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## Structure Reports

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**Cu<sub>2</sub>ZnSiS<sub>4</sub>**

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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{S}-\text{Si}) = 0.002$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.051; data-to-parameter ratio = 24.5.

Single crystals of Cu<sub>2</sub>ZnSiS<sub>4</sub>, dicopper(I) zinc silicon tetrasulfide, have been prepared *via* high-temperature solid-state synthesis. Cu<sub>2</sub>ZnSiS<sub>4</sub> was found to have the wurtz-stannite structure type, like that of Li<sub>2</sub>CdGeS<sub>4</sub>, Li<sub>2</sub>CdSnS<sub>4</sub>, and Cu<sub>2</sub>CdSiS<sub>4</sub>. Each sulfur anion is tetrahedrally coordinated by two Cu cations, one Si cation, and one Zn cation, forming a three-dimensional honeycomb structure. When viewed along the  $c$  axis, the atoms are aligned in rows in which each cation alternates with the sulfur anions.

## Related literature

For synthetic procedures, see: Himmrich & Haeuseler (1991); Nitsche *et al.* (1967); Yao *et al.* (1987). For related structures, see: Chapuis & Niggli (1972); Lekse *et al.* (2008, 2009); Schäfer & Nitsche (1974). For optical properties, see: Levenco *et al.* (2010).

## Experimental

## Crystal data

Cu<sub>2</sub>ZnSiS<sub>4</sub>  $V = 292.24$  (1) Å<sup>3</sup>  
 $M_r = 348.78$   $Z = 2$   
Orthorhombic,  $Pmn2_1$  Mo  $K\alpha$  radiation  
 $a = 7.4374$  (1) Å  $\mu = 12.77$  mm<sup>-1</sup>  
 $b = 6.4001$  (1) Å  $T = 296$  K  
 $c = 6.1394$  (1) Å  $0.13 \times 0.07 \times 0.06$  mm

## Data collection

Bruker SMART APEX diffractometer 5153 measured reflections  
Absorption correction: multi-scan (SADABS; Sheldrick, 2002) 1078 independent reflections  
 $T_{\min} = 0.290$ ,  $T_{\max} = 0.500$  1023 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   $\Delta\rho_{\text{max}} = 0.72$  e Å<sup>-3</sup>  
 $wR(F^2) = 0.051$   $\Delta\rho_{\text{min}} = -1.01$  e Å<sup>-3</sup>  
 $S = 1.14$  Absolute structure: Flack (1983),  
44 parameters 449 Friedel pairs  
1 restraint Flack parameter: 0.02 (1)

Table 1

Selected bond lengths (Å).

|                      |            |                       |            |
|----------------------|------------|-----------------------|------------|
| Cu1—S <sup>2i</sup>  | 2.3170 (7) | Zn1—S <sup>3iii</sup> | 2.3650 (7) |
| Cu1—S3               | 2.325 (1)  | Zn1—S <sup>3iv</sup>  | 2.3650 (7) |
| Cu1—S1               | 2.3270 (6) | Si1—S1                | 2.131 (1)  |
| Cu1—S <sup>3ii</sup> | 2.3426 (7) | Si1—S <sup>3v</sup>   | 2.136 (1)  |
| Zn1—S2               | 2.322 (1)  | Si1—S <sup>3vi</sup>  | 2.136 (1)  |
| Zn1—S1               | 2.322 (1)  | Si1—S <sup>3vii</sup> | 2.143 (3)  |

Symmetry codes: (i)  $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$ ; (ii)  $-x + \frac{1}{2}, -y, z + \frac{1}{2}$ ; (iii)  $-x, y, z + 1$ ; (iv)  $x, y, z + 1$ ; (v)  $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ; (vi)  $x - \frac{1}{2}, -y + 1, z + \frac{1}{2}$ ; (vii)  $x, y, z - 1$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2010); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2337).

