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$AuCuSe_4$: A Mixed Polychalcogenide with Se_3^{2-} and Se^{2-} Anions

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The polychalcogenide compound $AuCuSe_4$ crystallizes in the monoclinic space group $P2_1/m$ with $a = 4.318(2)$ Å, $b = 7.447(1)$ Å, $c = 8.099(1)$ Å, $\beta = 93.33(2)°$, and $Z = 2$. The structure of $AuCuSe_4$ is a unique three-dimensional framework assembled from formally Au^{3+} and Cu^+ ions and Se_3^{2-} and Se^{2-} fragments. Conceptually, the framework is composed of one-dimensional $[Au(Se_3)Se]_n^{n-}$ chains linked by Cu^+ atoms. The Au atoms adopt a square planar geometry while Cu atoms adopt a severely distorted tetrahedral geometry. The Se_3^{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-$ACuSe_4$[1a,2] (A = K, Rb, Cs), K_3AuSe_{13},[3] Na_3AuSe_8,[3] $KAuSe_5$,[4] $CsAuSe_3$,[4] Na_5AuSe_{12},[5]and $Cs_2Au_2Se_3$[6] containing polyselenide ligands from Se_2^{2-} to Se_5^{2-} have been reported. Many more examples with Se^{2-} ions include KCuSe,[7] $K_3Cu_8Se_6$,[8] $Cs_2Cu_5Se_4$,[9] $NaAuSe_2$,[4] $CsAu_3Se_2$,[10] K_3AuSe_2,[11] and AAuSe (A = Na,[12] K,[13] Rb[13]). 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 $AuCuTe_4$, which contains Te_2^{2-} ligands.[14] Here we report $AuCuSe_4$, the first mixed-metal ternary compound in the Au/Cu/Se system which crystallizes from K_2Se_x flux and features a novel structure type with Se_3^{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 (K_2Se) was prepared in liquid ammonia from potassium and elemental selenium in a 2:1 ratio.

$AuCuSe_4$. Method A. A 0.094 g (0.6 mmol) amount of K_2Se, 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 K_2Se_x with DMF, dark brown rod-shaped crystals were obtained together with $KAuSe_5$ (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. $AuCuSe_4$ 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 $AuCuSe_4$ and a small amount of unreacted Au (∼3%). To obtain a $AuCuSe_4$ phase totally free of Au, many attempts were made by varying the annealing temperature from the 220 to 360 °C and the isotherm periods form 12 h to 7days. 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 (×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 ∼±3−5%.

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 $AuCuSe_4$ 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. $BaSO_4$ 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 $AuCuSe_4$ were collected on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation using the $\omega\angle 2\theta$ 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 DIFABS[17] correction. The structure of $AuCuSe_4$ was solved with direct methods using SHELXS-86[18] and was refined with the TEXSAN[19] 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.

Table 1. Summary of Crystallographic Data for $AuCuSe_4$

empirical formula	$AuCuSe_4$
fw	576.35
temp (K)	296
cryst system	monoclinic
space group	$P2_1/m$ (No. 11)
a (Å)	4.318(2)
b (Å)	7.447(1)
c (Å)	8.099(1)
β (deg)	93.33(2)
V (Å^3)	260.0(1)
Z	2
μ(Mo Kα) (mm^{-1})	59.78
ρ_{calc} (g/cm^3)	7.36
final $R/R_w{}^a$ (%)	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 $AuCuSe_4$ with Their Estimated Standard Deviations in Parentheses

atom	x	y	z	$B_{eq}{}^a$ (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 $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Results and Discussion

Synthesis and Spectroscopy. During the investigation of ternary K/Cu/Se and K/Au/Se systems in liquid K_2Se_x we discovered several unusual polyselenides such as α-$KCuSe_4$,[1a,2a] K_3AuSe_{13},[3] and $KAuSe_5$.[4] On the basis of the considerations discussed above, we investigated the quaternary K/Au/Cu/Se system, which led to the discovery of $AuCuSe_4$. The K^+ ions were not incorporated but instead ended up in the competing ternary compounds. Therefore, the crystals of $AuCuSe_4$ were mixed with $KAuSe_5$, $KAuSe_2$, and sometimes α-$KCuSe_4$. Generally a low fraction of K_2Se is necessary in the reaction. Increasing the K_2Se fraction tends to favor competing alkali metal ternary phases and less or none of $AuCuSe_4$. Any efforts to prepare pure $AuCuSe_4$ in K_2Se_x flux were not successful. Therefore, we devised a direct synthesis for $AuCuSe_4$ by combining stoichiometric amounts of corresponding elements. Direct combination of the elements at 380 or 600 °C produced $AuCuSe_4$ 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 $AuCuSe_4$ (>97%) with only small amount of unreacted Au. Many attempts using various annealing temperatures and periods did not remove the Au.

