

Monoclinic $\text{Cu}_2\text{Se}_3\text{Sn}$ L. D. Gulay,^a M. Daszkiewicz,^{b*} T. A. Ostapyuk,^c O. S. Klymowych^c and O. F. Zmiy^c^aDepartment of Ecology and Protection of the Environment, Volyn National University, Voli Avenue 13, 43009 Lutsk, Ukraine, ^bW. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna Street 2, PO Box 1410, 50-950 Wrocław, Poland, and ^cDepartment of General and Inorganic Chemistry, Volyn National University, Voli Avenue 13, 43009 Lutsk, Ukraine

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A previously unknown modification of dicopper(I) triselenostannate(IV), $\text{Cu}_2\text{Se}_3\text{Sn}$, has been obtained from the Cu_2Se – SnSe_2 quasi-binary system and investigated using X-ray single-crystal diffraction. The Se atoms are stacked in a closest-packed arrangement with the layers in the sequence *ABC*. The Cu atoms occupy one-third of the tetrahedral interstices, whereas the Sn atoms are located in one-sixth of the tetrahedral interstices. All the atoms occupy general positions. The structure possesses pseudo-inversion symmetry. The $\text{Cu}_2\text{Se}_3\text{Sn}$ structure investigated in this paper (96 atoms per unit cell, ordered distribution of Cu and Sn over 12 cation positions) is a superstructure of the reported cubic (eight atoms per unit cell, random distribution of Cu and Sn over one cation position) and monoclinic (24 atoms per unit cell, ordered distribution of Cu and Sn over three cation positions) modifications.

Comment

As a continuation of our studies of ternary chalcogenides, we have examined the Cu_2Se – SnSe_2 system because of the reported formation of several phases of composition $\text{Cu}_2\text{Se}_3\text{Sn}$ that belong to the family of low-melting-point compounds having a tetrahedral lattice, which are of interest for their semiconducting and optical properties (Sharma *et al.*, 1977; Fernandez *et al.*, 1996). Knowledge of the crystal structure of the $\text{Cu}_2\text{Se}_3\text{Sn}$ compounds is important for understanding their properties. Sharma *et al.* (1977) indicated that $\text{Cu}_2\text{Se}_3\text{Sn}$ crystallizes in the cubic sphalerite structure (space group $F\bar{4}3m$, $a = 5.6877$ Å). Recently, Delgado *et al.* (2003) described the structure of $\text{Cu}_2\text{Se}_3\text{Sn}$ in a monoclinic unit cell [$a = 6.9670$ (3) Å, $b = 12.0493$ (7) Å and $c = 6.9453$ (3) Å, and $\beta = 109.19$ (1)°] of the Cu_2GeS_3 structure type (space group Cc). Both studies were based on X-ray powder diffraction data. We present here the crystal structure of a previously unknown

modification of $\text{Cu}_2\text{Se}_3\text{Sn}$ based on X-ray single-crystal diffraction analysis.

The asymmetric unit of the title compound contains eight Cu atoms, four Sn atoms and 12 Se atoms (Fig. 1). Each of the formally Cu^{I} and Sn^{IV} ions is surrounded by four Se^{2-} anions at distances that agree well with the sums of the respective ionic radii (Wiberg, 1995). The crystal lattice consists of corner-sharing $[\text{CuSe}_4]$ and $[\text{SnSe}_4]$ tetrahedra. Since the metal-centred tetrahedra are connected only by the corners, the Se-centred coordination environment is also tetrahedral. Similar values of the Cu–Se and Sn–Se interatomic distances for tetrahedral surroundings are observed in the structures of LnCuSe_2 and Eu_2SnSe_5 (Daszkiewicz *et al.*, 2008; Evenson & Dorhout, 2001). However, from the bond-valence point of view the eight symmetry-independent Cu^{I} ions are overbonded, because the bond-valence sums (BVS) for these ions [based on Cu–Se distances ranging from 2.380 (5) to 2.495 (5) Å] are greater than the formal oxidation state, ~ 1.40 (Table 1) (Brown, 1996). Similarly, each of the Se^{2-} anions is overbonded. In this case, the Sn^{4+} ions must be underbonded, as indicated by the calculated BVS [based on Sn–Se distances in the range 2.488 (3)–2.627 (3) Å] of ~ 3.74 , because the difference between the BVS for the cations and anions must be zero.

