

# The dehydrated copper silicate Na<sub>2</sub>[Cu<sub>2</sub>Si<sub>4</sub>O<sub>11</sub>]: a three-dimensional microporous framework with a linear Si—O—Si linkage

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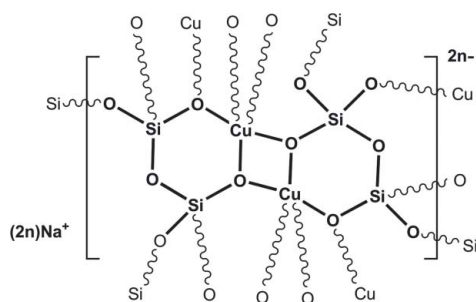
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{Si—O}) = 0.004$  Å;  
R factor = 0.043;  $wR$  factor = 0.120; data-to-parameter ratio = 11.9.

The structure of the title dehydrated copper silicate, disodium dicopper undecaoxide tetrasilicate, Na<sub>2</sub>(Cu<sub>2</sub>O<sub>11</sub>Si<sub>4</sub>), was determined by single-crystal X-ray diffraction from a non-merohedral twin. It exhibits an effective three-dimensional microporous framework with the major channels, in which the Na<sup>+</sup> cations are placed, running along the  $a$ -axis direction and smaller channels observed along the  $b$ -axis direction. The structure is unusual in that it contains a symmetry-constrained Si—O—Si angle of 180°. The Cu centre is coordinated to five O atoms, exhibiting a slightly distorted square-pyramidal coordination geometry. The Na cation is interacting with five neighbouring O atoms, exhibiting an uncharacteristic coordination environment.

## Related literature

For related literature, see: Brandão *et al.* (2005); Haile & Wuensch (2000); Liebau (1985); Rocha & Anderson (2000); Rocha & Lin (2005); dos Santos *et al.* (2005); Ananias *et al.* (2001, 2006); Anderson *et al.* (1994); Ferreira *et al.* (2003).



## Experimental

### Crystal data

Na <sub>2</sub> (Cu <sub>2</sub> O <sub>11</sub> Si <sub>4</sub> )	$\gamma = 100.461$ (7)°
$M_r = 461.44$	$V = 258.9$ (2) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 1$
$a = 5.190$ (2) Å	Mo $K\alpha$ radiation
$b = 6.299$ (3) Å	$\mu = 4.71$ mm <sup>-1</sup>
$c = 8.196$ (4) Å	$T = 298$ (2) K
$\alpha = 96.390$ (7)°	$0.28 \times 0.08 \times 0.04$ mm
$\beta = 97.281$ (7)°	

### Data collection

Bruker SMART CCD 1000 diffractometer	1587 measured reflections
Absorption correction: multi-scan (TWINABS; Sheldrick, 2002)	1043 independent reflections
$T_{\min} = 0.627$ , $T_{\max} = 0.834$	782 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	88 parameters
$wR(F^2) = 0.119$	$\Delta\rho_{\text{max}} = 1.40$ e Å <sup>-3</sup>
$S = 1.01$	$\Delta\rho_{\text{min}} = -1.58$ e Å <sup>-3</sup>
1043 reflections	

Table 1

Selected bond lengths (Å).

Cu1—O5 <sup>i</sup>	1.909 (3)	Cu1—O6	1.974 (3)
Cu1—O2	1.950 (4)	Cu1—O2 <sup>iii</sup>	2.316 (4)
Cu1—O6 <sup>ii</sup>	1.970 (4)		

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

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2003); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXTL (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2065).

