

AuCuSe₄: A Mixed Polychalcogenide with Se₃^{2−} and Se^{2−} Anions

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The polychalcogenide compound AuCuSe₄ crystallizes in the monoclinic space group *P*2₁/*m* with *a* = 4.318(2) Å, *b* = 7.447(1) Å, *c* = 8.099(1) Å, β = 93.33(2)°, and *Z* = 2. The structure of AuCuSe₄ is a unique three-dimensional framework assembled from formally Au³⁺ and Cu⁺ ions and Se₃^{2−} and Se^{2−} fragments. Conceptually, the framework is composed of one-dimensional [Au(Se₃)Se]_{*n*}[−] chains linked by Cu⁺ atoms. The Au atoms adopt a square planar geometry while Cu atoms adopt a severely distorted tetrahedral geometry. The Se₃^{2−} ligand in this structure shows an unprecedented ligation mode using both its terminal and internal selenium atoms. The material is a p-type narrow gap semiconductor with a band gap of ~0.52 eV.

Introduction

Molten alkali metal polychalcogenide salts have been an outstanding synthetic tool for discovery of new (poly)chalcogenide compounds at intermediate temperature.¹ Au and Cu in particular are among the most reactive toward polychalcogenide species (Q_{*x*}^{2−}; Q = S, Se, Te) giving rise to many phases with interesting structural features associated with the multidentate ligation modes of (poly)chalcogenide ligands. In the ternary A/M/Se (M = Cu, Au) systems, α-ACuSe₄^{1a,2} (A = K, Rb, Cs), K₃AuSe₁₃,³ Na₃AuSe₈,³ KAuSe₅,⁴ CsAuSe₃,⁴ Na₅AuSe₁₂,⁵ and Cs₂Au₂Se₃⁶ containing polyselenide ligands from Se₂^{2−} to Se₅^{2−} have been reported. Many more examples with Se^{2−} ions include KCuSe,⁷ K₃Cu₈Se₆,⁸ Cs₂Cu₅Se₄,⁹ NaAuSe₂,⁴ CsAu₃Se₂,¹⁰ K₃-AuSe₂,¹¹ and AAuSe (A = Na,¹² K,¹³ Rb¹³). One interesting aspect of Au and Cu chemistry is that these metals can potentially afford mixed formal oxidation states +1/+3 and +1/+2, respectively. Cu is often stabilized in a linear, trigonal planar, and tetrahedral geometries, but Au rigidly prefers either linear coordination, with +1 oxidation state, or square planar coordination, with +3 oxidation state. A natural question to ask is what type of structure is possible if both metals occurred in

a quaternary phase. In the literature there are no known quaternary or even ternary Au/Cu/Q (Q = S, Se) compounds except for the little known mineral kostovite AuCuTe₄, which contains Te₂^{2−} ligands.¹⁴ Here we report AuCuSe₄, the first mixed-metal ternary compound in the Au/Cu/Se system which crystallizes from K₂Se_{*x*} flux and features a novel structure type with Se₃^{2−} and Se^{2−} ligands.

Experimental Section

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. Potassium monoselenide (K₂Se) was prepared in liquid ammonia from potassium and elemental selenium in a 2:1 ratio.

AuCuSe₄. Method A. A 0.094 g (0.6 mmol) amount of K₂Se, 0.098 g (0.5 mmol) of Au, 0.032 g (0.5 mmol) of Cu, and 0.624 g (8.0 mmol) of Se powder were mixed together and loaded in a Pyrex tube (9 mm diameter) which was then flame-sealed under vacuum (~10^{−3} Torr). The tube was placed in a computer-controlled furnace, heated at 310 °C for 4 days, and then cooled slowly to 120 °C at a rate of 2 °C/h and then to 50 °C at a rate of 35 °C/h. Upon removal of the excess K₂Se_{*x*} with DMF, dark brown rod-shaped crystals were obtained together with KAuSe₅ (about 20%). A quantitative microprobe analysis performed on a large number of single crystals with the EDS/SEM system gave an average composition of Au_{1.0}Cu_{1.0}Se_{4.1}. This compound is insoluble in all common organic solvents and stable with respect to hydrolysis and air oxidation.

