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# Tetrakis[$\mu_2$-5-nitro-2-(phenylsulfanyl)benzoato-$\kappa^2O$:$O'$]bis[(acetonitrile-$\kappa N$)copper(II)]

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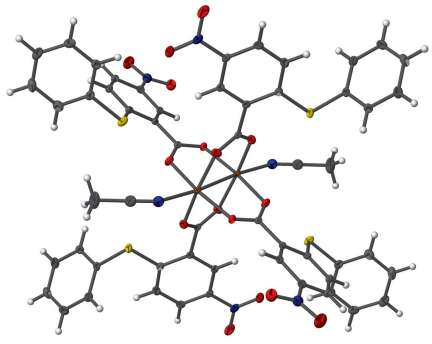
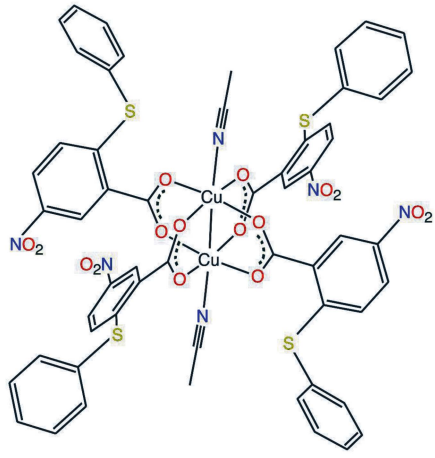
**Structural data**: full structural data are available from iucrdata.iucr.org

The title compound, $[Cu_2(\mu_2\text{-}O_2CC_{12}H_8NO_2S)_4(CH_3CN)_2]$, consists of a dinuclear and centrosymmetric complex based on two $Cu^{II}$ atoms coordinated by four 5-nitro-2-phenylsulfanyl-benzoate anions and two acetonitrile ligands. Each benzoate anion acts as a bis-monodentate ligand while each acetonitrile acts as a monodentate ligand, leading to a square-pyramidal $NO_4$ coordination environment for each $Cu^{II}$ atom with the acetonitrile N atom at the apex. The intramolecular Cu···Cu distance in the dimer is 2.6478 (3) Å. The cohesion of the crystal structure is ensured by $_{(phenyl)}C—H\cdots O_{(nitro)}$ hydrogen bonds and $_{(phenyl)}C—H\cdots\pi$ interactions.

**3D view**



**Chemical scheme**




## Structure description

The title compound was obtained serendipitously during efforts to make 5-nitro-2-phenylsulfanyl-benzoic acid by reacting 2-bromo-5-nitro-benzoic acid with benzenethiol through a modified Ullmann reaction with $Cu/Cu_2O$ as catalyst, $K_2CO_3$ as base, and ethoxyethanol as solvent (Liu *et al.*, 2007). The complex likely formed between $Cu^{II}$ generated *in situ* and 5-nitro-2-phenylsulfanyl-benzoate.

The title compound is a centrosymmetric dinuclear $Cu^{II}$ complex with two pairs of bis-monodentate 5-nitro-2-phenylsulfanyl-benzoate anions and a pair of acetonitrile molecules as ligands (Fig. 1). The coordination of each copper(II) atom is square-pyramidal, with the acetonitrile N atom at the apex of the $NO_4$ coordination set. The intramolecular Cu···Cu distance in the dimer is 2.6478 (3) Å (Fig. 1). The aromatic rings of the two independent benzoate moieties (denoted by suffix *A* and *B* for the two anions in the asymmetric unit) are nearly perpendicular with a dihedral angle of 86.55 (5)°. The negative charge of the carboxylate group is delocalized over the two O atoms in each of the anions, as indicated by the nearly identical length of the two C—O bonds [1.2574 (17) and 1.2624 (17) Å for molecule *A* and 1.2574 (17) and 1.2655 (16) Å for molecule *B*]. A

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

*Cg*4 is the centroid of the C8*B*–C13*B* ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C9*B*—H9*B*···O19*B*$^{i}$ | 0.95 | 2.39 | 3.2351 (19) | 148 |
| C10—H10*A*···*Cg*4$^{ii}$ | 0.95 | 2.63 | 3.4171 (17) | 140 |

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+1, -z$.

weak intermolecular hydrogen bond is formed between the C9*B*—H9*B* group of a phenyl ring and the O19*B* atom of an inversion-related ($-x$ + 1, $-y$ + 2, $-z$ + 1) $NO_2$ group (Table 1), leading to the formation of supramolecular pillars along [100] and [010] (Fig. 2). An additional C—H···$\pi$ interaction between C10*A*—H10*A* and the centroid of a neighbouring phenyl ring (Table 1) consolidates the three-dimensional network structure.

The molecular structure of the title complex is similar to that of tetrakis($\mu_2$-benzoato-*O,O*')-bis(dimethylsulfoxide)-dicopper(II) (Reyes-Ortega *et al.*, 2005) and other related copper complexes (Vives *et al.*, 2003).

