Inorg. Chem. **1998,** *37,* 5583−5587

Flux Synthesis of LiAuS and NaAuS: "Chicken-Wire-Like" Layer Formation by Interweaving of $(AuS)_n^{n-}$ Threads. Comparison with α-HgS and AAuS (A = K, Rb)

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Received April 2, 1998

From the reaction of Au with alkali metal polysulfide liquids, LiAuS and NaAuS were discovered. Orange crystals of LiAuS crystallize in the monoclinic space group *C*2/*c*, (no. 15), with $a = 8.994(2)$ Å, $b = 8.956(2)$ Å, $c = 7.201(3)$ Å, $\beta = 128.68(1)°$, and $Z = 8$. Light-yellow planks of NaAuS crystallize in the orthorhombic space group *Ccca*, (no. 68), with $a = 14.658(5)$ Å, $b = 21.043(7)$ Å, $c = 7.118(4)$ Å, and $Z = 32$. Both compounds contain infinite one-dimensional $(AuS)_n^{n-}$ chains, featuring alternating sulfide anions and linear coordinated Au centers. In LiAuS, the chains are zigzag and fully extended and they pack in two mutually perpendicular sets. In NaAuS, the same chains coil in an unusual fashion so that they become interwoven to form layers reminiscent of "chicken-wire". This novel coiling mode allows Au−Au contacts to form, which help to stabilize the structure. The structural relationships between LiAuS, NaAuS, $Na_7Au_5S_6$, AAuQ (A = K, Rb, Cs; Q = S, Se), and α-HgS are explored.

Introduction

Reactions of gold with polychalcogenide melts can go quickly to completion at temperatures as low as 190 °C.[1] This reactivity was pointed out by Bertholet in the early 1800's when he reported that gold dissolved in alkali metal polysulfide melts but not in molten sulfur.[2] This high reactivity makes the A/Au/Q systems (A = alkali metal; Q = S, Se, Te) interesting for study from a chemical standpoint because many ternary phases are possible. The strong affinity of gold for chalcogen atoms is evident in the number of ternary compounds that have been reported, NaAuSe,[3] KAuQ (Q = S, Se),[4] AAuQ (A = K, Rb, Cs), AAuTe (A = Na, K, Rb, Cs),[5] Na_3AuS_2,[6a] $Na_7Au_5S_6$,[6b] AAu_3S_2 (A = Cs, Rb),[7] $CsAu_3Se_2$,[7] $Cs_4Au_6S_5$,[8] $K_4Au_6S_5$,[9] $K_7Au_5S_7$,[9] and $AAuSe_2$[13] (A = Na, K), containing monochalcogenide ligands as well as K_3AuSe_{13},[10,11] Na_3AuSe_8,[10,11] K_5AuSe_{12},[12] $KAuQ_5$ (Q = S, Se),[12] and $CsAuSe_3$,[13] which feature long-chain polychalcogenides. Here, we describe LiAuS and NaAuS, both of which feature infinite $(AuS)_n^{n-}$ chains in remarkable conformations and arrangements.

Experimental Section

Reagents. Elemental sulfur was purchased from Spectrum Chemical Manufacturing Corporation. Sodium and lithium were obtained from Aldrich. Au metal (99.99%) was acquired from Liberty Coins, Lansing, MI. Chemicals were measured and loaded in Pyrex tubes under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. Lithium metal was manipulated under an argon atmosphere to avoid the formation of Li_3N.

Synthesis. a. Finely Divided Au Metal. A gold coin (99.99%, 31.1 g) was dissolved in 400 mL of aqua regia (300 mL of concentrated HCl and 100 mL of concentrated HNO_3). The solution was boiled in an acid-resistant fume hood to a volume of approximately 100 mL. The solution was neutralized with ammonium hydroxide, and the gold was reduced with excess hydrazine hydrochloride dissolved in 100 mL of distilled water. The resulting black suspension was heated gently, with stirring, for 1 h to allow particle aggregation. After the suspension was filtered and washed with copious amounts of distilled water and acetone, the resulting gold powder was heated in air for 2 h at 300 °C to drive off any remaining impurities, yielding 30.9 g of Au powder. Note: heating too long or at too high a temperature results in impractical grain sizes.