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## supporting information

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**Cu<sub>2</sub>ZnSiS<sub>4</sub>**

**Kimberly A. Rosmus and Jennifer A. Aitken**

**S1. Comment**

Cu<sub>2</sub>ZnSiS<sub>4</sub> was prepared as crystals *via* iodine vapor transport reactions as early as 1967 (Nitsche *et al.*, 1967); however, only lattice parameters were reported. Using the same synthetic method to prepare Cu<sub>2</sub>ZnSiS<sub>4</sub>, Yao *et al.* reported the infrared spectrum of this compound (Yao *et al.*, 1987). Alternatively Cu<sub>2</sub>ZnSiS<sub>4</sub> can be synthesized by grinding stoichiometric amounts of the elements and reacting them in a vibrational mill multiple times during the heating process (Himmrich & Haeuseler, 1991). More recently, the band gap of the title compound has been reported (Levcenco *et al.*, 2010). In this paper, Cu<sub>2</sub>ZnSiS<sub>4</sub> was prepared as relatively small single crystals using a simple high-temperature solid-state synthesis.

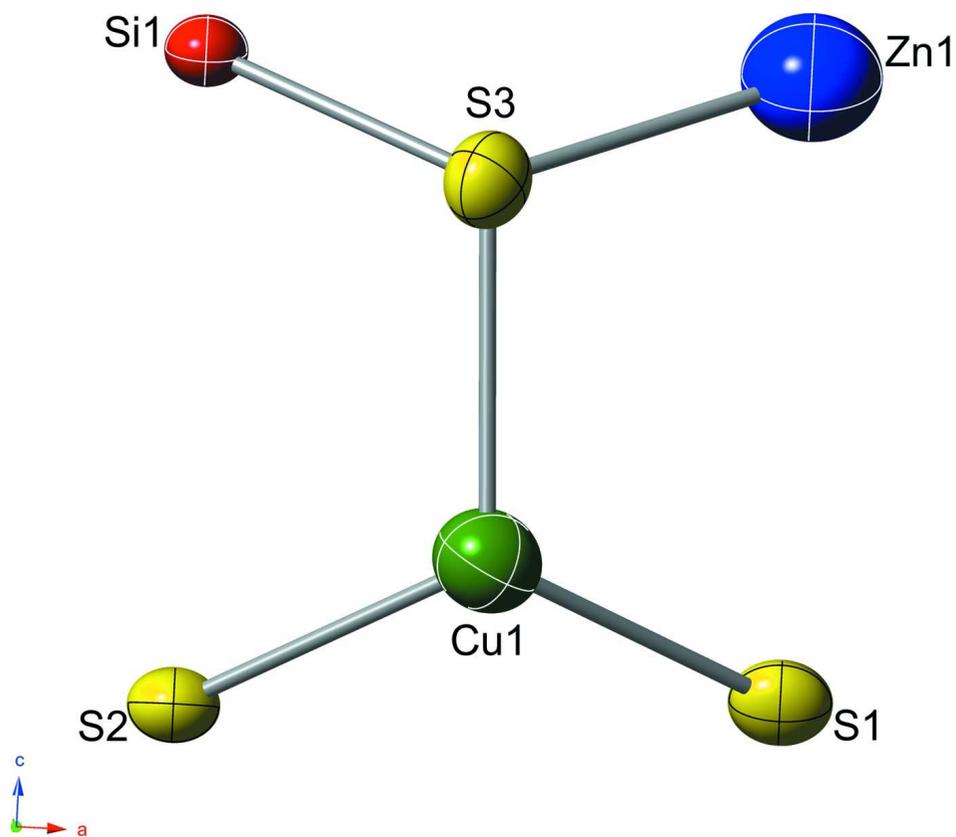
Cu<sub>2</sub>ZnSiS<sub>4</sub> possesses the wurtz-stannite structure type (Schäfer, & Nitsche, 1974) like that of Li<sub>2</sub>CdGeS<sub>4</sub>, Li<sub>2</sub>CdSnS<sub>4</sub> (Lekse *et al.*, 2009), and Cu<sub>2</sub>CdSiS<sub>4</sub> (Chapuis & Niggli, 1972). The asymmetric unit can be observed in Figure 1.