## Synthesis and crystallization

A mixture of benzenethiol (1.25 g, 11.4 mmol), 2-bromo-5-nitro-benzoic acid (2.16 g, 8.8 mmol), $K_2CO_3$ (1.21 g, 8.8 mmol), Cu powder (51 mg, 0.8 mmol), $Cu_2O$ (38 mg, 0.4 mmol) and 2-ethoxyethanol (3 ml) was heated to 403 K for 24 h. The reaction was cooled down to room temperature, and the solvent was removed under reduced pressure. The residue was poured into water (30 ml), treated with charcoal, and the resulting suspension was filtered through Celite. Acidification of the filtrate with dilute HCl (pH 5) gave a bluish precipitate

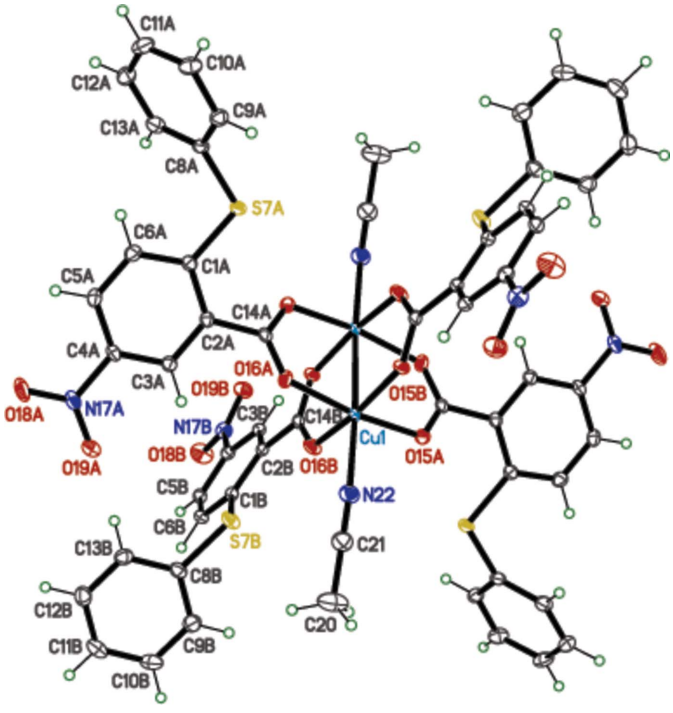



**Figure 1**
The molecular structure of the binuclear title complex, with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms). Non-labelled atoms are generated by inversion symmetry (symmetry code: $-x$ + 1, $-y$ + 2, $-z$).

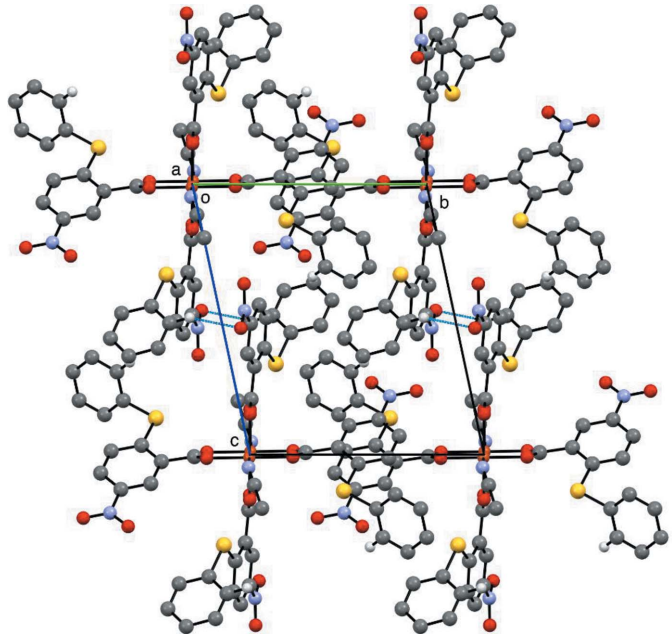



**Figure 2**
Packing of the molecules in the title compound, with intermolecular C—H···O hydrogen bonds indicated by blue dashed lines (H atoms not participating in hydrogen bonding are omitted).