b. Li_2S and Na_2S. Lithium sulfide and sodium sulfide were produced in liquid ammonia. In a nitrogen-filled glovebox, the stoichiometric amounts of alkali metal chunks and elemental sulfur powder necessary to produce 20 g of starting material were loaded into a 250 mL round-bottom flask. A Teflon stir bar was added, and each flask was closed to air with a glass adapter and valve. The apparatus was removed to a Schlenk line, where approximately 150 mL of liquid ammonia was condensed under nitrogen, with stirring, into the dry-ice/acetone-cooled round-bottom flask. After the flask was allowed to warm to room temperature, the apparatus was put under vacuum for several hours, followed by heating with a hot air gun to drive off any remaining ammonia. The apparatus was returned to the glovebox, and the product was ground to a fine powder before use. The resulting powders were pale yellow in color.

c. LiAuS. Orange crystals of LiAuS were obtained by the reaction of 1−4 equiv of Li_2S, 1 equiv of Au metal, and 8 equiv of elemental S. This charge was sealed inside an evacuated Pyrex tube. The tube was placed inside a computer-controlled furnace and heated at 500 °C

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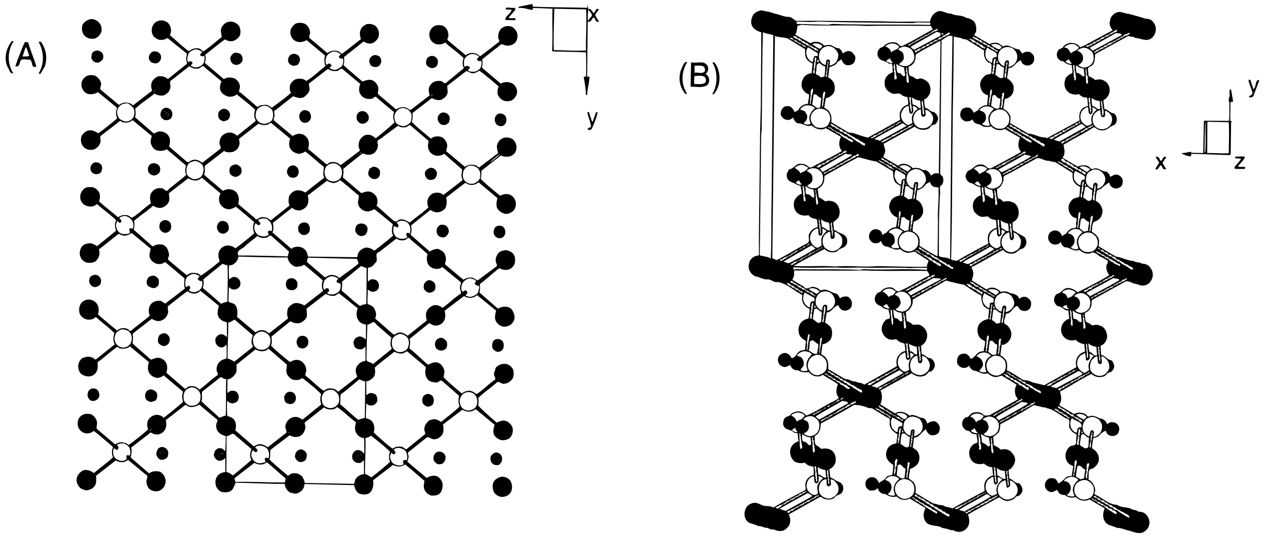

Figure 1. (A) A view of the structure of LiAuS along [1 0 0] (Au, black circles; S, open circles; Li, gray small circles) (50% probability). (B) The structure of LiAuS along [0 0 1]. The Li atoms are the small black circles.