Method B. AuCuSe₄ was also prepared by a direct stoichiometric reaction from a mixture of 0.197 g (1 mmol) of Au, 0.0635 g (1 mmol) of Cu, and 0.316 g (4 mmol) of Se. The mixture was loaded in a quartz tube which was then flame-sealed under vacuum (~10^{−4} Torr). The mixture was heated to form a complete melt using a mild flame and then was quenched to an ice–water bath. The melt, which turned out to be amorphous judging from X-ray diffraction, was ground finely and annealed at 320 °C for 24 h in an evacuated silica tube. X-ray diffraction of the product shows AuCuSe₄ and a small amount of unreacted Au (~3%). To obtain a AuCuSe₄ phase totally free of Au, many attempts were made by varying the annealing temperature from the 220 to 360 °C and the isotherm periods from 12 h to 7 days. However, trace amounts of unreacted Au were always observed.

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Physical Measurements. Microprobe Analyses. Quantitative microprobe analyses of the compounds were performed on a JEOL 35CF scanning electron microscopy equipped with Tracor Northern TN 5500 X-ray microanalysis attachment. Single crystals were carefully picked and mounted on an aluminum stub using conducting silver paint to help dissipate charges that developed on the sample surface during measurements. A standardless quantitative analysis program was used to analyze the X-ray spectra obtained. Since the Se ratio is always underestimated due to an artifact in the software program, a correction factor ($\times 1.86$), which was determined by calibrating with known K/Au/Se and K/Cu/Se ternary compounds, was used to better evaluate the selenium content. The accuracy of this type of analysis is typically $\sim \pm 3\text{--}5\%$.

Physicochemical Measurements. DTA experiments were performed on a computer-controlled Shimadzu DTA-50 thermal analyzer as described elsewhere.¹⁵ Residues of the DTA experiments were examined by X-ray powder diffraction. The stability/reproducibility of the samples was monitored by running multiple heating/cooling cycles. The FT-IR spectrum of AuCuSe₄ was obtained from a CsI pellet sample in the region 600–100 cm⁻¹ with a Nicolet 740 FT-IR spectrometer. Optical diffuse reflectance measurement was performed at room temperature with a Shimadzu UV-3101PC double-beam, double-monochromator spectrometer operating in the 200–2500 nm region. The instrument is equipped with an integrating sphere and controlled by a personal computer. BaSO₄ powder was used as a 100% reflectance standard. The reflectance versus wavelength data generated were used to estimate the material's band gap by converting reflectance to absorption data as described earlier.¹⁶ Raman spectra were collected on a Holoprobe Raman spectrograph equipped with a 633 nm He Ne laser and a CCD camera detector. Laser power at the sample was estimated to be about 1 mW, and the focused laser beam diameter was ca. 10 μm . A total of 12 scans were adequate to obtain good quality spectra. The accumulation time for each scan was 15 s.

X-ray Crystallographic Studies. The X-ray single-crystal data for AuCuSe₄ were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo K α radiation using the $\omega/2\theta$ scan mode. Accurate unit cell parameters were obtained from least-squares refinement of the 2θ , ω , χ , and ϕ values of 25 machine-centered reflections. The stability of the experimental setup and crystal integrity were verified by measuring three standard reflections periodically (every 100 reflections) during data collection. Two absorption corrections were applied to the data: an empirical absorption correction based on ψ scans for three reflections followed by a DIFABS¹⁷ correction. The structure of AuCuSe₄ was solved with direct methods using SHELXS-86¹⁸ and was refined with the TEXSAN¹⁹ package of crystallographic programs. All atoms were refined anisotropically. The data collection parameters and details of the structure solution and refinement are given in Table 1. The final coordinates, temperature factors, and their estimated standard deviations of all atoms are shown in Table 2.

