C21 | 1.2649 (17) | C11—H11 | 0.9500 |
| O1—C1 | 1.2595 (16) | C7—C6 | 1.389 (2) |
| O1'—C1 ⁱ | 1.2592 (17) | C7—H7 | 0.9500 |
| O2'—C21 ⁱ | 1.2578 (16) | C6—H6 | 0.9500 |
| N012—C29 | 1.3959 (18) | C2D—H03A | 0.9800 |
| N012—C28 | 1.4212 (18) | C2D—H03B | 0.9800 |
| N012—H012 | 0.80 (2) | C2D—H03C | 0.9800 |
| C14—C13 | 1.386 (2) | C4—C3 | 1.392 (2) |
| C14—C9 | 1.405 (2) | C4—H4 | 0.9500 |
| C28—C27 | 1.394 (2) | C26—C25 | 1.388 (2) |
| C28—C23 | 1.397 (2) | C26—H26 | 0.9500 |
| C8—C7 | 1.3966 (19) | C22—C23 | 1.511 (2) |
| C8—C3 | 1.401 (2) | C22—C21 | 1.5198 (19) |
| C8—N1 | 1.4193 (18) | C22—H22A | 0.9900 |
| N1—C9 | 1.4003 (19) | C22—H22B | 0.9900 |
| N1—H1 | 0.81 (2) | C32—C33 | 1.384 (2) |
| C31—C30 | 1.386 (2) | C32—H32 | 0.9500 |
| C31—C32 | 1.387 (2) | C21—O2 ⁱ | 1.2579 (16) |
| C31—H31 | 0.9500 | C23—C24 | 1.3992 (19) |
| C13—C12 | 1.389 (2) | C24—C25 | 1.390 (2) |
| C13—H13 | 0.9500 | C24—H24 | 0.9500 |
| C27—C26 | 1.388 (2) | C25—H25 | 0.9500 |
| C27—H27 | 0.9500 | C33—C34 | 1.386 (2) |
| C2—C3 | 1.5050 (19) | C33—H33 | 0.9500 |
| C2—C1 | 1.5203 (19) | C34—C29 | 1.402 (2) |
| C2—H2A | 0.9900 | | |
| O2—Cu1—O1 | 86.92 (5) | H02A—C1D—H02C | 109.5 |
| O2—Cu1—O2' | 167.83 (4) | H02B—C1D—H02C | 109.5 |
| O1—Cu1—O2' | 92.47 (6) | C6—C5—C4 | 119.31 (14) |
| O2—Cu1—O1' | 90.59 (5) | C6—C5—H5 | 120.3 |
| O1—Cu1—O1' | 167.60 (4) | C4—C5—H5 | 120.3 |
| O2'—Cu1—O1' | 87.41 (6) | C11—C12—C13 | 120.00 (14) |

| | | | |
|---------------------------|-------------|--------------------------|-------------|
| O2—Cu1—O1D | 97.11 (5) | C11—C12—H12 | 120.0 |
| O1—Cu1—O1D | 94.31 (4) | C13—C12—H12 | 120.0 |
| O2'—Cu1—O1D | 95.06 (4) | C10—C11—C12 | 119.50 (15) |
| O1'—Cu1—O1D | 98.06 (4) | C10—C11—H11 | 120.3 |
| O2—Cu1—Cu1 ⁱ | 86.45 (4) | C12—C11—H11 | 120.3 |
| O1—Cu1—Cu1 ⁱ | 85.35 (3) | C6—C7—C8 | 120.25 (13) |
| O2'—Cu1—Cu1 ⁱ | 81.39 (4) | C6—C7—H7 | 119.9 |
| O1'—Cu1—Cu1 ⁱ | 82.36 (3) | C8—C7—H7 | 119.9 |
| O1D—Cu1—Cu1 ⁱ | 176.41 (3) | C5—C6—C7 | 120.16 (13) |
| O1D—S1D—C1D | 106.71 (7) | C5—C6—H6 | 119.9 |
| O1D—S1D—C2D | 106.52 (7) | C7—C6—H6 | 119.9 |
| C1D—S1D—C2D | 98.13 (8) | S1D—C2D—H03A | 109.5 |
| C21—O2—Cu1 | 120.01 (9) | S1D—C2D—H03B | 109.5 |
| S1D—O1D—Cu1 | 133.22 (6) | H03A—C2D—H03B | 109.5 |
| C1—O1—Cu1 | 121.65 (9) | S1D—C2D—H03C | 109.5 |
| C1 ⁱ —O1'—Cu1 | 124.30 (9) | H03A—C2D—H03C | 109.5 |
| C21 ⁱ —O2'—Cu1 | 125.79 (9) | H03B—C2D—H03C | 109.5 |
| C29—N012—C28 | 119.75 (12) | C5—C4—C3 | 121.55 (14) |
| C29—N012—H012 | 116.5 (14) | C5—C4—H4 | 119.2 |
| C28—N012—H012 | 115.4 (14) | C3—C4—H4 | 119.2 |
| C13—C14—C9 | 122.73 (14) | C25—C26—C27 | 119.88 (14) |