Cu<sub>2</sub>ZnSiS<sub>4</sub> has a diamond-like structure, where every cation is tetrahedrally coordinated with sulfur anions. The bond lengths for M—S range from 2.3170 (7)–2.3426 (7) Å for M=Cu, 2.322 (1)–2.3650 (7) Å for M=Zn, and 2.131 (1)–2.143 (3) Å for M=Si (Table 1). Every MS<sub>4</sub> tetrahedron points in the same direction along the crystallographic *b* axis rendering the structure noncentrosymmetric (Fig.2). When viewed down the *c* axis, the ions are aligned in rows where each cation alternates with the sulfur anions (Fig.3).

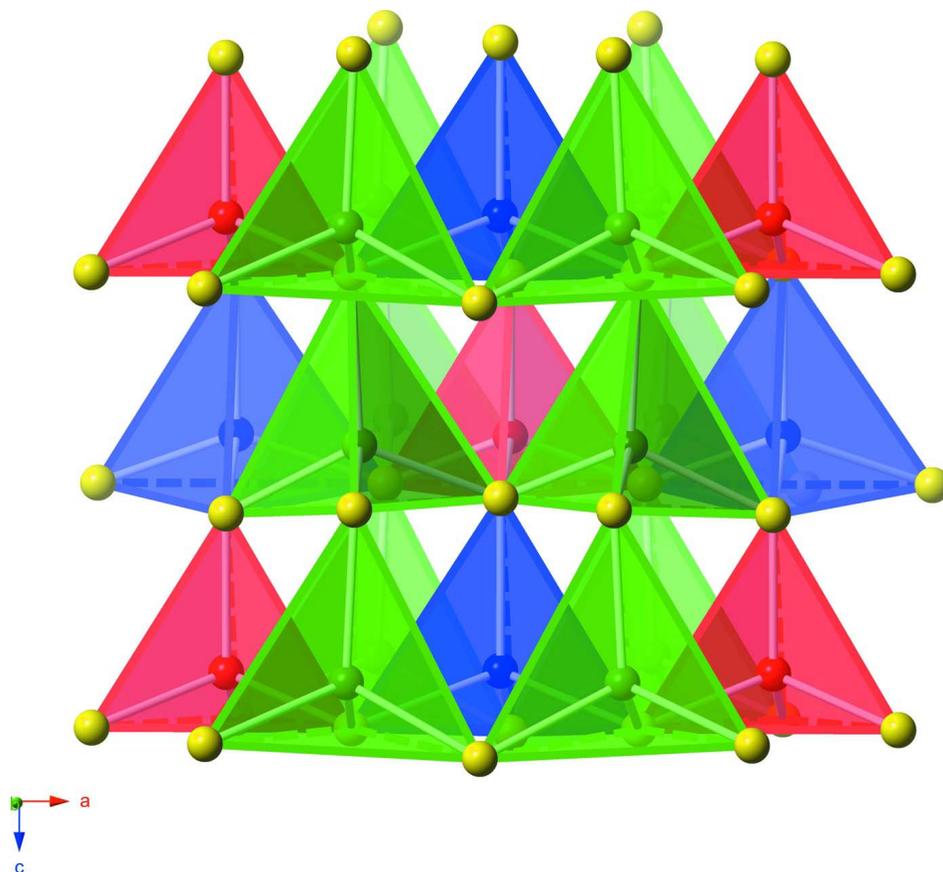
Recently second harmonic generation for a couple of compounds of this structure type, Li<sub>2</sub>CdGeS<sub>4</sub> and Li<sub>2</sub>CdSnS<sub>4</sub>, have been reported on powder samples (Lekse *et al.*, 2009). Therefore it is of interest to further study Cu<sub>2</sub>ZnSiS<sub>4</sub>.

**S2. Experimental**

Cu<sub>2</sub>ZnSiS<sub>4</sub> was prepared *via* high-temperature solid-state synthesis. Stoichiometric ratios of the elements were weighed and then ground for 30 min in an argon-filled glovebox using an agate mortar and pestle. The sample was placed into a graphite crucible, which was then inserted in a 12 mm outer diameter fused-silica tube. The tube was flame sealed under a vacuum of 10<sup>-3</sup> mbar and transported to a computer-controlled furnace. The sample was heated to 1000°C in 12hrs, held at 1000°C for 168hrs and then cooled at 7.5°C/hr to room temperature. When removed from the furnace, blue rod-like crystals of approximate size 0.13 x 0.07 x 0.6 mm were found under a light microscope.