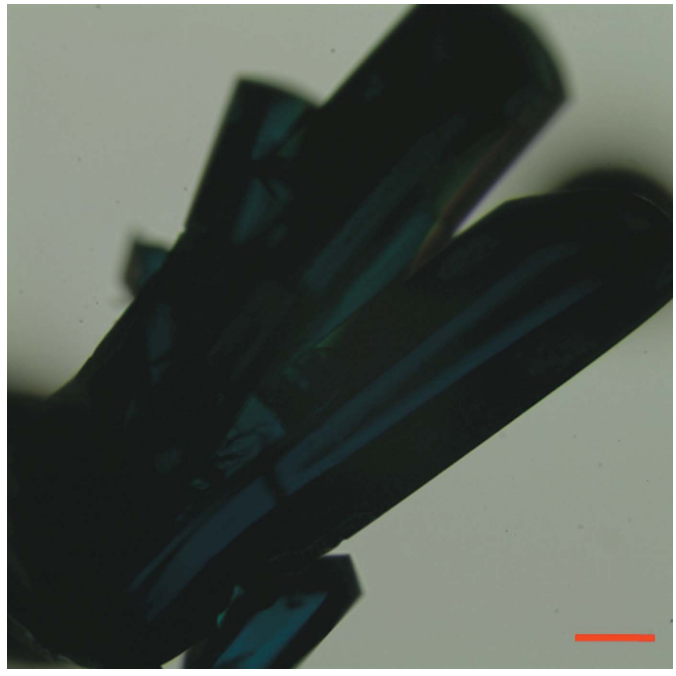


**Figure 3**
Crystals of the title complex. The length of the red scale bar represents 0.1 mm.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Cu_2(C_{13}H_8NO_4S)_4(C_2H_3N)_2]$ |
| $M_r$ | 1306.24 |
| Crystal system, space group | Triclinic, $P\overline{1}$ |
| Temperature (K) | 90 |
| $a, b, c$ (Å) | 10.7377 (1), 11.0957 (1), 12.4857 (2) |
| $\alpha, \beta, \gamma$ (°) | 77.9948 (5), 88.1362 (5), 72.3710 (5) |
| $V$ (Å$^3$) | 1385.97 (3) |
| $Z$ | 1 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.00 |
| Crystal size (mm) | 0.50 × 0.40 × 0.20 |
| | |
| Data collection | |
| Diffractometer | Nonius KappaCCD diffractometer |
| Absorption correction | Multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997) |
| $T_{min}$, $T_{max}$ | 0.636, 0.826 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12571, 6335, 5914 |
| $R_{int}$ | 0.016 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.650 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.023, 0.061, 1.05 |
| No. of reflections | 6335 |
| No. of parameters | 380 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.36, −0.39 |

Computer programs: *COLLECT* (Nonius, 2002), *DENZO-SMN* (Otwinowski & Minor, 1997), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

(crude product). The crude product was dissolved in aqueous $Na_2CO_3$ solution (5%$_{wt}$, 100 ml) and the solution was filtered through Celite and subjected to acidification and subsequent precipitation to give a pure product. Blue rod-shaped crystals were grown from $CH_3CN$ solution by slow evaporation (Fig. 3).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.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# full crystallographic data

*IUCrData* (2020). **5**, x200801 [https://doi.org/10.1107/S2414314620008019]

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**Tetrakis[$\mu_2$-5-nitro-2-(phenylsulfanyl)benzoato-$\kappa^2O$:$O'$]bis[(acetonitrile-$\kappa N$)copper(II)]**

*Crystal data*

$[Cu_2(C_{13}H_8NO_4S)_4(C_2H_3N)_2]$
$M_r$ = 1306.24
Triclinic, $P\overline{1}$
$a$ = 10.7377 (1) Å
$b$ = 11.0957 (1) Å
$c$ = 12.4857 (2) Å
$\alpha$ = 77.9948 (5)°
$\beta$ = 88.1362 (5)°
$\gamma$ = 72.3710 (5)°
$V$ = 1385.97 (3) Å$^3$
$Z$ = 1
$F(000)$ = 666
$D_x$ = 1.565 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 6289 reflections
$\theta$ = 1.0–27.5°
$\mu$ = 1.00 mm$^{-1}$
$T$ = 90 K
Rod, blue
0.50 × 0.40 × 0.20 mm