| C13—C14—Cl2 | 118.27 (11) | C25—C26—H26 | 120.1 |
| C9—C14—Cl2 | 118.98 (11) | C27—C26—H26 | 120.1 |
| C27—C28—C23 | 120.00 (13) | C23—C22—C21 | 111.97 (11) |
| C27—C28—N012 | 121.21 (13) | C23—C22—H22A | 109.2 |
| C23—C28—N012 | 118.79 (13) | C21—C22—H22A | 109.2 |
| C7—C8—C3 | 120.06 (13) | C23—C22—H22B | 109.2 |
| C7—C8—N1 | 121.86 (13) | C21—C22—H22B | 109.2 |
| C3—C8—N1 | 118.07 (12) | H22A—C22—H22B | 107.9 |
| C9—N1—C8 | 123.36 (12) | C33—C32—C31 | 119.92 (13) |
| C9—N1—H1 | 111.4 (14) | C33—C32—H32 | 120.0 |
| C8—N1—H1 | 113.6 (14) | C31—C32—H32 | 120.0 |
| C30—C31—C32 | 119.23 (13) | C11—C10—C9 | 122.69 (14) |
| C30—C31—H31 | 120.4 | C11—C10—Cl1 | 118.58 (12) |
| C32—C31—H31 | 120.4 | C9—C10—Cl1 | 118.73 (11) |
| C14—C13—C12 | 119.40 (14) | O2 ^h —C21—O2 | 125.72 (13) |
| C14—C13—H13 | 120.3 | O2 ^h —C21—C22 | 117.28 (12) |
| C12—C13—H13 | 120.3 | O2—C21—C22 | 116.98 (12) |
| C26—C27—C28 | 120.68 (14) | C28—C23—C24 | 118.49 (13) |
| C26—C27—H27 | 119.7 | C28—C23—C22 | 120.72 (12) |
| C28—C27—H27 | 119.7 | C24—C23—C22 | 120.72 (13) |
| C3—C2—C1 | 115.83 (11) | C4—C3—C8 | 118.60 (12) |
| C3—C2—H2A | 108.3 | C4—C3—C2 | 120.36 (13) |
| C1—C2—H2A | 108.3 | C8—C3—C2 | 121.01 (12) |
| C3—C2—H2B | 108.3 | C25—C24—C23 | 121.42 (14) |
| C1—C2—H2B | 108.3 | C25—C24—H24 | 119.3 |
| H2A—C2—H2B | 107.4 | C23—C24—H24 | 119.3 |
| N1—C9—C14 | 122.05 (14) | C26—C25—C24 | 119.44 (14) |

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| N1—C9—C10 | 122.15 (13) | C26—C25—H25 | 120.3 |
| C14—C9—C10 | 115.66 (13) | C24—C25—H25 | 120.3 |
| O1 ^h —C1—O1 | 125.60 (12) | C32—C33—C34 | 119.82 (13) |
| O1 ^h —C1—C2 | 117.90 (12) | C32—C33—H33 | 120.1 |
| O1—C1—C2 | 116.48 (12) | C34—C33—H33 | 120.1 |
| C31—C30—C29 | 122.77 (13) | C33—C34—C29 | 122.24 (13) |
| C31—C30—C13 | 118.42 (11) | C33—C34—C14 | 119.09 (11) |
| C29—C30—C13 | 118.81 (10) | C29—C34—C14 | 118.66 (10) |
| S1D—C1D—H02A | 109.5 | N012—C29—C30 | 120.60 (13) |
| S1D—C1D—H02B | 109.5 | N012—C29—C34 | 123.50 (13) |
| H02A—C1D—H02B | 109.5 | C30—C29—C34 | 115.89 (12) |
| S1D—C1D—H02C | 109.5 | | |
| O1—Cu1—O2—C21 | -80.75 (10) | C3—C8—C7—C6 | 1.2 (2) |
| O2'—Cu1—O2—C21 | 6.7 (3) | N1—C8—C7—C6 | -177.75 (13) |
| O1'—Cu1—O2—C21 | 87.09 (10) | C4—C5—C6—C7 | -1.9 (2) |
| O1D—Cu1—O2—C21 | -174.72 (10) | C8—C7—C6—C5 | 1.2 (2) |
| Cu1 ⁱ —Cu1—O2—C21 | 4.78 (10) | C6—C5—C4—C3 | 0.2 (2) |
| C1D—S1D—O1D—Cu1 | 54.37 (10) | C28—C27—C26—C25 | 0.5 (2) |
| C2D—S1D—O1D—Cu1 | -49.71 (10) | C30—C31—C32—C33 | 1.5 (2) |
| O2—Cu1—O1D—S1D | -106.94 (9) | C12—C11—C10—C9 | 0.8 (2) |
| O1—Cu1—O1D—S1D | 165.63 (8) | C12—C11—C10—C11 | -179.88 (11) |