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**supplementary materials**

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## The dehydrated copper silicate $\text{Na}_2[\text{Cu}_2\text{Si}_4\text{O}_{11}]$ : a three-dimensional microporous framework with a linear Si-O-Si linkage

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### Comment

Molecular sieves containing metal cations with a range of coordination geometries have been extensively studied due to their novel topologies, interesting chemical properties and potential applications in optoelectronics, batteries, magnetic materials and sensors (besides the traditional applications of zeolites) (Rocha & Anderson, 2000; Rocha & Lin, 2005). In the last decade, we have been interested in the synthesis and structural characterization of novel open-frameworks containing Si and metal cations (such as Ti, V, Cr, Nb, Zr and Sn) in tetrahedral and (more commonly) octahedral coordination environments, and lanthanide silicates exhibiting interesting photoluminescence properties (Anderson *et al.*, 1994; Ananias *et al.*, 2001; Ferreira *et al.*, 2003; Ananias *et al.*, 2006). As part of this research line, we prepared and characterized the hydrated copper silicate  $\text{Na}_2(\text{Cu}_2\text{Si}_4\text{O}_{11})\cdot 2\text{H}_2\text{O}$  (Brandão *et al.*, 2005). This compound was dehydrated and the magnetic properties of both hydrated and dehydrated forms were investigated (Santos *et al.*, 2005), however the crystalline structure of the dehydrated compound was not reported. Here we describe the structure of the dehydrated microporous copper silicate,  $\text{Na}_2(\text{Cu}_2\text{Si}_4\text{O}_{11})$  (I).

The asymmetric unit of the copper silicate (I) comprises one Cu(II) cation, two corner-shared  $\text{SiO}_4$  groups and one  $\text{Na}^+$  counter-cation (Figure 1). The crystallographic unique Cu(II) metal centre is coordinated to five O-atoms from five distinct  $\text{SiO}_4$  tetrahedral moieties (four basal  $\text{SiO}_4$  and one apical  $\text{SiO}_4$ ), in a geometry resembling a distorted square pyramid for which the apical Cu—O bond is longer than the basal ones (Figure 2a and Table 1).

Adjacent  $\text{SiO}_4$  tetrahedral moieties are linked along the *a* direction by corner-shared oxygen atoms (O3 and O4 are shared alternately) leading to the formation of zigzag metallic anionic chains,  $[(\text{Cu}_2\text{Si}_4\text{O}_{11})_\infty]^{2-}$ , in which the Cu...Cu distances alternate between 2.9921 (8) Å (*via* bridging basal  $\text{SiO}_4$ , green bonds in Fig. 2 b) and 3.1031 (10) Å (*via* the apical  $\text{SiO}_4$  tetrahedron, yellow bonds in Fig. 2 b).  $[(\text{Cu}_2\text{Si}_4\text{O}_{11})_\infty]^{2-}$  chains are interconnected *via* corner-sharing  $\text{SiO}_4$  tetrahedra through linear interactions Si1—O1—Si<sup>iv</sup> [angle is 180.0°; symmetry code: (iv) 2 - x, -y, 1 - z] to form infinite layers (Fig. 2c). This linear Si—O—Si interaction is very rare and represents a remarkable structural feature of the copper silicate (I) framework. We note that such occurrence was also recently reported in the lanthanide silicate  $\text{K}_3(\text{NdSi}_7\text{O}_{17})$  (Haile & Wuensch, 2000). From the evaluation of the structures of several hundred silicates it was concluded that the average of an unstrained Si—O—Si bond angle is *ca* 139° and that truly linear bonds are energetically unfavorable (Liebau, 1985). In fact, the crystallographically determined values of 180° are more likely to represent a time average rather than the actual value of the bond angle. The bond, at any instant in time, should have an O-atom displaced from its average position such that the instantaneous value of Si—O—Si is less than 180° (Haile & Wuensch, 2000). This structural feature is ultimately reflected in the anisotropic displacement parameters associated with this bridging O-atom. Indeed, the thermal parameters associated with this atom are unusually large, with the greatest displacement occurring in the plane perpendicular to the Si1...Si1<sup>iv</sup> vector (Figure 2c).