*Data collection*

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 18 pixels mm$^{-1}$
$\omega$ scans at fixed $\chi$=55°
Absorption correction: multi-scan (*Scalepack*; Otwinowski & Minor, 1997)
$T_{min}$ = 0.636, $T_{max}$ = 0.826
12571 measured reflections
6335 independent reflections
5914 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.016
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.7°
$h$ = −13→13
$k$ = −14→14
$l$ = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.061
$S$ = 1.05
6335 reflections
380 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
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2 + 0.9758P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.39 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.37846 (2) | 0.99509 (2) | 0.01065 (2) | 0.00993 (5) |
| C20 | 0.00546 (18) | 1.0018 (2) | 0.19864 (15) | 0.0383 (4) |
| H20A | 0.021784 | 0.918044 | 0.249462 | 0.057* |
| H20B | −0.082418 | 1.027638 | 0.165040 | 0.057* |
| H20C | 0.012133 | 1.066883 | 0.238691 | 0.057* |
| C21 | 0.10207 (15) | 0.99118 (16) | 0.11335 (13) | 0.0219 (3) |
| N22 | 0.17853 (12) | 0.98250 (13) | 0.04760 (11) | 0.0210 (3) |
| C1A | 0.73172 (13) | 0.54587 (13) | −0.03417 (11) | 0.0129 (3) |
| C2A | 0.63214 (13) | 0.61581 (13) | 0.02586 (10) | 0.0121 (3) |
| C3A | 0.57027 (13) | 0.55063 (13) | 0.10719 (11) | 0.0131 (3) |
| H3A | 0.502908 | 0.597453 | 0.147404 | 0.016* |
| C4A | 0.60775 (13) | 0.41742 (13) | 0.12878 (11) | 0.0135 (3) |
| C5A | 0.70116 (14) | 0.34601 (13) | 0.06829 (11) | 0.0154 (3) |
| H5A | 0.723021 | 0.254424 | 0.082499 | 0.018* |
| C6A | 0.76180 (14) | 0.41077 (14) | −0.01307 (12) | 0.0161 (3) |
| H6A | 0.825160 | 0.362840 | −0.055605 | 0.019* |
| S7A | 0.81150 (3) | 0.63183 (3) | −0.13466 (3) | 0.01537 (8) |
| C8A | 0.90777 (13) | 0.50792 (13) | −0.20027 (11) | 0.0141 (3) |
| C9A | 0.87216 (14) | 0.50745 (14) | −0.30608 (12) | 0.0164 (3) |
| H9A | 0.796224 | 0.570717 | −0.341701 | 0.020* |
| C10A | 0.94849 (14) | 0.41366 (15) | −0.35961 (12) | 0.0199 (3) |
| H10A | 0.925925 | 0.414027 | −0.432642 | 0.024* |
| C11A | 1.05753 (15) | 0.31967 (15) | −0.30620 (13) | 0.0220 (3) |
| H11A | 1.108205 | 0.254619 | −0.342354 | 0.026* |
| C12A | 1.09315 (14) | 0.31990 (15) | −0.20054 (13) | 0.0211 (3) |
| H12A | 1.167443 | 0.254741 | −0.164227 | 0.025* |
| C13A | 1.01995 (14) | 0.41563 (15) | −0.14789 (12) | 0.0176 (3) |
| H13A | 1.046003 | 0.418341 | −0.076659 | 0.021* |
| C14A | 0.58662 (13) | 0.76073 (13) | 0.00758 (10) | 0.0119 (2) |
| O15A | 0.32797 (9) | 1.18158 (9) | 0.00850 (8) | 0.0148 (2) |
| O16A | 0.46503 (10) | 0.81172 (9) | 0.01343 (8) | 0.0167 (2) |
| N17A | 0.54354 (12) | 0.34971 (12) | 0.21587 (9) | 0.0167 (2) |
| O18A | 0.57926 (13) | 0.23095 (10) | 0.23492 (9) | 0.0291 (3) |
| O19A | 0.45741 (11) | 0.41481 (10) | 0.26574 (9) | 0.0218 (2) |
| C1B | 0.47177 (13) | 0.84097 (13) | 0.39310 (11) | 0.0132 (3) |
| C2B | 0.55474 (13) | 0.90071 (13) | 0.32621 (11) | 0.0123 (3) |
| C3B | 0.66210 (13) | 0.91810 (13) | 0.37284 (11) | 0.0132 (3) |
| H3B | 0.718486 | 0.957058 | 0.328018 | 0.016* |
| C4B | 0.68656 (13) | 0.87855 (13) | 0.48456 (11) | 0.0135 (3) |