| O2'—Cu1—O1D—S1D | 72.77 (9) | N1—C9—C10—C11 | 176.25 (13) |
| O1'—Cu1—O1D—S1D | -15.32 (9) | C14—C9—C10—C11 | 0.3 (2) |
| O2—Cu1—O1—C1 | 84.24 (11) | N1—C9—C10—C11 | -3.02 (18) |
| O2'—Cu1—O1—C1 | -83.59 (11) | C14—C9—C10—C11 | -179.00 (10) |
| O1'—Cu1—O1—C1 | 5.6 (3) | Cu1—O2—C21—O2 ^h | -9.74 (19) |
| O1D—Cu1—O1—C1 | -178.85 (10) | Cu1—O2—C21—C22 | 168.74 (9) |
| Cu1 ⁱ —Cu1—O1—C1 | -2.44 (10) | C23—C22—C21—O2 ^h | 116.54 (13) |
| O2—Cu1—O1'—C1 ⁱ | -93.06 (12) | C23—C22—C21—O2 | -62.08 (16) |
| O1—Cu1—O1'—C1 ⁱ | -14.8 (3) | C27—C28—C23—C24 | -3.4 (2) |
| O2'—Cu1—O1'—C1 ⁱ | 74.93 (11) | N012—C28—C23—C24 | 177.69 (13) |
| O1D—Cu1—O1'—C1 ⁱ | 169.68 (11) | C27—C28—C23—C22 | 173.79 (13) |
| Cu1 ⁱ —Cu1—O1'—C1 ⁱ | -6.72 (11) | N012—C28—C23—C22 | -5.15 (19) |
| O2—Cu1—O2'—C21 ⁱ | 2.2 (3) | C21—C22—C23—C28 | 85.23 (16) |
| O1—Cu1—O2'—C21 ⁱ | 89.04 (12) | C21—C22—C23—C24 | -97.69 (15) |
| O1'—Cu1—O2'—C21 ⁱ | -78.54 (11) | C5—C4—C3—C8 | 2.1 (2) |
| O1D—Cu1—O2'—C21 ⁱ | -176.41 (11) | C5—C4—C3—C2 | -175.91 (13) |
| Cu1 ⁱ —Cu1—O2'—C21 ⁱ | 4.12 (11) | C7—C8—C3—C4 | -2.8 (2) |
| C29—N012—C28—C27 | -26.4 (2) | N1—C8—C3—C4 | 176.17 (12) |
| C29—N012—C28—C23 | 152.56 (13) | C7—C8—C3—C2 | 175.18 (12) |
| C7—C8—N1—C9 | -13.2 (2) | N1—C8—C3—C2 | -5.80 (19) |
| C3—C8—N1—C9 | 167.83 (13) | C1—C2—C3—C4 | -100.88 (15) |
| C9—C14—C13—C12 | 1.3 (2) | C1—C2—C3—C8 | 81.12 (16) |
| C12—C14—C13—C12 | -177.01 (11) | C28—C23—C24—C25 | 2.1 (2) |
| C23—C28—C27—C26 | 2.1 (2) | C22—C23—C24—C25 | -175.05 (13) |
| N012—C28—C27—C26 | -178.99 (14) | C27—C26—C25—C24 | -1.8 (2) |
| C8—N1—C9—C14 | -63.1 (2) | C23—C24—C25—C26 | 0.5 (2) |

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|---------------------------|--------------|------------------|--------------|
| C8—N1—C9—C10 | 121.19 (16) | C31—C32—C33—C34 | -2.6 (2) |
| C13—C14—C9—N1 | -177.33 (13) | C32—C33—C34—C29 | 0.3 (2) |
| C12—C14—C9—N1 | 0.95 (18) | C32—C33—C34—C14 | -179.55 (11) |
| C13—C14—C9—C10 | -1.3 (2) | C28—N012—C29—C30 | -59.39 (19) |
| C12—C14—C9—C10 | 176.94 (10) | C28—N012—C29—C34 | 121.85 (15) |
| Cu1—O1—C1—O1 ⁱ | 8.65 (19) | C31—C30—C29—N012 | 177.19 (14) |
| Cu1—O1—C1—C2 | -169.98 (9) | C13—C30—C29—N012 | -3.74 (19) |
| C3—C2—C1—O1 ⁱ | 3.49 (18) | C31—C30—C29—C34 | -4.0 (2) |
| C3—C2—C1—O1 | -177.76 (12) | C13—C30—C29—C34 | 175.12 (10) |
| C32—C31—C30—C29 | 1.9 (2) | C33—C34—C29—N012 | -178.30 (13) |
| C32—C31—C30—C13 | -177.23 (11) | C14—C34—C29—N012 | 1.52 (19) |
| C14—C13—C12—C11 | -0.1 (2) | C33—C34—C29—C30 | 2.9 (2) |
| C13—C12—C11—C10 | -0.9 (2) | C14—C34—C29—C30 | -177.30 (10) |

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