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As observed for the chains, adjacent layers are also interconnected *via* corner-sharing SiO<sub>4</sub> tetrahedra generating a three-dimensional microporous framework with the major channels running along the *a* direction, formed by eight-membered rings and having a cross-section of *ca* 7.5 × 4.3 Å (Figure 3a). Interestingly, the Na<sup>+</sup> cations are located within the channels but are remarkably close to the previously described layers, creating an effective porous copper framework (Figure 3a). In addition, remarkably large channels are also observed along the *b* direction, which are formed by six-membered rings and display a cross-section of *ca* 5.2 × 4.6 Å (Figure 3 b).

### Experimental

Chemicals were purchased from commercial sources and used without further purification. An alkaline solution was prepared by mixing 13.86 g of a sodium silicate solution (Na<sub>2</sub>O 8 wt%, SiO<sub>2</sub> 27 wt%), 16.13 g H<sub>2</sub>O and 4.11 g NaOH, and a second solution was prepared by mixing 17.87 g H<sub>2</sub>O with 7.60 g of Cu(SO<sub>4</sub>).15H<sub>2</sub>O. These two solutions were combined, stirred thoroughly during 2 h and the resulting gel, with a molar composition of CuO: 3.1SiO<sub>2</sub>: 1.4Na<sub>2</sub>O: 94.5H<sub>2</sub>O, was autoclaved for 10 days at 503 K. A crystalline material was obtained [Na<sub>2</sub>(Cu<sub>2</sub>Si<sub>4</sub>O<sub>11</sub>)·2H<sub>2</sub>O], filtered and treated thermally at 573 K for six hours leads to the removal of the crystallization water molecules.

### Refinement

Even though crystals of the title compound could be indexed with the unit-cell parameters summarized in Table 1, a visual inspection of the centered reflections using RLATT showed the presence of a rotational twin (non-merohedral). A full sphere of reflections was collected and a partial data set was then deconvoluted using CELL\_NOW (Sheldrick 2004) into a two-component twin. Data integration was performed by assuming that the second twin domain was identical to the first. The final structural model exhibits a large average *U*(i,j) tensor, most likely due to the applied twinning correction which ultimately seems to lead to large *U*3/*U*1 ratios.

### Figures

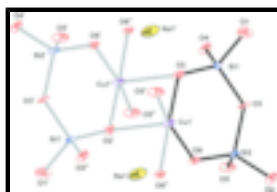


Fig. 1. Fragment of the crystal structure of the title compound with the atoms represented as thermal displacement ellipsoids drawn at the 50% probability level [Symmetry codes: (i) 2 - *x*, -*y*, 2 - *z*; (ii) *x*, -1 + *y*, *z*; (iii) 1 - *x*, -*y*, 2 - *z*; (iv) 2 - *x*, 1 - *y*, 2 - *z*; (v) *x*, *y*, 1 + *z*; (vi) 1 + *x*, *y*, *z*].

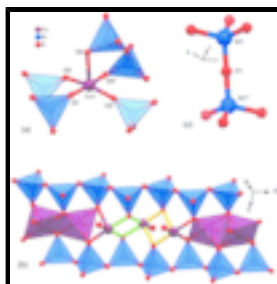


Fig. 2. (a) Mixed ball-and-stick and polyhedral representation of the coordination environment of the Cu(II) cations and (b) the metallic chain [(Cu<sub>2</sub>Si<sub>4</sub>O<sub>11</sub>)<sub>n</sub>]<sup>2-</sup> running along the *a* direction of the unit cell. (c) Schematic representation of the linear Si—O—Si bond connecting adjacent Si1 centres *via* the O1 atom. [Symmetry codes: (i) 2 - *x*, -*y*, 2 - *z*; (ii) *x*, -1 + *y*, *z*; (iii) 1 - *x*, -*y*, 2 - *z*; (iv) 2 - *x*, -*y*, 1 - *z*].