| | | | | |
|---|---|---|---|---|
| C5B | 0.60457 (14) | 0.82457 (13) | 0.55299 (11) | 0.0146 (3) |
| H5B | 0.620979 | 0.800878 | 0.630000 | 0.018* |
| C6B | 0.49851 (13) | 0.80600 (13) | 0.50678 (11) | 0.0146 (3) |
| H6B | 0.442099 | 0.768585 | 0.553019 | 0.017* |
| S7B | 0.34082 (3) | 0.80704 (4) | 0.33483 (3) | 0.01856 (8) |
| C8B | 0.28760 (13) | 0.71437 (14) | 0.45143 (11) | 0.0161 (3) |
| C9B | 0.18868 (14) | 0.77613 (15) | 0.51410 (13) | 0.0203 (3) |
| H9B | 0.148411 | 0.866897 | 0.493867 | 0.024* |
| C10B | 0.14911 (15) | 0.70463 (16) | 0.60623 (13) | 0.0228 (3) |
| H10B | 0.082094 | 0.746774 | 0.649382 | 0.027* |
| C11B | 0.20682 (15) | 0.57216 (16) | 0.63558 (12) | 0.0221 (3) |
| H11B | 0.181478 | 0.523963 | 0.700033 | 0.026* |
| C12B | 0.30193 (15) | 0.50986 (15) | 0.57050 (13) | 0.0210 (3) |
| H12B | 0.339840 | 0.418677 | 0.589475 | 0.025* |
| C13B | 0.34171 (14) | 0.58063 (14) | 0.47772 (12) | 0.0177 (3) |
| H13B | 0.405530 | 0.537858 | 0.432525 | 0.021* |
| C14B | 0.53438 (13) | 0.94456 (13) | 0.20461 (11) | 0.0127 (3) |
| O15B | 0.36927 (9) | 1.03736 (9) | −0.14980 (8) | 0.01443 (19) |
| O16B | 0.42258 (10) | 0.95862 (10) | 0.16679 (8) | 0.0179 (2) |
| N17B | 0.80353 (12) | 0.89184 (12) | 0.53147 (10) | 0.0176 (2) |
| O18B | 0.81739 (12) | 0.86967 (12) | 0.63151 (9) | 0.0276 (3) |
| O19B | 0.88348 (10) | 0.92404 (11) | 0.46750 (9) | 0.0218 (2) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.01075 (8) | 0.00931 (8) | 0.00903 (8) | −0.00330 (6) | 0.00151 (6) | −0.00015 (6) |
| C20 | 0.0299 (9) | 0.0581 (13) | 0.0299 (9) | −0.0159 (9) | 0.0122 (8) | −0.0135 (9) |
| C21 | 0.0170 (7) | 0.0264 (8) | 0.0228 (8) | −0.0082 (6) | −0.0015 (6) | −0.0034 (6) |
| N22 | 0.0148 (6) | 0.0245 (7) | 0.0233 (6) | −0.0080 (5) | 0.0009 (5) | −0.0010 (5) |
| C1A | 0.0140 (6) | 0.0137 (6) | 0.0112 (6) | −0.0047 (5) | 0.0003 (5) | −0.0022 (5) |
| C2A | 0.0143 (6) | 0.0115 (6) | 0.0104 (6) | −0.0037 (5) | −0.0011 (5) | −0.0018 (5) |
| C3A | 0.0150 (6) | 0.0133 (6) | 0.0105 (6) | −0.0037 (5) | 0.0001 (5) | −0.0025 (5) |
| C4A | 0.0173 (6) | 0.0136 (6) | 0.0099 (6) | −0.0068 (5) | 0.0002 (5) | 0.0000 (5) |
| C5A | 0.0183 (7) | 0.0106 (6) | 0.0163 (6) | −0.0035 (5) | −0.0010 (5) | −0.0019 (5) |
| C6A | 0.0169 (7) | 0.0140 (7) | 0.0177 (7) | −0.0037 (5) | 0.0028 (5) | −0.0055 (5) |
| S7A | 0.01914 (17) | 0.01343 (16) | 0.01462 (16) | −0.00625 (13) | 0.00703 (13) | −0.00429 (12) |
| C8A | 0.0141 (6) | 0.0146 (6) | 0.0146 (6) | −0.0054 (5) | 0.0047 (5) | −0.0040 (5) |
| C9A | 0.0135 (6) | 0.0179 (7) | 0.0165 (7) | −0.0030 (5) | 0.0004 (5) | −0.0036 (5) |
| C10A | 0.0186 (7) | 0.0262 (8) | 0.0175 (7) | −0.0068 (6) | 0.0016 (5) | −0.0103 (6) |
| C11A | 0.0177 (7) | 0.0212 (8) | 0.0286 (8) | −0.0039 (6) | 0.0068 (6) | −0.0122 (6) |
| C12A | 0.0136 (7) | 0.0202 (7) | 0.0256 (8) | −0.0014 (6) | 0.0008 (6) | −0.0015 (6) |
| C13A | 0.0154 (7) | 0.0230 (7) | 0.0142 (6) | −0.0067 (6) | 0.0008 (5) | −0.0022 (5) |
| C14A | 0.0165 (6) | 0.0115 (6) | 0.0070 (6) | −0.0035 (5) | 0.0009 (5) | −0.0012 (5) |
| O15A | 0.0164 (5) | 0.0110 (5) | 0.0177 (5) | −0.0050 (4) | 0.0039 (4) | −0.0039 (4) |
| O16A | 0.0149 (5) | 0.0102 (5) | 0.0231 (5) | −0.0029 (4) | 0.0014 (4) | −0.0009 (4) |