The $\text{Cu}_2\text{Se}_3\text{Sn}$ structure described here, with 96 atoms in the unit cell, is a superstructure of the cubic (Sharma *et al.*, 1977)

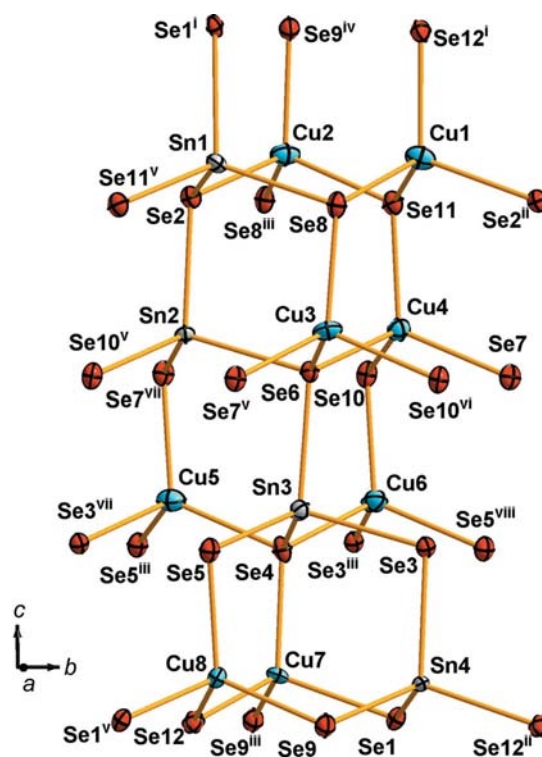


Figure 1

The coordination environments for the four symmetry-independent Sn and eight Cu atoms in the asymmetric unit of $\text{Cu}_2\text{Se}_3\text{Sn}$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (iii) $x - 1, y, z$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (vi) $x + 1, y, z$; (vii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (viii) $x - \frac{1}{2}, y + \frac{1}{2}, z$.]

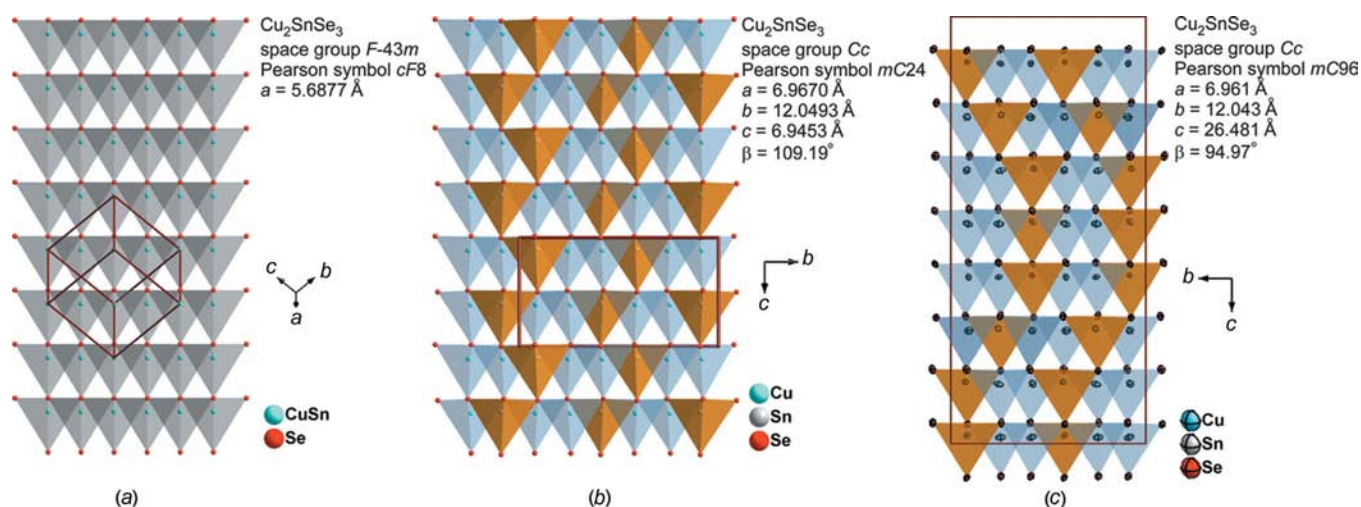


Figure 2

The packing of the Cu- and Sn-centred tetrahedra in (a) the cubic (Sharma *et al.*, 1977), (b) the first monoclinic (Delgado *et al.*, 2003) and (c) the second monoclinic (this work) modifications of $\text{Cu}_2\text{Se}_3\text{Sn}$.