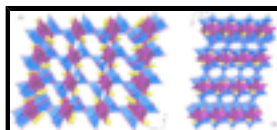


Fig. 3. Perspective views of the crystal packing arrangement along the (a) [100] and (b) [010] directions of unit cell.

**disodium dicopper undecaoxide tetrasilicate**

*Crystal data*

Na <sub>2</sub> (Cu <sub>2</sub> O <sub>11</sub> Si <sub>4</sub> )	Z = 1
$M_r = 461.44$	$F_{000} = 224$
Triclinic, $P\bar{1}$	$D_x = 2.960 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 5.190 (2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 6.299 (3) \text{ \AA}$	Cell parameters from 758 reflections
$c = 8.196 (4) \text{ \AA}$	$\theta = 8.1\text{--}58.1^\circ$
$\alpha = 96.390 (7)^\circ$	$\mu = 4.71 \text{ mm}^{-1}$
$\beta = 97.281 (7)^\circ$	$T = 298 (2) \text{ K}$
$\gamma = 100.461 (7)^\circ$	Plate, black
$V = 258.9 (2) \text{ \AA}^3$	$0.28 \times 0.08 \times 0.04 \text{ mm}$

*Data collection*

Bruker SMART CCD 1000 diffractometer	1043 independent reflections
Radiation source: fine-focus sealed tube	782 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.042$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 26.4^\circ$
$\omega$ scans	$\theta_{\text{min}} = 3.9^\circ$
Absorption correction: multi-scan (TWINABS; Sheldrick, 2002)	$h = -6 \rightarrow 6$
$T_{\text{min}} = 0.627$ , $T_{\text{max}} = 0.834$	$k = -7 \rightarrow 7$
1587 measured reflections	$l = 0 \rightarrow 10$

*Refinement*

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1043 reflections	$\Delta\rho_{\text{max}} = 1.40 \text{ e \AA}^{-3}$
88 parameters	$\Delta\rho_{\text{min}} = -1.58 \text{ e \AA}^{-3}$
	Extinction correction: none

*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

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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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.70666 (10)	-0.10891 (9)	0.93472 (8)	0.0096 (3)