Results and Discussion

Synthesis and Spectroscopy. During the investigation of ternary K/Cu/Se and K/Au/Se systems in liquid K₂Se_x we discovered several unusual polyselenides such as α -KCuSe₄,^{1a,2a} K₃AuSe₁₃,³ and KAuSe₅.⁴ On the basis of the considerations discussed above, we investigated the quaternary K/Au/Cu/Se system, which led to the discovery of AuCuSe₄. The K⁺ ions were not incorporated but instead ended up in the competing

Table 1. Summary of Crystallographic Data for AuCuSe₄

empirical formula	AuCuSe ₄
fw	576.35
temp (K)	296
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>m</i> (No. 11)
<i>a</i> (Å)	4.318(2)
<i>b</i> (Å)	7.447(1)
<i>c</i> (Å)	8.099(1)
β (deg)	93.33(2)
<i>V</i> (Å ³)	260.0(1)
<i>Z</i>	2
$\mu(\text{Mo K}\alpha)$ (mm ⁻¹)	59.78
ρ_{calc} (g/cm ³)	7.36
final <i>R</i> / <i>R</i> _w ^a (%)	5.1/5.5

$$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|. R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}.$$

Table 2. Fractional Atomic Coordinates and *B*_{eq} Values for AuCuSe₄ with Their Estimated Standard Deviations in Parentheses

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} ^a (Å ²)
Au	1/2	0	0	0.60(3)
Se(1)	0.4162(3)	0.0013(2)	0.6951(2)	0.80(5)
Se(2)	0.0742(4)	1/4	0.6384(2)	0.86(6)
Se(3)	0.1445(4)	1/4	1.0623(2)	0.66(6)
Cu	-0.0248(6)	1/4	1.3423(3)	1.5(1)

^a *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{\text{eq}} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

ternary compounds. Therefore, the crystals of AuCuSe₄ were mixed with KAuSe₅, KAuSe₂, and sometimes α -KCuSe₄. Generally a low fraction of K₂Se is necessary in the reaction. Increasing the K₂Se fraction tends to favor competing alkali metal ternary phases and less or none of AuCuSe₄. Any efforts to prepare pure AuCuSe₄ in K₂Se_x flux were not successful. Therefore, we devised a direct synthesis for AuCuSe₄ by combining stoichiometric amounts of corresponding elements. Direct combination of the elements at 380 or 600 °C produced AuCuSe₄ along with unreacted Au and competing Cu/Se and Au/Se binary phases. Annealing experiments at 2/3 the compound's melting point did not increase the homogeneity of the sample.

Another more successful approach was devised in which we form an *amorphous phase* by quenching a molten stoichiometric combination of the elements in ice–water temperature, followed by annealing of the sample at 320 °C. This procedure results in fairly pure AuCuSe₄ (>97%) with only small amount of unreacted Au. Many attempts using various annealing temperatures and periods did not remove the Au.

Even though AuCuSe₄ seems to be relatively stable in air, its thermal stability is relatively low, typical for polychalcogenide compounds.²⁰ DTA experiments show two endothermic peaks on heating at 417 and 430 °C, suggesting decomposition of the phase and one exothermic peak on cooling at 402 °C; see Figure 1. This thermal treatment produces Cu₂Se and Au and Se as identified with X-ray diffraction of the sample after the DTA experiment. Repeating the heating cycle up to 450 °C clearly shows the appearance of additional endothermic peaks at 220 °C (attributed to Se melting).

In the far-IR region AuCuSe₄ exhibits absorptions in the range of 170–235 cm⁻¹ due to Se–Se, Au–Se, and Cu–Se stretching vibrations; see Figure 2a. The absorptions at 235 and 228 cm⁻¹ can be assigned to Se–Se and Au–Se stretching vibrations.

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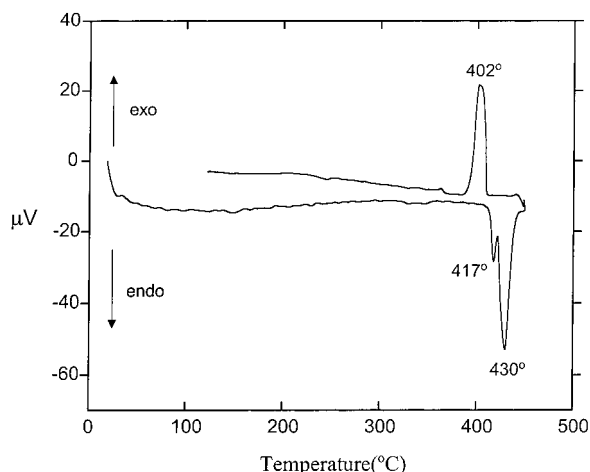


Figure 1. DTA diagram of AuCuSe₄ (experiment run under vacuum; heating/cooling rate 10 °C/min).