(space group $\bar{F}43m$, eight atoms per unit cell) and monoclinic (Delgado *et al.*, 2003) (space group Cc , 24 atoms per unit cell) modifications reported earlier. The known modifications were investigated using X-ray powder diffraction, while the present monoclinic superstructure was investigated using X-ray single-crystal diffraction. The structures are similar (Fig. 2), in that the Se atoms in all modifications of $\text{Cu}_2\text{Se}_3\text{Sn}$ are stacked in a closest-packed arrangement with the layers in the sequence ABC (cubic closest packing). In the cubic modification, a mixture of randomly distributed Cu^+ and Sn^{4+} ions ($\frac{2}{3}\text{Cu} + \frac{1}{3}\text{Sn}$) occupy half of the tetrahedral interstices. In the structures of both monoclinic modifications, the Cu^+ ions occupy one-third of the tetrahedral interstices, whereas the Sn^{4+} ions are located in one-sixth of the tetrahedral interstices. The distribution of the cation positions in both monoclinic modifications is ordered. In both modifications, the Sn-centred tetrahedra create zigzag chains along the c axis. However, the period of the chain is one-quarter as long in the previously reported structure than in the present superstructure, and this is reflected in the relation of the lattice parameters, $c \simeq 4c'$. Moreover, the amplitude of the chain is 1.5 times larger in the superstructure.

The presence of three structures for $\text{Cu}_2\text{Se}_3\text{Sn}$ can be explained in two ways. The first is that the three modifications really exist. The cubic modification (random distribution of Cu^+ and Sn^{4+} atoms over one position) is a high-temperature modification, while the monoclinic modifications with different ordered distributions of the positions of Cu and Sn are low-temperature modifications. The second is that only one or two modifications exist. The basic fragments of the structures for all three structures are similar. It is possible that the superstructure reflections measured in the X-ray single-crystal investigation were missed in the previous powder studies. Further work will be required on the $\text{Cu}_2\text{Se}-\text{SnSe}_2$ system to determine how many structural modifications actually exist.

Experimental

A sample of composition $\text{Cu}_2\text{Se}_3\text{Sn}$ was prepared by melting the high-purity (better than 99.9 wt%) elements in an evacuated silica tube. The ampoule was heated at a rate of 100 K h^{-1} in a tube furnace to a temperature of 770 K, then heated at a rate of 20 K h^{-1} to a maximum temperature of 1380 K and kept at this temperature for 2 h. The ampoule was then cooled slowly (at a rate of 10 K h^{-1}) to 620 K and annealed at this temperature for 500 h. After annealing, the sample was quenched in cold water. A diffraction-quality single crystal was selected from the sample.

Crystal data

$\text{Cu}_2\text{Se}_3\text{Sn}$	$V = 2211.7 (8) \text{ \AA}^3$
$M_r = 482.65$	$Z = 16$
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 6.9612 (14) \text{ \AA}$	$\mu = 31.69 \text{ mm}^{-1}$
$b = 12.043 (2) \text{ \AA}$	$T = 295 \text{ K}$
$c = 26.481 (5) \text{ \AA}$	$0.10 \times 0.09 \times 0.05 \text{ mm}$
$\beta = 94.97 (3)^\circ$	

Data collection

Kuma KM-4 diffractometer with a CCD area detector	12585 measured reflections
Absorption correction: numerical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	4780 independent reflections
$T_{\min} = 0.038$, $T_{\max} = 0.212$	2338 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.095$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	$\Delta\rho_{\text{max}} = 1.87 \text{ e \AA}^{-3}$
$wR(F^2) = 0.104$	$\Delta\rho_{\text{min}} = -1.14 \text{ e \AA}^{-3}$
$S = 0.76$	Absolute structure: Flack (1983),
4780 reflections	with 2258 Friedel pairs
219 parameters	Flack parameter: 0.078 (15)
2 restraints	

The systematic absences were found to be consistent with the space group Cc , which was assigned for the crystal structure determination. Eight positions for Cu, four for Sn and 12 for Se were determined. All positions are fully occupied. A mixed occupation of

Table 1

Bond-valence sums for the symmetry-independent Cu⁺, Sn⁴⁺ and Se²⁻ ions.

Cu1	1.401	Sn1	3.742	Se5	2.122
Cu2	1.390	Sn2	3.762	Se6	2.210
Cu3	1.395	Sn3	3.690	Se7	2.181
Cu4	1.394	Sn4	3.781	Se8	2.180
Cu5	1.405	Se1	2.205	Se9	2.192
Cu6	1.401	Se2	2.222	Se10	2.133
Cu7	1.397	Se3	2.203	Se11	2.141
Cu8	1.391	Se4	2.195	Se12	2.162

Cu and Sn on each cation site was checked, but in all cases the refinement was unstable. The structure was checked with *PLATON* (Spek, 2009), which detected a pseudo-inversion centre. A refinement in *C2/c* was unsuccessful. The structure was refined as a twinned model with a twin fraction of 0.058 (14), because the Flack parameter (Flack, 1983) initially refined to 0.078 (15).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg,

2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3242). Services for accessing these data are described at the back of the journal.

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