Na1	0.8700 (4)	0.3540 (3)	1.1990 (3)	0.0235 (6)
Si1	1.0175 (2)	0.1358 (2)	0.67930 (18)	0.0087 (4)
Si2	0.5954 (3)	0.3456 (2)	0.80969 (18)	0.0089 (4)
O1	1.0000	0.0000	0.5000	0.0217 (13)
O2	1.0064 (7)	-0.0190 (6)	0.8196 (5)	0.0127 (8)
O3	0.7804 (6)	0.2736 (6)	0.6719 (5)	0.0126 (8)
O4	0.2923 (6)	0.3209 (5)	0.7137 (5)	0.0144 (8)
O5	0.7200 (7)	0.5899 (6)	0.8873 (5)	0.0170 (9)
O6	0.5974 (6)	0.1760 (5)	0.9452 (5)	0.0107 (8)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0054 (4)	0.0083 (4)	0.0159 (4)	0.0011 (2)	0.0051 (2)	0.0018 (2)
Na1	0.0137 (11)	0.0161 (12)	0.0396 (16)	0.0021 (9)	0.0072 (10)	-0.0030 (10)
Si1	0.0048 (7)	0.0096 (7)	0.0124 (8)	0.0018 (5)	0.0034 (5)	0.0009 (5)
Si2	0.0040 (6)	0.0078 (7)	0.0155 (8)	0.0013 (5)	0.0042 (5)	0.0018 (5)
O1	0.020 (3)	0.024 (3)	0.021 (3)	0.006 (2)	0.007 (2)	-0.006 (2)
O2	0.0078 (17)	0.0137 (18)	0.018 (2)	0.0033 (13)	0.0040 (14)	0.0045 (14)
O3	0.0057 (16)	0.0169 (19)	0.018 (2)	0.0068 (14)	0.0049 (14)	0.0018 (14)
O4	0.0063 (16)	0.0140 (18)	0.023 (2)	0.0017 (14)	0.0014 (14)	0.0061 (15)
O5	0.0145 (18)	0.0100 (18)	0.028 (2)	0.0000 (14)	0.0129 (16)	0.0016 (15)
O6	0.0082 (16)	0.0111 (17)	0.016 (2)	0.0039 (13)	0.0061 (14)	0.0050 (14)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cu1—O5 <sup>i</sup>	1.909 (3)	Si1—O4 <sup>iv</sup>	1.642 (4)
Cu1—O2	1.950 (4)	Si2—O5	1.583 (4)
Cu1—O6 <sup>ii</sup>	1.970 (4)	Si2—O6	1.625 (4)
Cu1—O6	1.974 (3)	Si2—O4	1.639 (3)
Cu1—O2 <sup>iii</sup>	2.316 (4)	Si2—O3	1.650 (4)
Cu1—Cu1 <sup>ii</sup>	2.9921 (13)	Si2—Cu1 <sup>ii</sup>	3.1221 (19)
Cu1—Cu1 <sup>iii</sup>	3.1031 (15)	O1—Si1 <sup>v</sup>	1.5991 (14)
Cu1—Si2 <sup>ii</sup>	3.1221 (19)	O2—Cu1 <sup>iii</sup>	2.316 (4)
Cu1—Si1	3.1673 (19)	O4—Si1 <sup>vi</sup>	1.642 (4)