Table 1. Summary of Crystallographic Data for LiAuS and NaAuS

formula	NaAuS	LiAuS
fw	252.02 g/mol	235.97 g/mol
a	14.658(5) Å	8.994(2) Å
b	21.043(7) Å	8.956(2) Å
c	7.118(4) Å	7.201(3) Å
β	90°	128.68(1)°
V	2195(3) Å^3	452.8(5) Å^3
space group	*Ccca* (no. 68)	*C*2/*c* (no. 15)
Z	32	8
d_{calc}	6.10 g/cm^3	6.92 g/cm^3
μ(Mo Kα)	539.68 cm^{-1}	652.2 cm^{-1}
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
R/R_w[a]	5.6%/8.3%	2.6%/3.2%

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, $w = 1/\sigma^2(F)$.

Table 2. Fractional Atomic Coordinates and B_{eq}[a] Values for LiAuS, with Estimated Standard Deviations in Parentheses

atom	Wyckoff symbol	x	y	z	B_{eq}
Au1	4a	0.0	0.0	0.0	1.32(3)
Au2	4d	0.25	0.25	0.5	1.31(3)
S	8f	0.2864(6)	0.1252(5)	0.2500(6)	1.2(1)
Li	8f	0.149(5)	0.377(1)	0.043(5)	2.3(9)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

for 4 days and then cooled at 4 °C/h to 100 °C and at 20 °C/h to room temperature. The product was isolated with methanol under a nitrogen atmosphere. The compound is stable in H_2O and common organic solvents such as alcohols, acetonitrile, and acetone, but it slowly decomposes in air over several days. Analysis on a number of these crystals by SEM/EDS indicated the present of Au and S. (Li is too light to be detected through the Be window of the detector.) For the purposes of phase identification, a measured powder pattern was compared to one calculated[14] from the appropriate structural parameters.

Table 3. Fractional Atomic Coordinates and B_{eq}[a] Values for NaAuS, with Estimated Standard Deviations in Parentheses

atom	Wyckoff symbol	x	y	z	B_{eq}
Au1	16i	0.1180(2)	0.3733(2)	0.2196(5)	2.1(1)
Au2	8g	0.0	0.25	0.465(1)	2.7(4)
Au3	8d	0.0	0.5	0.0	2.1(3)
S1	16i	0.128(6)	0.313(1)	0.491(3)	2(1)
S2	16i	0.129(5)	0.440(1)	−0.040(3)	2(1)
Na1	8e	0.249(4)	0.25	0.75	3(3)
Na2	8f	1.0	0.138(2)	0.75	2(2)
Na3	16i	0.691(3)	0.066(2)	0.092(4)	2(2)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

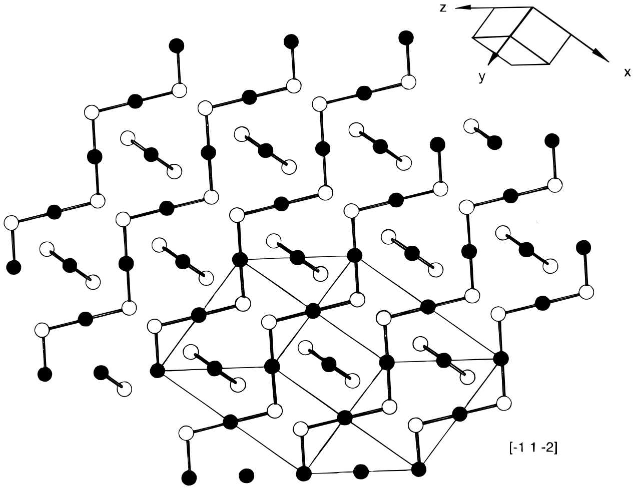

Figure 2. A projection view of the structure of LiAuS along [−1 1 −2]. For clarity, Li atoms have been deleted (Au, black circles; S, open circles).

d. NaAuS. Light-yellow rods of NaAuS were obtained from the reaction of 0.195 g (2.5 mmol) of Na_2S, 0.098 g (0.5 mmol) of Au metal, and 0.128 g (4.0 mmol) of elemental S. The charge was sealed inside an evacuated Pyrex tube, which was then placed inside a computer-controlled furnace. The tube was heated at 550 °C for 3 days and then cooled at 5 °C/h to 200 °C and at 20 °C/h to room temperature. The product was isolated with methanol under a nitrogen atmosphere. The compound is insoluble in H_2O and common organic solvents and is stable to air exposure for over a week. For the purposes of phase identification, a measured powder pattern was compared to one calculated[14] from the appropriate structural parameters.