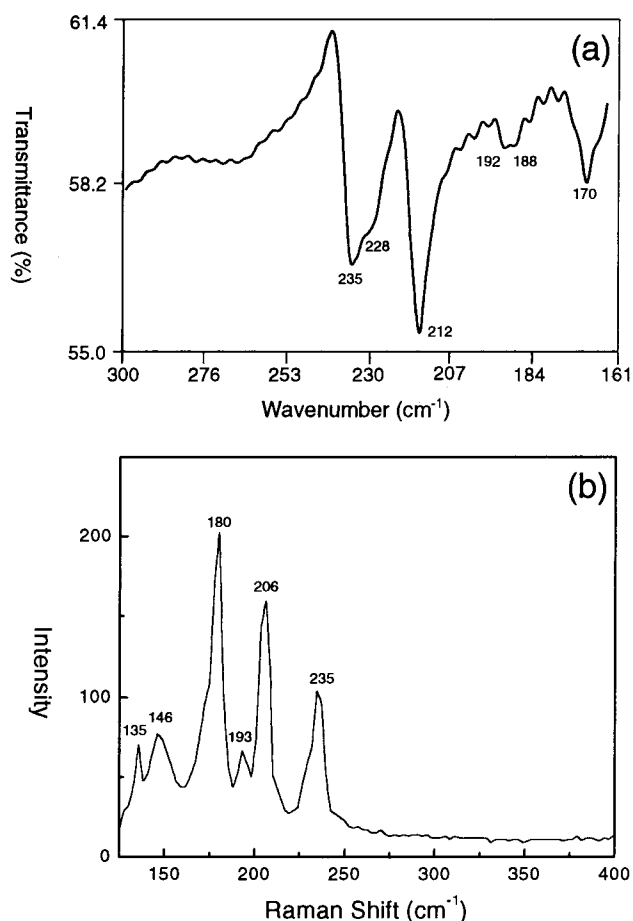


Figure 2. (a) FT-IR spectrum (CsI pellet) and (b) Raman spectrum of AuCuSe₄.

For Cu and Au polyselenide compounds, a spectral absorption due to Se–Se stretching vibrations is observed in the range 242–264 cm^{−1}; for example, see α-KCuSe₄ at 246–252 cm^{−1}, KAuSe₅ at 244–257 cm^{−1}, CsAuSe₃ at 243 cm^{−1}, and unbound polyselenide (Ph₄P)₂Se₅ at 267 cm^{−1}. Therefore, the peak at 235 cm^{−1} is a bit low in energy for a typical Se–Se stretching vibration. However, the unusual *pentadentate* bridging ligation mode of the Se₃^{2−} ligand in AuCuSe₄ serves to shift the frequency to lower values and closer to the energies of the Au–Se stretching vibrations. The monoselenide Au³⁺ compounds of KAuSe₂ and NaAuSe₂ show Au–Se stretching vibrations at

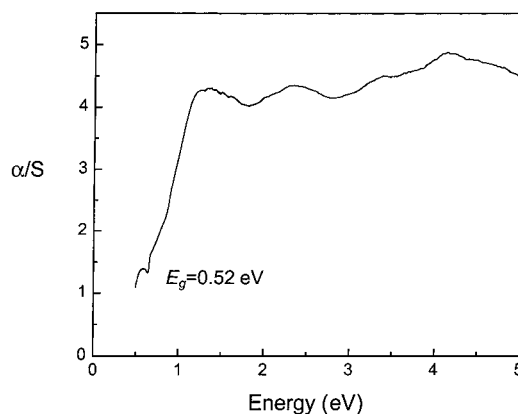


Figure 3. Optical absorption spectrum of AuCuSe₄ derived from diffuse reflectance data.