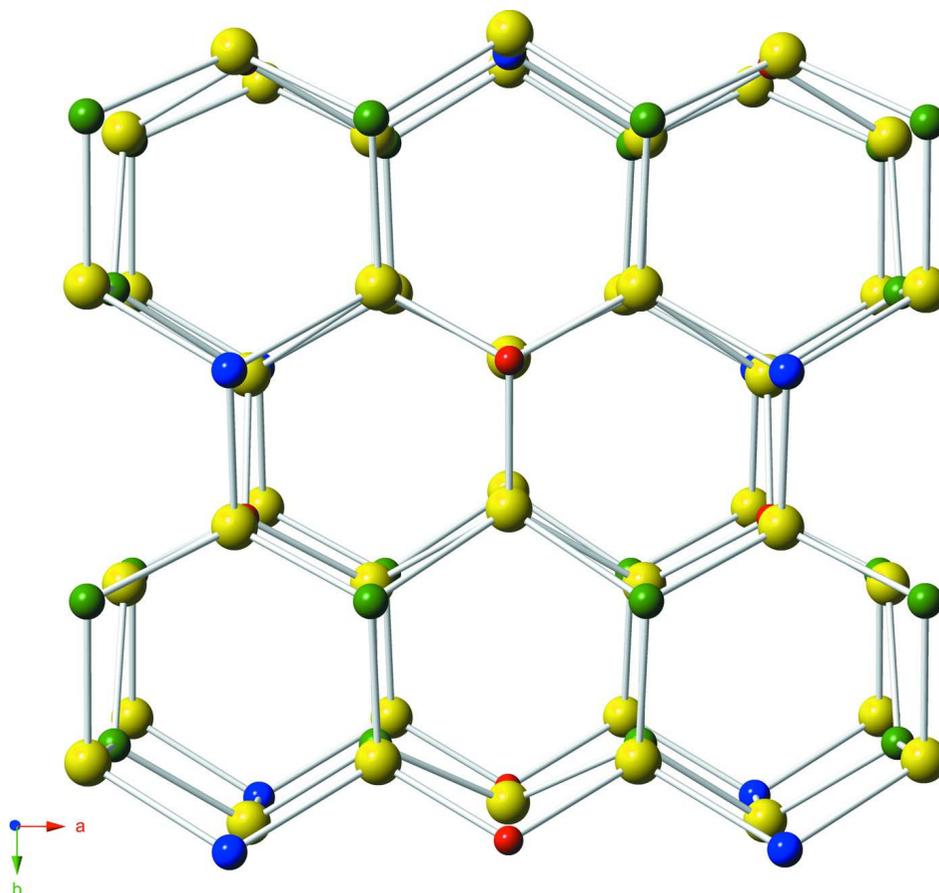
**Figure 1**

Asymmetric unit of  $\text{Cu}_2\text{ZnSiS}_4$  using 95% probability thermal ellipsoids.



**Figure 2**

Polyhedral view down the  $b$  axis of  $\text{Cu}_2\text{ZnSiS}_4$  with sulfur anions as the corners of each tetrahedron.

**Figure 3**

$\text{Cu}_2\text{ZnSiS}_4$  viewed along the  $c$  axis showing a three-dimensional honeycomb structure where the atoms are aligned in rows with each cation alternating with sulfur anions. Color code: Cu - green, Zn - blue, Si - red, and S - yellow.