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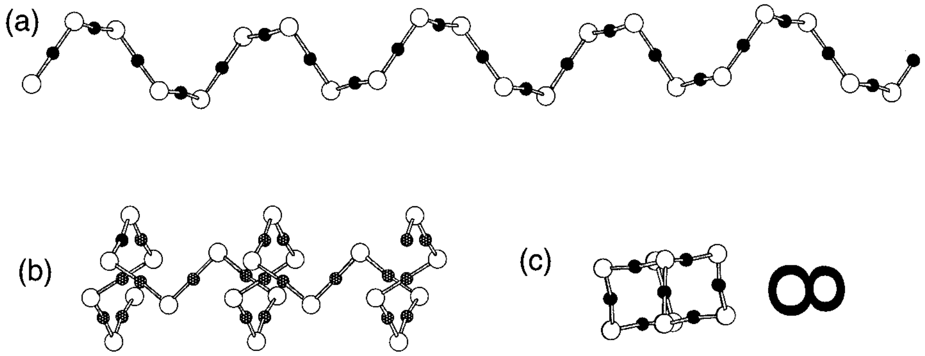

Figure 3. Three views of the coiling of the $(AuS)_n^{n-}$ chains in NaAuS (Au, black circles; S, open circles).

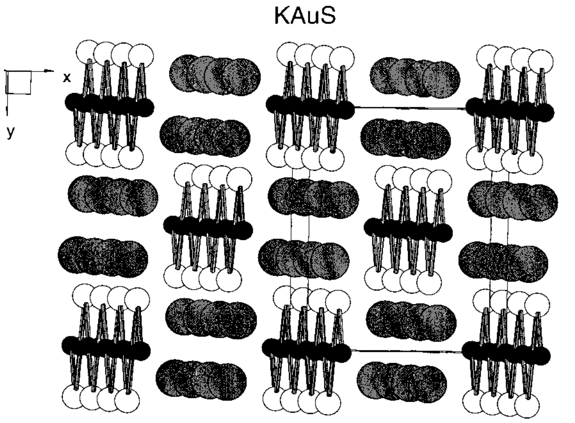

Figure 4. A projection view of the structure of KAuS along [0 0 1] (Au, black circles; S, open circles; K, gray circles).

Table 4. Selected Bond Distances for LiAuS and NaAuS, with Standard Deviations in Parentheses[a]

atom−atom	distance (Å)	atom−atom	distance (Å)
	LiAuS		
Au1−Au2	3.1732(6)	Li−S	2.51(3)
Au1−S	2.310(4)	Li−S	2.54(3)
Au2−S	2.309(4)	Li−S	2.53(3)
Li−S	2.56(3)		
	NaAuS		
Au2−Au2	3.06(1)	Na2−S1	2.82(6)
Au1−S1	2.32(3)	Na2−S2	2.92(5)
Au1−S2	2.32(2)	Na3−S1	2.81(5)
Au2−S1	2.30(7)	Na3−S2	2.78(4)
Au3−S2	2.30(6)	Na3−S2	2.96(4)
Na1−S1	2.87(7)	Na3−S2	2.80(7)
Na1−S1	2.82(7)		

[a] The estimated standard deviations in the mean bond length are calculated by the equation $\sigma l = \{\sum_n (l_n - l)^2/n(n-1)\}^{1/2}$, where l_n is the length of the nth bond, l is the mean length, and n is the number of bonds.

Crystallographic Studies. a. Single-Crystal X-ray Diffraction. Single-crystal X-ray diffraction data for LiAuS and NaAuS were collected on a computer-controlled Rigaku AFC6S four-circle autodiffractometer (Mo Kα radiation, graphite monochromated, at 23 °C). The cell parameters were determined by least-squares refinement of 16−25 computer-centered reflections. The intensity data were collected with the $\omega-2\theta$ scan technique at the speed of 4.0 deg/min. None of the crystals showed significant decay as judged by three check reflections measured every 150 reflections throughout their respective data sets. The space groups were determined from the systematic absences and intensity statistics. The structures were solved by the direct methods routine of SHELXS-86[15] and refined by the full-matrix least-squares techniques of the TEXSAN package of crystallographic programs.[16] An empirical absorption correction based on ψ-scans was applied to each data set, followed by a DIFABS[17] correction to the isotropically refined structure. All atoms were eventually refined anisotropically. All calculations were performed on a VAX Station 3100/76 computer. The complete parameters and details of the structure