| N17A | 0.0243 (6) | 0.0150 (6) | 0.0116 (5) | −0.0087 (5) | 0.0004 (5) | −0.0004 (4) |
| O18A | 0.0527 (8) | 0.0130 (5) | 0.0222 (6) | −0.0134 (5) | 0.0126 (5) | −0.0016 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O19A | 0.0243 (5) | 0.0208 (5) | 0.0188 (5) | −0.0072 (4) | 0.0082 (4) | −0.0015 (4) |
| C1B | 0.0130 (6) | 0.0118 (6) | 0.0127 (6) | −0.0017 (5) | 0.0005 (5) | −0.0013 (5) |
| C2B | 0.0140 (6) | 0.0098 (6) | 0.0109 (6) | −0.0008 (5) | 0.0020 (5) | −0.0017 (5) |
| C3B | 0.0149 (6) | 0.0108 (6) | 0.0133 (6) | −0.0028 (5) | 0.0034 (5) | −0.0031 (5) |
| C4B | 0.0135 (6) | 0.0125 (6) | 0.0147 (6) | −0.0032 (5) | 0.0003 (5) | −0.0043 (5) |
| C5B | 0.0182 (7) | 0.0133 (6) | 0.0104 (6) | −0.0025 (5) | 0.0010 (5) | −0.0016 (5) |
| C6B | 0.0154 (6) | 0.0151 (7) | 0.0118 (6) | −0.0042 (5) | 0.0032 (5) | −0.0007 (5) |
| S7B | 0.01666 (17) | 0.02532 (19) | 0.01348 (16) | −0.01036 (14) | −0.00195 (13) | 0.00278 (13) |
| C8B | 0.0139 (6) | 0.0204 (7) | 0.0144 (6) | −0.0077 (5) | 0.0000 (5) | −0.0006 (5) |
| C9B | 0.0181 (7) | 0.0177 (7) | 0.0269 (8) | −0.0069 (6) | 0.0033 (6) | −0.0066 (6) |
| C10B | 0.0210 (7) | 0.0297 (8) | 0.0239 (8) | −0.0124 (6) | 0.0093 (6) | −0.0134 (6) |
| C11B | 0.0228 (7) | 0.0304 (8) | 0.0163 (7) | −0.0158 (7) | 0.0014 (6) | −0.0007 (6) |
| C12B | 0.0194 (7) | 0.0187 (7) | 0.0226 (7) | −0.0060 (6) | −0.0029 (6) | 0.0015 (6) |
| C13B | 0.0133 (6) | 0.0209 (7) | 0.0178 (7) | −0.0036 (5) | 0.0000 (5) | −0.0041 (6) |
| C14B | 0.0167 (6) | 0.0088 (6) | 0.0111 (6) | −0.0020 (5) | 0.0016 (5) | −0.0018 (5) |
| O15B | 0.0153 (5) | 0.0167 (5) | 0.0099 (4) | −0.0040 (4) | 0.0027 (4) | −0.0015 (4) |
| O16B | 0.0172 (5) | 0.0245 (5) | 0.0104 (4) | −0.0073 (4) | 0.0004 (4) | 0.0017 (4) |
| N17B | 0.0187 (6) | 0.0177 (6) | 0.0180 (6) | −0.0065 (5) | −0.0004 (5) | −0.0059 (5) |
| O18B | 0.0295 (6) | 0.0413 (7) | 0.0168 (5) | −0.0159 (5) | −0.0035 (4) | −0.0080 (5) |
| O19B | 0.0196 (5) | 0.0248 (6) | 0.0243 (5) | −0.0116 (4) | 0.0030 (4) | −0.0053 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—O16B | 1.9505 (10) | C13A—H13A | 0.9500 |
| Cu1—O16A | 1.9576 (10) | C14A—O15A$^{i}$ | 1.2574 (17) |
| Cu1—O15B | 1.9588 (9) | C14A—O16A | 1.2624 (17) |
| Cu1—O15A | 1.9685 (10) | N17A—O18A | 1.2287 (16) |
| Cu1—N22 | 2.2206 (12) | N17A—O19A | 1.2287 (16) |
| Cu1—Cu1$^{i}$ | 2.6478 (3) | C1B—C6B | 1.4062 (18) |
| C20—C21 | 1.460 (2) | C1B—C2B | 1.4176 (18) |
| C20—H20A | 0.9800 | C1B—S7B | 1.7746 (14) |
| C20—H20B | 0.9800 | C2B—C3B | 1.3893 (19) |
| C20—H20C | 0.9800 | C2B—C14B | 1.4966 (18) |
| C21—N22 | 1.139 (2) | C3B—C4B | 1.3808 (19) |
| C1A—C6A | 1.4032 (19) | C3B—H3B | 0.9500 |
| C1A—C2A | 1.4123 (18) | C4B—C5B | 1.3862 (19) |
| C1A—S7A | 1.7734 (14) | C4B—N17B | 1.4623 (18) |
| C2A—C3A | 1.3919 (18) | C5B—C6B | 1.381 (2) |
| C2A—C14A | 1.5017 (18) | C5B—H5B | 0.9500 |
| C3A—C4A | 1.3785 (19) | C6B—H6B | 0.9500 |
| C3A—H3A | 0.9500 | S7B—C8B | 1.7839 (14) |
| C4A—C5A | 1.3865 (19) | C8B—C13B | 1.391 (2) |
| C4A—N17A | 1.4654 (17) | C8B—C9B | 1.392 (2) |
| C5A—C6A | 1.3816 (19) | C9B—C10B | 1.388 (2) |
| C5A—H5A | 0.9500 | C9B—H9B | 0.9500 |
| C6A—H6A | 0.9500 | C10B—C11B | 1.385 (2) |
| S7A—C8A | 1.7840 (14) | C10B—H10B | 0.9500 |
| C8A—C9A | 1.3887 (19) | C11B—C12B | 1.390 (2) |