Si1—O2	1.588 (4)	O5—Cu1 <sup>vii</sup>	1.909 (3)
Si1—O1	1.5991 (14)	O6—Cu1 <sup>ii</sup>	1.970 (4)
Si1—O3	1.629 (3)		
O5 <sup>i</sup> —Cu1—O2	92.49 (15)	O2 <sup>iii</sup> —Cu1—Si1	100.98 (10)
O5 <sup>i</sup> —Cu1—O6 <sup>ii</sup>	91.91 (15)	Cu1 <sup>ii</sup> —Cu1—Si1	115.23 (4)
O2—Cu1—O6 <sup>ii</sup>	175.60 (13)	Cu1 <sup>iii</sup> —Cu1—Si1	64.33 (4)
O5 <sup>i</sup> —Cu1—O6	164.27 (15)	Si2 <sup>ii</sup> —Cu1—Si1	179.25 (4)
O2—Cu1—O6	94.42 (14)	O2—Si1—O1	111.33 (15)
O6 <sup>ii</sup> —Cu1—O6	81.32 (16)	O2—Si1—O3	112.6 (2)
O5 <sup>i</sup> —Cu1—O2 <sup>iii</sup>	105.60 (16)	O1—Si1—O3	108.16 (15)
O2—Cu1—O2 <sup>iii</sup>	87.05 (15)	O2—Si1—O4 <sup>iv</sup>	111.48 (19)
O6 <sup>ii</sup> —Cu1—O2 <sup>iii</sup>	91.76 (14)	O1—Si1—O4 <sup>iv</sup>	108.08 (16)
O6—Cu1—O2 <sup>iii</sup>	88.87 (14)	O3—Si1—O4 <sup>iv</sup>	104.92 (18)
O5 <sup>i</sup> —Cu1—Cu1 <sup>ii</sup>	131.06 (12)	O1—Si1—Cu1	115.96 (7)
O2—Cu1—Cu1 <sup>ii</sup>	135.03 (10)	O3—Si1—Cu1	84.08 (15)
O6 <sup>ii</sup> —Cu1—Cu1 <sup>ii</sup>	40.70 (10)	O4 <sup>iv</sup> —Si1—Cu1	129.55 (15)
O6—Cu1—Cu1 <sup>ii</sup>	40.62 (10)	O5—Si2—O6	113.2 (2)
O2 <sup>iii</sup> —Cu1—Cu1 <sup>ii</sup>	90.41 (9)	O5—Si2—O4	111.75 (19)
O5 <sup>i</sup> —Cu1—Cu1 <sup>iii</sup>	103.18 (12)	O6—Si2—O4	109.3 (2)
O2—Cu1—Cu1 <sup>iii</sup>	48.19 (11)	O5—Si2—O3	107.1 (2)
O6 <sup>ii</sup> —Cu1—Cu1 <sup>iii</sup>	130.50 (11)	O6—Si2—O3	107.00 (19)
O6—Cu1—Cu1 <sup>iii</sup>	91.93 (10)	O4—Si2—O3	108.15 (19)
O2 <sup>iii</sup> —Cu1—Cu1 <sup>iii</sup>	38.86 (9)	O5—Si2—Cu1 <sup>ii</sup>	109.62 (16)
Cu1 <sup>ii</sup> —Cu1—Cu1 <sup>iii</sup>	116.74 (4)	O4—Si2—Cu1 <sup>ii</sup>	81.61 (15)
O5 <sup>i</sup> —Cu1—Si2 <sup>ii</sup>	73.75 (12)	O3—Si2—Cu1 <sup>ii</sup>	134.72 (14)
O2—Cu1—Si2 <sup>ii</sup>	156.11 (11)	Si1 <sup>v</sup> —O1—Si1	180.0
O6 <sup>ii</sup> —Cu1—Si2 <sup>ii</sup>	26.72 (10)	Si1—O2—Cu1	126.8 (2)
O6—Cu1—Si2 <sup>ii</sup>	103.96 (11)	Si1—O2—Cu1 <sup>iii</sup>	116.29 (18)
O2 <sup>iii</sup> —Cu1—Si2 <sup>ii</sup>	78.31 (10)	Cu1—O2—Cu1 <sup>iii</sup>	92.95 (15)
Cu1 <sup>ii</sup> —Cu1—Si2 <sup>ii</sup>	64.59 (4)	Si1—O3—Si2	132.7 (3)
Cu1 <sup>iii</sup> —Cu1—Si2 <sup>ii</sup>	115.04 (5)	Si2—O4—Si1 <sup>vi</sup>	137.0 (2)
O5 <sup>i</sup> —Cu1—Si1	106.73 (13)	Si2—O5—Cu1 <sup>vii</sup>	152.9 (2)
O2—Cu1—Si1	23.68 (11)	Si2—O6—Cu1 <sup>ii</sup>	120.24 (18)
O6 <sup>ii</sup> —Cu1—Si1	153.39 (10)	Si2—O6—Cu1	130.3 (2)
O6—Cu1—Si1	75.74 (11)	Cu1 <sup>ii</sup> —O6—Cu1	98.68 (16)