Table 5. Selected Bond Angles for LiAuS and NaAuS, with Standard Deviations in Parentheses[a]

atom−atom−atom	angle (deg)	atom−atom−atom	angle (deg)
	LiAuS		
S−Au1−S	180	S−Li−S	112(1)
S−Au2−S	180	S−Li−S	114(1)
Au1−S−Au2	102.1(2)	S−Li−S	102(1)
S−Li−S	125(1)	S−Li−S	98.9(9)
S−Li−S	102(1)		
	NaAuS		
S1−Au1−S2	171.5(8)	S1−Na2−S2	96.3(7)
S1−Au2−S1	171(1)	S1−Na2−S2	107(6)
S2−Au3−S2	180	S2−Na2−S2	112(2)
Au1−S1−Au2	101(2)	S1−Na3−S2	105(2)
Au1−S2−Au3	100(2)	S1−Na3−S2	130(1)
S1−Na1−S1	125(1)	S1−Na3−S2	100(1)
S1−Na1−S1	103(2)	S2−Na3−S2	99(2)
S1−Na1−S1	104(3)	S2−Na3−S2	128(2)
S1−Na1−S1	100(3)	S2−Na3−S2	98(2)
S1−Na1−S1	137(2)		

[a] The estimated standard deviations in the mean bond angles are calculated by the equation $\sigma l = \{\sum_n (l_n - l)^2/n(n-1)\}^{1/2}$, where l_n is the angle of the nth bond, l is the mean angle, and n is the number of angles.

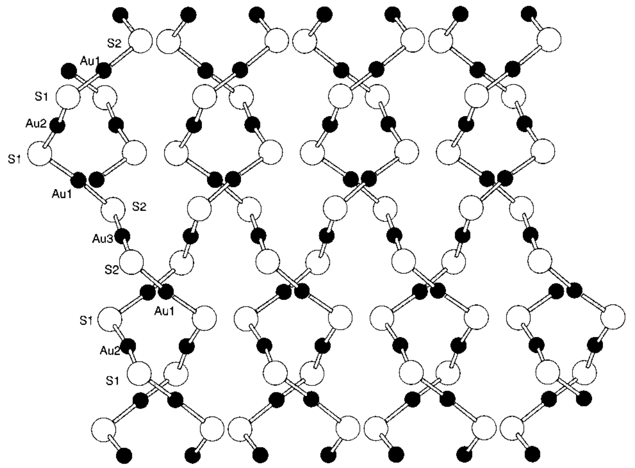

Figure 5. A view of the interweaving pattern of the $(AuS)_n^{n-}$ chains in NaAuS (Au, black circles; S, open circles).

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(15) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175−89.