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|---|---|---|---|
| C8A—C13A | 1.397 (2) | C11B—H11B | 0.9500 |
| C9A—C10A | 1.392 (2) | C12B—C13B | 1.391 (2) |
| C9A—H9A | 0.9500 | C12B—H12B | 0.9500 |
| C10A—C11A | 1.387 (2) | C13B—H13B | 0.9500 |
| C10A—H10A | 0.9500 | C14B—O16B | 1.2574 (17) |
| C11A—C12A | 1.386 (2) | C14B—O15B$^{i}$ | 1.2655 (16) |
| C11A—H11A | 0.9500 | N17B—O18B | 1.2267 (16) |
| C12A—C13A | 1.389 (2) | N17B—O19B | 1.2349 (16) |
| C12A—H12A | 0.9500 | | |

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|---|---|---|---|
| O16B—Cu1—O16A | 87.64 (4) | C12A—C13A—C8A | 119.63 (13) |
| O16B—Cu1—O15B | 168.27 (4) | C12A—C13A—H13A | 120.2 |
| O16A—Cu1—O15B | 91.98 (4) | C8A—C13A—H13A | 120.2 |
| O16B—Cu1—O15A | 89.65 (4) | O15A$^{i}$—C14A—O16A | 126.72 (13) |
| O16A—Cu1—O15A | 168.31 (4) | O15A$^{i}$—C14A—C2A | 117.69 (12) |
| O15B—Cu1—O15A | 88.37 (4) | O16A—C14A—C2A | 115.55 (12) |
| O16B—Cu1—N22 | 90.57 (4) | C14A$^{i}$—O15A—Cu1 | 119.40 (9) |
| O16A—Cu1—N22 | 97.89 (5) | C14A—O16A—Cu1 | 125.20 (9) |
| O15B—Cu1—N22 | 101.10 (4) | O18A—N17A—O19A | 123.80 (12) |
| O15A—Cu1—N22 | 93.50 (4) | O18A—N17A—C4A | 118.00 (12) |
| O16B—Cu1—Cu1$^{i}$ | 83.35 (3) | O19A—N17A—C4A | 118.21 (11) |
| O16A—Cu1—Cu1$^{i}$ | 81.95 (3) | C6B—C1B—C2B | 118.05 (12) |
| O15B—Cu1—Cu1$^{i}$ | 84.98 (3) | C6B—C1B—S7B | 120.91 (10) |
| O15A—Cu1—Cu1$^{i}$ | 86.45 (3) | C2B—C1B—S7B | 121.02 (10) |
| N22—Cu1—Cu1$^{i}$ | 173.92 (4) | C3B—C2B—C1B | 119.99 (12) |
| C21—C20—H20A | 109.5 | C3B—C2B—C14B | 117.13 (12) |
| C21—C20—H20B | 109.5 | C1B—C2B—C14B | 122.86 (12) |
| H20A—C20—H20B | 109.5 | C4B—C3B—C2B | 119.77 (12) |
| C21—C20—H20C | 109.5 | C4B—C3B—H3B | 120.1 |
| H20A—C20—H20C | 109.5 | C2B—C3B—H3B | 120.1 |
| H20B—C20—H20C | 109.5 | C3B—C4B—C5B | 121.79 (13) |
| N22—C21—C20 | 179.27 (17) | C3B—C4B—N17B | 118.98 (12) |
| C21—N22—Cu1 | 142.80 (12) | C5B—C4B—N17B | 119.22 (12) |
| C6A—C1A—C2A | 118.39 (12) | C6B—C5B—C4B | 118.55 (12) |
| C6A—C1A—S7A | 122.63 (10) | C6B—C5B—H5B | 120.7 |
| C2A—C1A—S7A | 118.97 (10) | C4B—C5B—H5B | 120.7 |
| C3A—C2A—C1A | 120.17 (12) | C5B—C6B—C1B | 121.77 (13) |
| C3A—C2A—C14A | 116.23 (12) | C5B—C6B—H6B | 119.1 |
| C1A—C2A—C14A | 123.60 (12) | C1B—C6B—H6B | 119.1 |
| C4A—C3A—C2A | 119.31 (13) | C1B—S7B—C8B | 101.35 (6) |
| C4A—C3A—H3A | 120.3 | C13B—C8B—C9B | 120.08 (13) |
| C2A—C3A—H3A | 120.3 | C13B—C8B—S7B | 120.24 (11) |
| C3A—C4A—C5A | 121.98 (12) | C9B—C8B—S7B | 119.66 (11) |
| C3A—C4A—N17A | 118.85 (12) | C10B—C9B—C8B | 119.76 (14) |
| C5A—C4A—N17A | 119.13 (12) | C10B—C9B—H9B | 120.1 |
| C6A—C5A—C4A | 118.65 (13) | C8B—C9B—H9B | 120.1 |
| C6A—C5A—H5A | 120.7 | C11B—C10B—C9B | 120.33 (14) |
| C4A—C5A—H5A | 120.7 | C11B—C10B—H10B | 119.8 |

| | | | |
|---|---|---|---|
| C5A—C6A—C1A | 121.35 (13) | C9B—C10B—H10B | 119.8 |
| C5A—C6A—H6A | 119.3 | C10B—C11B—C12B | 119.85 (14) |
| C1A—C6A—H6A | 119.3 | C10B—C11B—H11B | 120.1 |
| C1A—S7A—C8A | 102.32 (6) | C12B—C11B—H11B | 120.1 |
| C9A—C8A—C13A | 120.39 (13) | C11B—C12B—C13B | 120.19 (14) |
| C9A—C8A—S7A | 118.87 (11) | C11B—C12B—H12B | 119.9 |
| C13A—C8A—S7A | 120.69 (11) | C13B—C12B—H12B | 119.9 |
| C8A—C9A—C10A | 119.57 (13) | C12B—C13B—C8B | 119.66 (14) |
| C8A—C9A—H9A | 120.2 | C12B—C13B—H13B | 120.2 |
| C10A—C9A—H9A | 120.2 | C8B—C13B—H13B | 120.2 |
| C11A—C10A—C9A | 119.95 (14) | O16B—C14B—O15B$^{i}$ | 126.33 (12) |
| C11A—C10A—H10A | 120.0 | O16B—C14B—C2B | 116.29 (12) |
| C9A—C10A—H10A | 120.0 | O15B$^{i}$—C14B—C2B | 117.37 (12) |
| C12A—C11A—C10A | 120.55 (14) | C14B$^{i}$—O15B—Cu1 | 121.32 (9) |
| C12A—C11A—H11A | 119.7 | C14B—O16B—Cu1 | 123.77 (9) |
| C10A—C11A—H11A | 119.7 | O18B—N17B—O19B | 123.72 (12) |
| C11A—C12A—C13A | 119.84 (14) | O18B—N17B—C4B | 118.56 (12) |
| C11A—C12A—H12A | 120.1 | O19B—N17B—C4B | 117.72 (12) |
| C13A—C12A—H12A | 120.1 | | |