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

Fig. 1

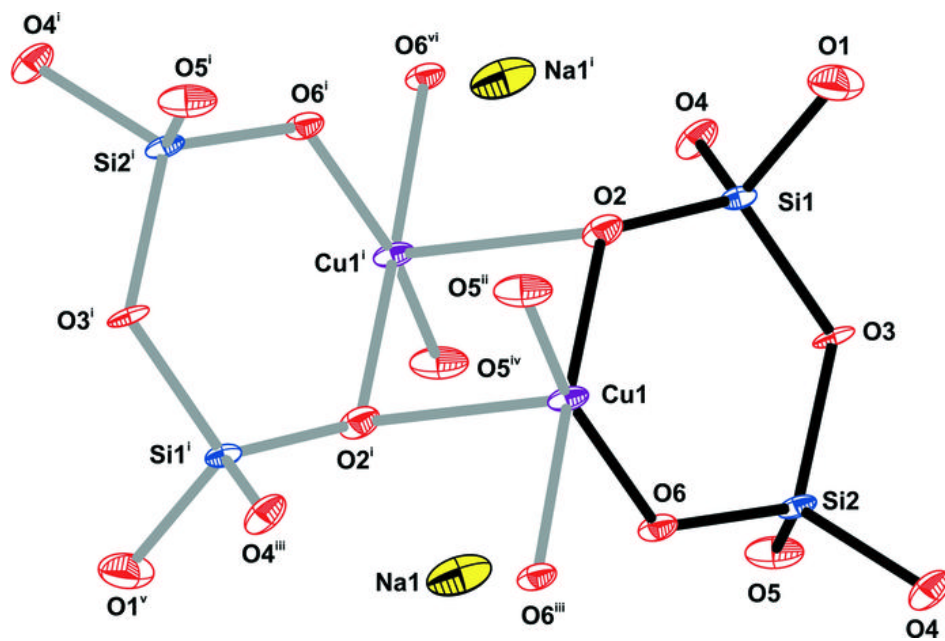


Fig. 2

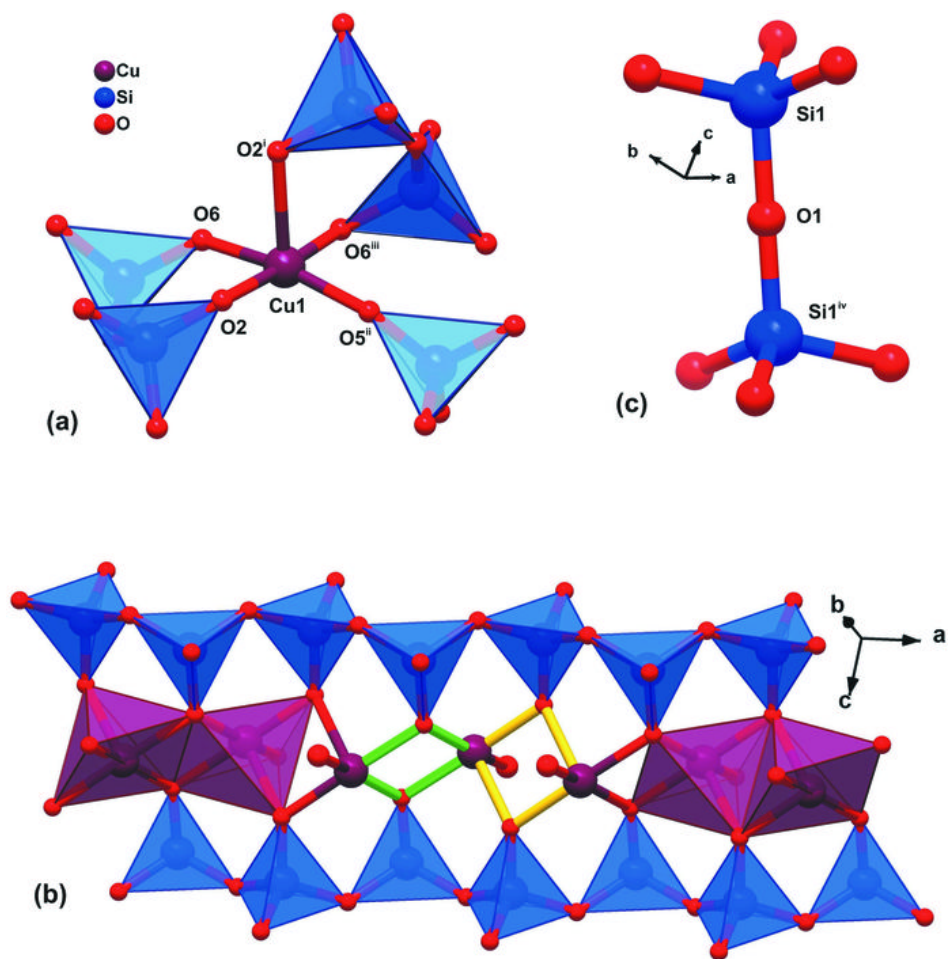


Fig. 3