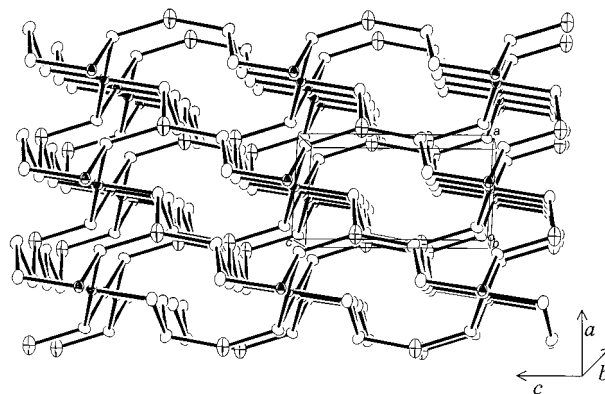


Figure 4. ORTEP representation of the three-dimensional framework of AuCuSe₄ looking down the *b* axis (90% probability ellipsoids); shaded octant ellipsoids, Au; crossed ellipsoids, Cu; boundary ellipsoids, Se.

231 cm^{−1} and 236, 230, and 222 cm^{−1}, respectively. Thus, we can assign the 235, 228, and 212 cm^{−1} bands to both Se–Se and Au–Se stretching vibrations. The Raman spectrum of AuCuSe₄, Figure 2b, displays major shifts at 180, 206, and 235 cm^{−1}, which can be respectively assigned to Au–Se, Cu–Se, and Se–Se stretching vibrations.²¹

On the basis of the formal oxidation states of Cu⁺ and Au³⁺, we have a valence precise compound, which should give rise to a completely filled valence band. Thus AuCuSe₄ should be a semiconductor. Indeed, the UV–visible–near-IR reflectance spectroscopy on AuCuSe₄ at room temperature reveals the presence of a band gap at 0.52 eV; see Figure 3. The magnitude of the band gap is rather narrow, and the electronic absorption associated with it is attributed to charge transfer excitations from mainly Se orbitals to primarily Cu and Au *s*, *p* orbitals. The electrical conductivity and thermopower measurements on a pressed pellet show 12 S/cm and +22.4 μV/K at room temperature, respectively, consistent with a *p*-type semiconductor.

Structure of AuCuSe₄. To the best of our knowledge, the structure of AuCuSe₄ is unique. It is a three-dimensional covalent framework with two types of small empty tunnels; see Figure 4. As revealed by the local metal coordination, this is formally a Au³⁺/Cu⁺ compound with Se₃^{2−} and Se^{2−} fragments.

(21) These interpretations could be an oversimplification because it is not trivial to interpret the IR and Raman spectra of metal polychalcogenide compounds without ambiguity. The M–Se and Se–Se stretching frequencies fall in the same spectroscopic region, and there is a paucity of detailed in-depth vibrational spectroscopic studies for the various ligands (Q_x^{2−}, *x* = 2–6) and metal polychalcogenide compounds.

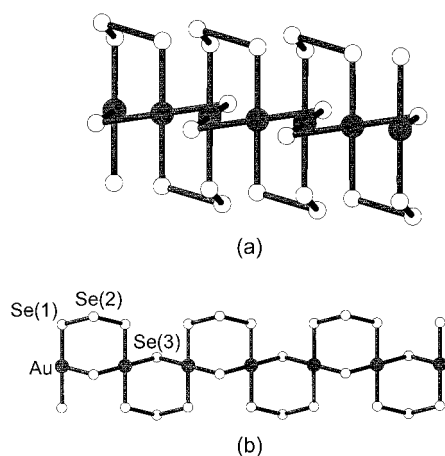


Figure 5. Two side views of the hypothetical $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chain running parallel to the b axis with atom-labeling scheme.

The structure is clearly anisotropic. Conceptually, we can decompose it into one-dimensional $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chains linked by Cu^+ atoms. Two views of the $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chain are shown in Figure 5. In this chain, the Se_3^{2-} ligands bridge the Au atoms via their terminal Se(1) which span the Au–Au distance of 3.7234(7) Å. The square planar coordination of Au atoms is completed by the bridging monoselenides, Se(3). The chains are centrosymmetric and run parallel to the crystallographic b axis. The Au atoms are located on an inversion center. The average Au–Se bond distance is 2.479(5) Å and is similar to those in other Au^{3+} compounds.^{3,4} The $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chain is somewhat reminiscent of the $[\text{Au}(\text{Se}_3)(\text{Se}_5)_2]_n^{3n-}$ chain of $\text{K}_3\text{AuSe}_{13}$.³ Like the $[\text{Au}(\text{Se}_3)(\text{Se}_5)_2]_n^{3n-}$ chain, the $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chain can be perceived as an oxidative addition product of a neutral Se atom to the Au^+ atoms of the known $[\text{Au}(\text{Se}_3)]_n^{n-}$ chain as shown in eq 1.