### dicopper(I) zinc silicon tetrasulfide

#### Crystal data

$\text{Cu}_2\text{ZnSiS}_4$

$M_r = 348.78$

Orthorhombic,  $Pmn2_1$

Hall symbol: P 2ac -2

$a = 7.4374$  (1) Å

$b = 6.4001$  (1) Å

$c = 6.1394$  (1) Å

$V = 292.24$  (1) Å<sup>3</sup>

$Z = 2$

$F(000) = 332$

$D_x = 3.964$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 3127 reflections

$\theta = 3.2\text{--}32.2^\circ$

$\mu = 12.77$  mm<sup>-1</sup>

$T = 296$  K

Rod, blue

$0.13 \times 0.07 \times 0.06$  mm

#### Data collection

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2002)

$T_{\min} = 0.290$ ,  $T_{\max} = 0.500$

5153 measured reflections

1078 independent reflections

1023 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$   
 $\theta_{\text{max}} = 32.9^\circ$ ,  $\theta_{\text{min}} = 3.2^\circ$   
 $h = -11 \rightarrow 11$

$k = -9 \rightarrow 9$   
 $l = -9 \rightarrow 9$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.051$   
 $S = 1.14$   
 1078 reflections  
 44 parameters  
 1 restraint  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

$w = 1/[\sigma^2(F_o^2) + (0.0067P)^2 + 0.2702P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.72 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.01 \text{ e } \text{Å}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick,  
 2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.025 (1)  
 Absolute structure: Flack (1983), **449 Friedel  
 pairs**  
 Absolute structure parameter: 0.02 (1)

*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 ( $\text{Å}^2$ )*

|     | $x$         | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| Cu1 | 0.24741 (3) | 0.17426 (4) | 0.33723 (8)  | 0.0133 (1)                       |
| Zn1 | 0.0000      | 0.34747 (7) | 0.84124 (15) | 0.0211 (1)                       |
| Si1 | 0.0000      | 0.6743 (1)  | 0.3451 (4)   | 0.0071 (1)                       |
| S1  | 0.0000      | 0.3611 (1)  | 0.4632 (1)   | 0.0094 (1)                       |
| S2  | 0.0000      | 0.6784 (1)  | 0.9961 (2)   | 0.0089 (2)                       |
| S3  | 0.26269 (8) | 0.1724 (1)  | -0.0411 (1)  | 0.0100 (1)                       |

*Atomic displacement parameters ( $\text{Å}^2$ )*

|     | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|------------|------------|------------|-------------|-------------|-------------|
| Cu1 | 0.0141 (1) | 0.0135 (1) | 0.0125 (2) | -0.0007 (1) | -0.0008 (1) | 0.0000 (2)  |
| Zn1 | 0.0235 (2) | 0.0210 (2) | 0.0191 (3) | 0.000       | 0.000       | -0.0016 (3) |
| Si1 | 0.0078 (3) | 0.0077 (3) | 0.0058 (5) | 0.000       | 0.000       | 0.0007 (4)  |
| S1  | 0.0126 (3) | 0.0072 (3) | 0.0085 (5) | 0.000       | 0.000       | 0.0011 (4)  |
| S2  | 0.0099 (3) | 0.0104 (3) | 0.0064 (6) | 0.000       | 0.000       | -0.0001 (3) |
| S3  | 0.0089 (2) | 0.0101 (3) | 0.0110 (5) | -0.0012 (1) | 0.0006 (3)  | 0.0000 (3)  |