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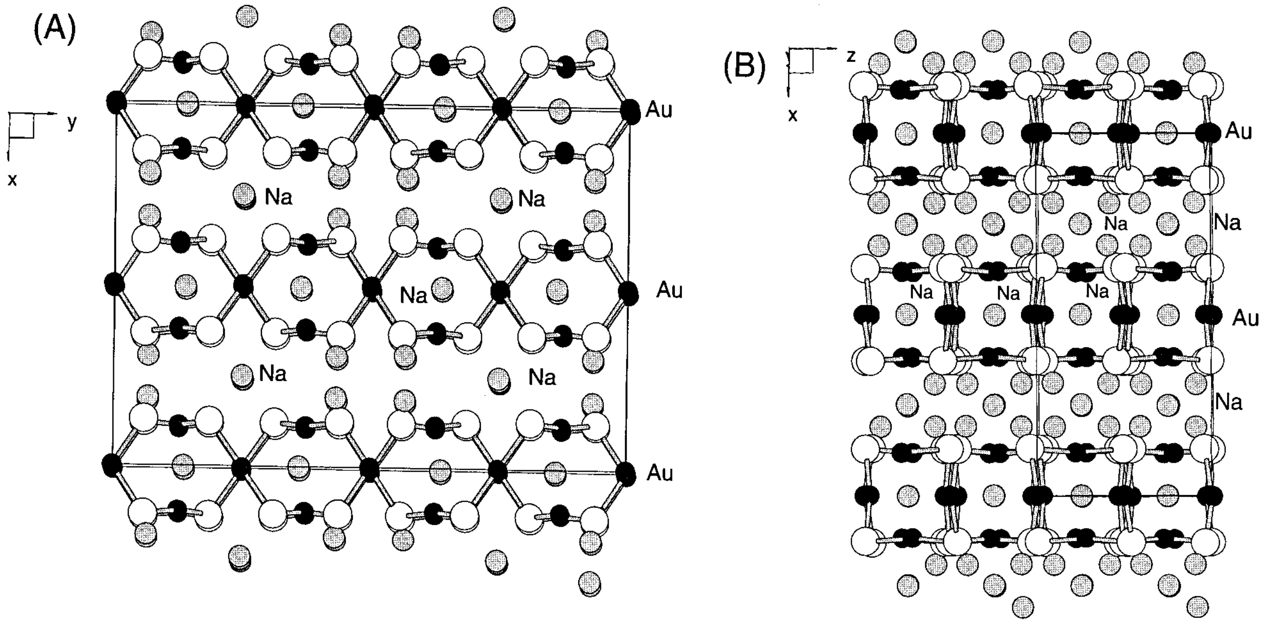

Figure 6. (A) A projection view of the structure of NaAuS along [0 0 1]. (B) A view of the structure of NaAuS along [0 1 0].

solution and refinement for the compounds are given in Table 1. The higher *R* values and thermal parameters in NaAuS are due to the poor crystal quality of the sample. The coordinates of all atoms, isotropic equivalent temperature factors, site multiplicities, and their standard deviations are given in Tables 2 and 3.

b. Powder X-ray Diffraction. The compounds were examined by X-ray powder diffraction to check for phase purity and for identification. The products obtained by the above methods of preparation were pure as judged by optical examination as well as X-ray powder diffraction. Powder patterns obtained on a Philips XRG-3000 powder diffractometer and a Rigaku rotating anode (Cu Kα) X-ray powder diffractometer, Rigaku-Denki/Rw400F2 (RotaFlex), provided accurate d_{hkl} spacings.

Results and Discussion

Structure Description. a. LiAuS. The structure of LiAuS consists of two nearly perpendicular sets of $(AuS)_n^{n-}$ zigzag chains, as seen in the projection view along [1 0 0] in Figure 1A. In this figure, Au atoms are black, sulfur atoms are white, and Li atoms are gray. The Au−S distances are normal, with Au1−S at 2.310(4) Å and Au2−S at 2.309(4) Å. The S−Au−S angle is constrained by symmetry to be 180°, a normal bond angle about Au.

Another view nearly along the [0 0 1] direction also reveals the two parallel sets of chains. In addition, channels are visible along this direction. Interestingly, the lithium atoms are situated near the sulfur columns and not in the middle of the channel; see Figure 1B. The immediate environment of the Li ions is tetrahedral, with Li−S distances varying from 2.51(3) to 2.56(3) Å.

To better see that the chains are in fact separate from each other, a projection view down the [−1 1 −2] direction is useful. One set of chains is in the plane of Figure 2, while one set is directed vertically out of the page. Within the set of chains in the plane of the figure, the Au−Au distance is half of the *b*-axis length, or 4.478 Å (i.e., the distance between two adjacent gold atoms in a given $(AuS)_n^{n-}$ chain). The shortest Au−Au distance occurs between chains, at 3.1732(6) Å. Distances of this order have been seen before in the $A_2Au_2Cd_2S_4$ (A = Rb, Cs) compounds.[18] In this compound, the chains have a simple zigzag pattern and are stretched out in a linear manner. With all the freedom about the linearly coordinated gold atoms, more complicated chain geometries are possible; see below.