The reduced Se atoms (Se^{2-} in the $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chain) act to bridge the Au^{3+} ions in the chain, Figure 5. The $[\text{Au}(\text{Se}_3)\text{Se}]_n^{n-}$ chains are connected by Cu atoms which join them along the crystallographic bc plane but also perpendicular to it to form the final framework. The Cu centers are found in a highly distorted tetrahedral environment being bonded to two terminal selenium atoms (Se(1)) of adjacent Se_3^{2-} ligands along the crystallographic b axis, one internal selenium atom (Se(2)) of a third Se_3^{2-} ligand, and one bridging Se(3) atom, Figure 6a. As a result, the Se_3^{2-} ligands bind to five metal atoms simultaneously, Figure 6b.

There is only one crystallographically unique Cu atom in the structure with an extremely distorted tetrahedral coordination. One of the tetrahedral Cu bond angles ($\text{Se}(2)\text{--Cu--Se}(3)$) is very large at $152.3(1)^\circ$. The Cu–Se(2) and Cu–Se(3) bond distances are relatively short at 2.411(3) and 2.423(3) Å, while Cu–Se(1) bond distances are longer at 2.528(2) Å. The structure creates two types of empty tunnels along the b axis, which are composed

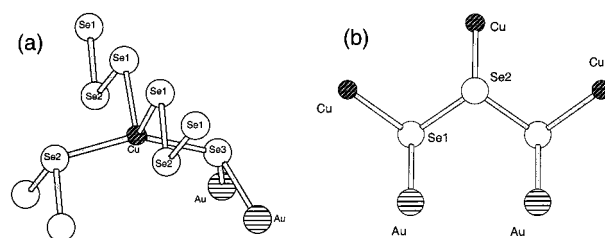


Figure 6. (a) Immediate coordination environment of Cu. (b) Pentadentate ligation mode of the Se_3^{2-} fragment in AuCuSe_4 with atom-labeling scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for AuCuSe_4 with Standard Deviations in Parentheses

bond		angle	
Au–Se(1)	2.475(1) (×2)	Se(1)–Au–Se(1)	180.00
Au–Se(3)	2.483(1) (×2)	Se(3)–Au–Se(3)	180.00
		Se(1)–Au–Se(3)	98.26(5) (×2)
		Se(1)–Au–Se(3)	81.74(5) (×2)
		Se(1)–Cu–Se(1)	95.5(1)
CuSe(1)	2.528(2) (×2)	Se(1)–Cu–Se(2)	101.40(8) (×2)
CuSe(2)	2.411(3)	Se(1)–Cu–Se(3)	97.12(8) (×2)
CuSe(3)	2.423(3)	Se(2)–Cu–Se(3)	152.3(1)
		Au–Se(1)–Se(2)	104.28(6)
Se(1)Se(2)	2.396(2) (×2)	Au–Se(1)–Cu	100.05(7)
		Se(2)–Se(1)–Cu	98.57(7)
		Se(1)–Se(2)–Se(1)	101.23 (9)
		Se(1)–Se(2)–Cu	105.19(7)
		Au–Se(3)–Au	97.13(6)
		Au–Se(3)–Cu	114.44(6) (×2)

of 10-membered rings and 8-membered rings. These tunnels are quite small: the short dimensions are 3.254(3) Å for Cu–Se(1) and 3.283(3) Å for Se(1)–Se(1) in the 10-membered ring and 4.036(1) Å for Se(3)–Se(3) in the 8-membered ring. Selected bond distances and angles are given in Table 3.

It is worth noting that the structure of AuCuSe_4 bears no relationship to other polychalcogenide compounds of copper such as KCuSe_4 , KAuSe_5 , and CsAuSe_3 . This is obvious since the last three compounds contain a single polychalcogenide species. Interestingly, AuCuSe_4 is not at all related to its analogue AuCuTe_4 either, which instead contains two Te_2^{2-} anions and has a layered orthorhombic structure. The origin of this stark difference between these two compounds should be investigated.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, anisotropic displacement parameters of all atoms, and bond angles and distances for the structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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