## Geometric parameters (Å, °)

|   |            |  |            |
|---|------------|--|------------|
| Cu1—S2 <sup>i</sup>                     | 2.3170 (7) | Si1—S3 <sup>vi</sup>                     | 2.136 (1)  |
| Cu1—S3                                  | 2.325 (1)  | Si1—S2 <sup>vii</sup>                    | 2.143 (3)  |
| Cu1—S1                                  | 2.3270 (6) | S1—Cu1 <sup>viii</sup>                   | 2.3270 (6) |
| Cu1—S3 <sup>ii</sup>                    | 2.3426 (7) | S2—Si1 <sup>iv</sup>                     | 2.143 (3)  |
| Zn1—S2                                  | 2.322 (1)  | S2—Cu1 <sup>vi</sup>                     | 2.3170 (7) |
| Zn1—S1                                  | 2.322 (1)  | S2—Cu1 <sup>v</sup>                      | 2.3170 (7) |
| Zn1—S3 <sup>iii</sup>                   | 2.3650 (7) | S3—Si1 <sup>i</sup>                      | 2.136 (1)  |
| Zn1—S3 <sup>iv</sup>                    | 2.3650 (7) | S3—Cu1 <sup>ix</sup>                     | 2.3426 (7) |
| Si1—S1                                  | 2.131 (1)  | S3—Zn1 <sup>vii</sup>                    | 2.3650 (7) |
| Si1—S3 <sup>v</sup>                     | 2.136 (1)  |  |            |
| S2 <sup>i</sup> —Cu1—S3                 | 112.51 (4) | Si1—S1—Zn1                               | 112.05 (8) |
| S2 <sup>i</sup> —Cu1—S1                 | 106.98 (3) | Si1—S1—Cu1 <sup>viii</sup>               | 111.72 (5) |
| S3—Cu1—S1                               | 111.92 (4) | Zn1—S1—Cu1 <sup>viii</sup>               | 108.24 (4) |
| S2 <sup>i</sup> —Cu1—S3 <sup>ii</sup>   | 106.09 (4) | Si1—S1—Cu1                               | 111.72 (5) |
| S3—Cu1—S3 <sup>ii</sup>                 | 108.38 (3) | Zn1—S1—Cu1                               | 108.24 (4) |
| S1—Cu1—S3 <sup>ii</sup>                 | 110.82 (4) | Cu1 <sup>viii</sup> —S1—Cu1              | 104.51 (4) |
| S2—Zn1—S1                               | 112.01 (5) | Si1 <sup>iv</sup> —S2—Cu1 <sup>vi</sup>  | 115.21 (4) |
| S2—Zn1—S3 <sup>iii</sup>                | 107.88 (4) | Si1 <sup>iv</sup> —S2—Cu1 <sup>v</sup>   | 115.21 (4) |
| S1—Zn1—S3 <sup>iii</sup>                | 108.84 (4) | Cu1 <sup>vi</sup> —S2—Cu1 <sup>v</sup>   | 108.34 (5) |
| S2—Zn1—S3 <sup>iv</sup>                 | 107.88 (4) | Si1 <sup>iv</sup> —S2—Zn1                | 113.46 (6) |
| S1—Zn1—S3 <sup>iv</sup>                 | 108.84 (4) | Cu1 <sup>vi</sup> —S2—Zn1                | 101.47 (4) |
| S3 <sup>iii</sup> —Zn1—S3 <sup>iv</sup> | 111.40 (5) | Cu1 <sup>v</sup> —S2—Zn1                 | 101.47 (4) |
| S1—Si1—S3 <sup>v</sup>                  | 108.68 (7) | Si1 <sup>i</sup> —S3—Cu1                 | 111.38 (7) |
| S1—Si1—S3 <sup>vi</sup>                 | 108.68 (7) | Si1 <sup>i</sup> —S3—Cu1 <sup>ix</sup>   | 110.92 (5) |
| S3 <sup>v</sup> —Si1—S3 <sup>vi</sup>   | 111.40 (7) | Cu1—S3—Cu1 <sup>ix</sup>                 | 108.76 (3) |
| S1—Si1—S2 <sup>vii</sup>                | 110.60 (9) | Si1 <sup>i</sup> —S3—Zn1 <sup>vii</sup>  | 111.42 (5) |
| S3 <sup>v</sup> —Si1—S2 <sup>vii</sup>  | 108.74 (7) | Cu1—S3—Zn1 <sup>vii</sup>                | 105.21 (4) |
| S3 <sup>vi</sup> —Si1—S2 <sup>vii</sup> | 108.74 (7) | Cu1 <sup>ix</sup> —S3—Zn1 <sup>vii</sup> | 108.95 (3) |

Symmetry codes: (i)  $-x+1/2, -y+1, z-1/2$ ; (ii)  $-x+1/2, -y, z+1/2$ ; (iii)  $-x, y, z+1$ ; (iv)  $x, y, z+1$ ; (v)  $-x+1/2, -y+1, z+1/2$ ; (vi)  $x-1/2, -y+1, z+1/2$ ; (vii)  $x, y, z-1$ ; (viii)  $-x, y, z$ ; (ix)  $-x+1/2, -y, z-1/2$ .