b. NaAuS. The structure of NaAuS also consists of infinitely one-dimensional $(AuS)_n^{n-}$ chains; see Figure 3a. Such chains are not unusual in and of themselves; they exist in the isoelectronic compounds AAuQ[4] (A = K, Rb; Q = S, Se) and α-HgS.[19] An end-on view of one of the chains in α-HgS would reveal a triangular cross section. Interestingly, no $(AuS)_n^{n-}$ chain has yet been found to adopt a HgS-type of conformation. In NaAuS, the conformation and packing of the isoelectronic chains are much more elaborate than in any of the other analogues. Meanwhile, KAuS forms straight chains reminiscent of those seen above in LiAuS. In KAuS, the chains do not form perpendicular sets but line up in a parallel fashion; see Figure 4. In NaAuS, the coiling and packing is unique. In an elaborate corkscrew manner, the chains trace figure eights as they propagate, circling first in a clockwise manner and then in a counterclockwise manner; see Figure 3B. Of course, the projection view of one of these chains would appear to be a figure eight; see Figure 3C. In contrast, the chains in α-HgS coil into simple spirals with a projection down their axis being a simple equilateral triangle. In these chains, the Au−S bond lengths are normal, ranging from 2.30(7) to 2.32(2) Å. The S−Au−S angles, at 171.5(8)°, 171(1)°, and 180° for Au1, Au2, and Au3, respectively, are normal (Tables 4 and 5). Each sodium atom is coordinated by four sulfur atoms in a tetrahedral fashion. The Na−S distances vary from 2.80(7) to 2.96(4) Å.

In NaAuS, $(AuS)_n^{n-}$ chains pack together by interweaving with each other. Each chain weaves through the two chains on either side of it, resulting in a "chicken-wire-like" mesh; see Figure 5. There are Au2−Au2 contacts between chains, at a distance of 3.06(1) Å. Other Au−Au distances are longer, ranging from 3.486(7) to 3.752(4) Å. The meshes form layers which include Na atoms; see Figure 6. There are also interlayer Na^+ cations, as seen in Figure 6 as well.

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(19) Auvray, P.; Genet, F. *Bull. Soc. Fr. Mineral. Cristallogr.* **1973**, *96*, 218−219.

NaAuS and $Na_7Au_5S_6$[6] both contain this unusual "chicken-wire-like" layer. In the latter compound, the meshes are further separated by a layer of linear discrete AuS_2^{3-} anions as well as the Na^+ cations necessary to balance the charge. These AuS_2^{3-} dumbbell anions are observed by themselves in the compound Na_3AuS_2.[5] Upon reflection then, it is easy to see how the compounds are related stoichiometrically.

$$Na_4Au_4S_4\ (NaAuS) + Na_3AuS_2 = Na_7Au_5S_6$$

The band gap of LiAuS was determined to be 2.1 eV, while the melting point and the crystallization point were determined to be 573 and 553 °C, respectively, by techniques standard in this laboratory.[20] By comparison, the band gap of NaAuS is 2.7 eV, considerably larger than that of the Li analogue; this suggests that the Li ions interact with the $[AuS]^-$ substructure much more strongly than the Na ions. This is consistent with the expected trend in alkali metal atoms where the degree of covalency in A−S (or A−O) bonds increases from the bottom to the top of the group. The surprising moisture stability of LiAuS also suggests that this material has characteristics that are closer to those of a three-dimensional material than to those of a low-dimensional material.

The variability in the packing of the chains in the AAuS series (A = alkali metal) suggests that mixed cation reactions may be interesting and may yield other coiling motifs of the highly flexible $(AuS)_n^{n-}$ species.

Acknowledgment. Financial support from the National Science Foundation DMR-9527347 is gratefully acknowledged. M.G.K. is an A. P. Sloan Foundation and a Camille and Henry Dreyfus Teacher Scholar 1993−98. This work made use of the SEM facilities of the Center for Electron Optics at Michigan State University.

Supporting Information Available: Tables listing crystallographic data, atomic positional coordinates of all atoms, and bond lengths and angles for LiAuS and NaAuS (12 pages). Ordering information is given on any current masthead page.

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