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|---|---|---|---|
| C6A—C1A—C2A—C3A | 2.85 (19) | C6B—C1B—C2B—C3B | 2.74 (19) |
| S7A—C1A—C2A—C3A | −178.32 (10) | S7B—C1B—C2B—C3B | −175.48 (10) |
| C6A—C1A—C2A—C14A | −177.17 (12) | C6B—C1B—C2B—C14B | −178.72 (12) |
| S7A—C1A—C2A—C14A | 1.66 (18) | S7B—C1B—C2B—C14B | 3.05 (18) |
| C1A—C2A—C3A—C4A | 0.4 (2) | C1B—C2B—C3B—C4B | −0.8 (2) |
| C14A—C2A—C3A—C4A | −179.61 (12) | C14B—C2B—C3B—C4B | −179.46 (12) |
| C2A—C3A—C4A—C5A | −3.2 (2) | C2B—C3B—C4B—C5B | −1.8 (2) |
| C2A—C3A—C4A—N17A | 178.95 (12) | C2B—C3B—C4B—N17B | 177.03 (12) |
| C3A—C4A—C5A—C6A | 2.6 (2) | C3B—C4B—C5B—C6B | 2.4 (2) |
| N17A—C4A—C5A—C6A | −179.52 (12) | N17B—C4B—C5B—C6B | −176.42 (12) |
| C4A—C5A—C6A—C1A | 0.8 (2) | C4B—C5B—C6B—C1B | −0.4 (2) |
| C2A—C1A—C6A—C5A | −3.4 (2) | C2B—C1B—C6B—C5B | −2.1 (2) |
| S7A—C1A—C6A—C5A | 177.77 (11) | S7B—C1B—C6B—C5B | 176.08 (11) |
| C6A—C1A—S7A—C8A | 7.14 (13) | C6B—C1B—S7B—C8B | −5.99 (13) |
| C2A—C1A—S7A—C8A | −171.63 (11) | C2B—C1B—S7B—C8B | 172.19 (11) |
| C1A—S7A—C8A—C9A | 108.76 (12) | C1B—S7B—C8B—C13B | −89.83 (12) |
| C1A—S7A—C8A—C13A | −73.62 (12) | C1B—S7B—C8B—C9B | 92.16 (12) |
| C13A—C8A—C9A—C10A | 0.5 (2) | C13B—C8B—C9B—C10B | 3.4 (2) |
| S7A—C8A—C9A—C10A | 178.11 (11) | S7B—C8B—C9B—C10B | −178.58 (12) |
| C8A—C9A—C10A—C11A | 1.5 (2) | C8B—C9B—C10B—C11B | −0.5 (2) |
| C9A—C10A—C11A—C12A | −1.5 (2) | C9B—C10B—C11B—C12B | −2.1 (2) |
| C10A—C11A—C12A—C13A | −0.6 (2) | C10B—C11B—C12B—C13B | 1.7 (2) |
| C11A—C12A—C13A—C8A | 2.6 (2) | C11B—C12B—C13B—C8B | 1.2 (2) |
| C9A—C8A—C13A—C12A | −2.6 (2) | C9B—C8B—C13B—C12B | −3.7 (2) |
| S7A—C8A—C13A—C12A | 179.85 (11) | S7B—C8B—C13B—C12B | 178.26 (11) |
| C3A—C2A—C14A—O15A$^{i}$ | 138.82 (13) | C3B—C2B—C14B—O16B | −162.85 (12) |
| C1A—C2A—C14A—O15A$^{i}$ | −41.16 (18) | C1B—C2B—C14B—O16B | 18.58 (19) |
| C3A—C2A—C14A—O16A | −39.11 (17) | C3B—C2B—C14B—O15B$^{i}$ | 17.83 (18) |

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|---|---|---|---|
| C1A—C2A—C14A—O16A | 140.91 (13) | C1B—C2B—C14B—O15B$^{i}$ | −160.74 (13) |
| O15A$^{i}$—C14A—O16A—Cu1 | −5.3 (2) | O15B$^{i}$—C14B—O16B—Cu1 | 6.7 (2) |
| C2A—C14A—O16A—Cu1 | 172.44 (8) | C2B—C14B—O16B—Cu1 | −172.57 (9) |
| C3A—C4A—N17A—O18A | −179.13 (13) | C3B—C4B—N17B—O18B | 172.27 (13) |
| C5A—C4A—N17A—O18A | 2.94 (19) | C5B—C4B—N17B—O18B | −8.87 (19) |
| C3A—C4A—N17A—O19A | 0.73 (19) | C3B—C4B—N17B—O19B | −8.25 (19) |
| C5A—C4A—N17A—O19A | −177.20 (13) | C5B—C4B—N17B—O19B | 170.61 (13) |

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

*Hydrogen-bond geometry (Å, º)*

*Cg*4 is the centroid of the C8*B*–C13*B* ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C6*B*—H6*B*···O18*A*$^{ii}$ | 0.95 | 2.65 | 3.2785 (17) | 124 |
| C9*B*—H9*B*···O19*B*$^{iii}$ | 0.95 | 2.39 | 3.2351 (19) | 148 |
| C10—H10*A*···*Cg*4$^{iv}$ | 0.95 | 2.63 | 3.4171 (17) | 140 |

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+2, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*.