Even though $AuCuSe_4$ 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 Cu_2Se 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 $AuCuSe_4$ 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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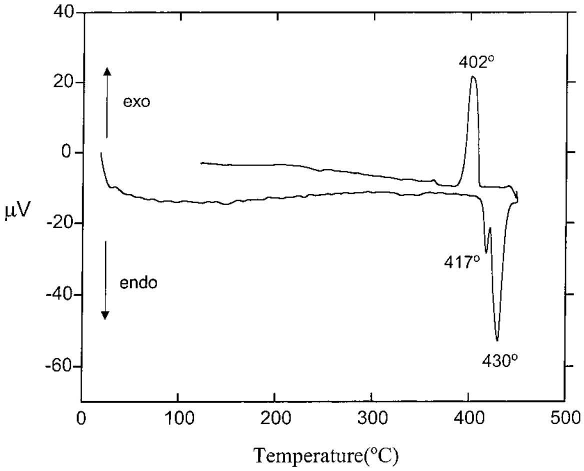

Figure 1. DTA diagram of $AuCuSe_4$ (experiment run under vacuum; heating/cooling rate 10 °C/min).

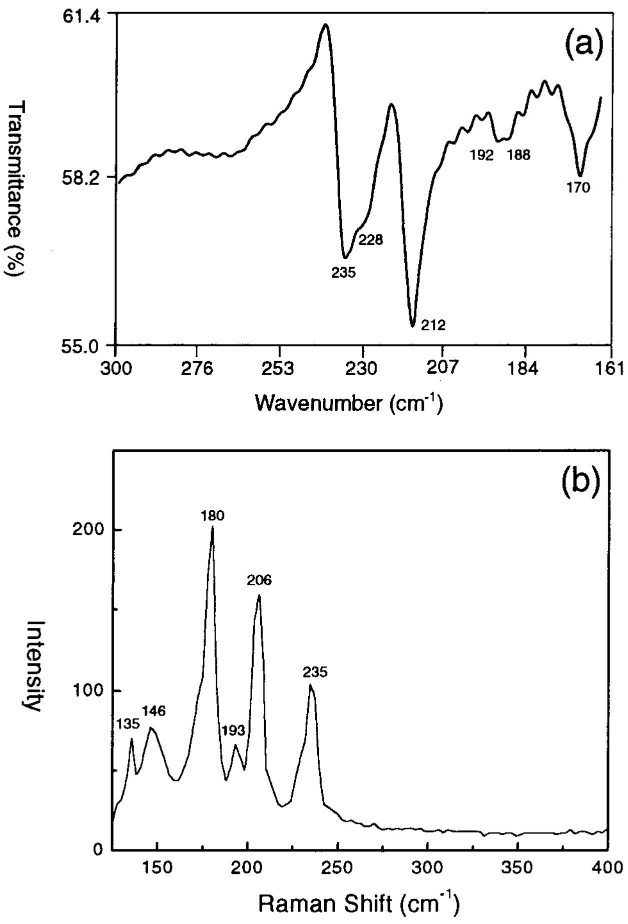

Figure 2. (a) FT-IR spectrum (CsI pellet) and (b) Raman spectrum of $AuCuSe_4$.

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-$KCuSe_4$ at 246−252 cm^{-1}, $KAuSe_5$ at 244−257 cm^{-1}, $CsAuSe_3$ at 243 cm^{-1}, and unbound polyselenide $(Ph_4P)_2Se_5$ 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 Se_3^{2-} ligand in $AuCuSe_4$ serves to shift the frequency to lower values and closer to the energies of the Au−Se stretching vibrations. The monoselenide Au^{3+} compounds of $KAuSe_2$ and $NaAuSe_2$ show Au−Se stretching vibrations at 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 $AuCuSe_4$, 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]

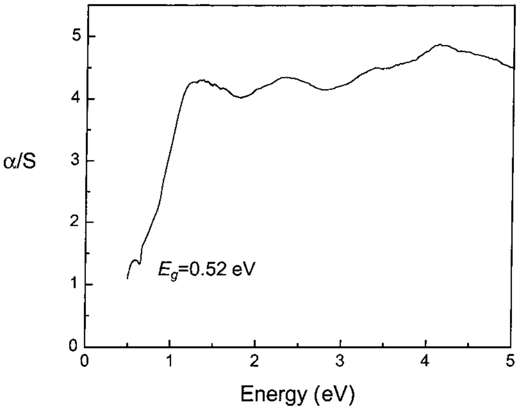

Figure 3. Optical absorption spectrum of $AuCuSe_4$ derived from diffuse reflectance data.

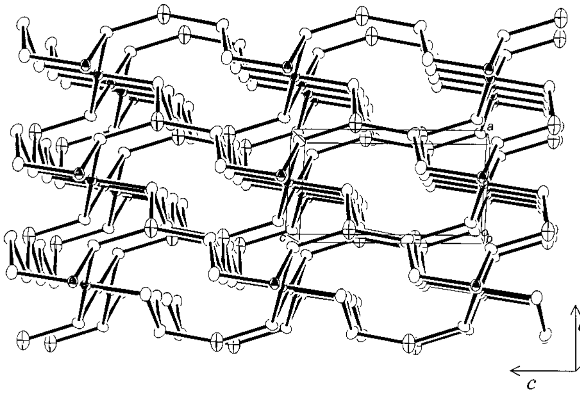

Figure 4. ORTEP representation of the three-dimensional framework of $AuCuSe_4$ looking down the *b* axis (90% probability ellipsoids): shaded octant ellipsoids, Au; crossed ellipsoids, Cu; boundary ellipsoids, Se.

On the basis of the formal oxidation states of Cu^+ and Au^{3+}, we have a valence precise compound, which should give rise to a completely filled valence band. Thus $AuCuSe_4$ should be a semiconductor. Indeed, the UV−visible−near-IR reflectance spectroscopy on $AuCuSe_4$ 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 $AuCuSe_4$. To the best of our knowledge, the structure of $AuCuSe_4$ 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 Au^{3+}/Cu^+ compound with Se_3^{2-} and Se^{2-} fragments.

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[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.

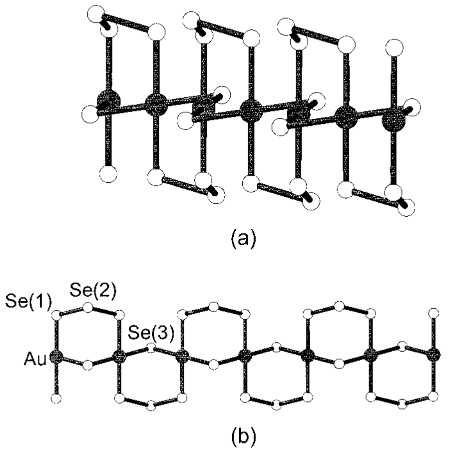

Figure 5. Two side views of the hypothetical $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chain running parallel to the *b* axis with atom-labeling scheme.

The structure is clearly anisotropic. Conceptually, we can decompose it into one-dimensional $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chains linked by $\mathrm{Cu^+}$ atoms. Two views of the $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chain are shown in Figure 5. In this chain, the $\mathrm{Se_3}^{2-}$ 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 $\mathrm{Au^{3+}}$ compounds.[3,4] The $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chain is somewhat reminiscent of the $[\mathrm{Au(Se_3)(Se_5)_2}]_n^{3n-}$ chain of $\mathrm{K_3AuSe_{13}}$.[3] Like the $[\mathrm{Au(Se_3)(Se_5)_2}]_n^{3n-}$ chain, the $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chain can be perceived as an oxidative addition product of a neutral Se atom to the $\mathrm{Au^+}$ atoms of the known $[\mathrm{Au(Se_3)}]_n^{n-}$ chain as shown in eq 1.

$$[\mathrm{Au(Se_3)}]_n^{\ n-} + n\mathrm{Se} \rightarrow [\mathrm{Au(Se_3)Se}]_n^{\ n-} \tag{1}$$

The reduced Se atoms ($\mathrm{Se^{2-}}$ in the $[\mathrm{Au(Se_3)Se}]_n^{n-}$ chain) act to bridge the $\mathrm{Au^{3+}}$ ions in the chain, Figure 5. The $[\mathrm{Au(Se_3)Se}]_n^{n-}$ 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 $\mathrm{Se_3}^{2-}$ ligands along the crystallographic *b* axis, one internal selenium atom (Se(2)) of a third $\mathrm{Se_3}^{2-}$ ligand, and one bridging Se(3) atom, Figure 6a. As a result, the $\mathrm{Se_3}^{2-}$ ligands bind to five metal atoms simultaneously, Figure 6b.

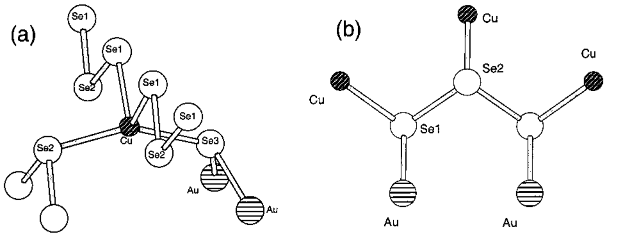

Figure 6. (a) Immediate coordination environment of Cu. (b) Pentadentate ligation mode of the $\mathrm{Se_3}^{2-}$ fragment in $\mathrm{AuCuSe_4}$ with atom-labeling scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{AuCuSe_4}$ 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)

There is only one crystallographically unique Cu atom in the structure with an extremely distorted tetrahedral coordination. One of the tetrahedral Cu bond angles (Se(2)−Cu-Se(3)) is very large at 152.3(1)°. 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 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 $\mathrm{AuCuSe_4}$ bears no relationship to other polychalcogenide compounds of copper such as $\mathrm{KCuSe_4}$, $\mathrm{KAuSe_5}$, and $\mathrm{CsAuSe_3}$. This is obvious since the last three compounds contain a single polychalcogenide species. Interestingly, $\mathrm{AuCuSe_4}$ is not at all related to its analogue $\mathrm{AuCuTe_4}$ either, which instead contains two $\mathrm{Te_2}^{2-}$ 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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