Inorg. Chem. **2001,** *40,* 1397−1398

Syntheses and Structures of LiAuS and Li_3AuS_2

Fu Qiang Huang, Yuting Yang,
Christine Flaschenriem, and James A. Ibers*

Department of Chemistry, Northwestern University,
2145 Sheridan Road, Evanston, Illinois 60208-3113

Received September 29, 2000

Introduction

Gold nanoparticles and gold complexes have attracted considerable attention because of their remarkable luminescent properties.[1−7] These gold complexes exhibit attractive $Au^+\cdots Au^+$ interactions, for example an interaction of 3.308(2) Å in $[Au_3(CH_3N{=}COCH_3)_3]$, a compound that shows remarkable solvent-stimulated luminescence.[2] Contacts between linearly coordinated Au^+ centers that are shorter than 3.5 Å in length are considered attractive.[2−6] Such weakly attractive interactions, which are ca. 7−11 kcal/mol in energy,[7−9] are the result of correlation effects enhanced by relativistic effects.[10,11]

In a search for extended solid-state structures that exhibit short $Au^+\cdots Au^+$ interactions our attention has turned to several ternary alkali metal (A) gold (Au) chalcogenides (Q) synthesized recently by means of the reactive flux technique[12] with AQ_x ($x \geq 2$) fluxes.[13−15] One such report[15] presented a monoclinic cell and atomic coordinates for LiAuS that immediately suggested an incorrect crystal system. Subsequent examination of the cell and coordinates with the programs MISSYM[16] and XPREP[17] suggested that the structure of LiAuS should be described in the orthorhombic system. Since no intensity data were available, it was necessary to resynthesize the compound to ascertain if the monoclinic cell was incorrect. In the course of this synthesis, the compound Li_3AuS_2 was also synthesized. Here we report its structure along with the correct crystal structure for LiAuS. In both structures, short interactions exist between linear two-coordinated Au^+ cations.

Table 1. Crystal Data and Structure Refinements for LiAuS and Li_3AuS_2

	LiAuS	Li_3AuS_2
formula weight	235.97	281.91
space group	*Fddd*	*Ibam*
a (Å)	8.9252(15)	5.763(1)
b (Å)	8.9686(15)	11.281(2)
c (Å)	11.2062(19)	6.276(1)
V (Å^3)	897.0(3)	408.1(1)
Z	16	4
T (K)	153(2)	153(2)
λ (Mo Kα, Å)	0.710 73	0.710 73
ρ_{calc} (g/cm^3)	6.989	4.589
μ (cm^{-1})	660.58	368.3
$R(F)^a$ ($F_o^2 > 2\sigma(F_o^2)$)	0.0270	0.0304
$R_w(F_o^2)^b$ (all data)	0.0682	0.0757

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

Experimental Section

Synthesis. The following reagents were used as obtained: Li (Alfa, 99.9%), Au (Alfa, 99.96+%), and S (Alfa, 99.5%). Li_2S, the reactive flux[12] employed in the syntheses, was synthesized from a reaction of stoichiometric amounts of elemental Li and S, dissolved in liquid ammonia at 194 K under an N_2 atmosphere. The compounds LiAuS and Li_3AuS_2 were prepared by the reactions of mixtures of 2.0 mmol Li_2S, 0.5 mmol Au, and 4.0 mmol S. These mixtures were loaded into fused-silica tubes under an Ar atmosphere in a glovebox. Two tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The tubes were kept at 793 and 773 K, respectively, for 96 h, and then cooled at 3 K/h to 298 K. The reaction mixtures were washed free of alkali chalcogenides with dimethylformamide and then dried with acetone. Orange blocks of LiAuS were found in the first tube, and light yellow flat needles of Li_3AuS_2 as well as orange blocks of LiAuS were found in the second. EDX analyses with a Hitachi S-4500 scanning electron microscope confirmed the existence of Au and S in both the light yellow and orange samples. Both materials decompose in air. This has prevented the measurement of their luminescence properties.

Crystallographic Studies. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[18] The collection of the intensity data was carried out with the program SMART.[18] Cell refinement and data reduction were carried out with the use of the program SAINT,[18] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[17] Then the program SADABS[18] was employed to make incident beam and decay corrections.

The structures were solved with the direct-methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL.PC suite of programs.[19] Each final refinement included anisotropic displacement parameters and a secondary extinction correction. Additional experimental details are shown in Table 1. Table 2 gives positional parameters and equivalent isotropic displacement parameters and Table 3 presents selected bond distances and bond angles.

The structure of LiAuS was reported previously in a monoclinic cell ($a' = 8.994(2)$ Å, $b' = 8.956(2)$ Å, $c' = 7.201(3)$ Å, $\beta' = 128.68(1)°$) in space group *C*2/*c*.[15] This incorrect cell is related to the present correct orthorhombic cell (space group *Fddd*) by the transformation

---

(1) Ottersen, O. P.; Zhang, N.; Walberg, F. *Neuroscience* **1992**, *46*, 519−534.
(2) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179−1181.
(3) Van Calcar, P. M.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1997**, *36*, 5231−5238.
(4) Toronto, D. V.; Weissbart, B.; Timi, D. S.; Balch, A. L. *Inorg. Chem.* **1996**, *35*, 2484−2489.
(5) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319−322.
(6) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391−400.
(7) Sato, T.; Ahmed, H.; Brown, D.; Johnson, B. F. G. *J. Appl. Phys.* **1997**, *82*, 696−701.
(8) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636.
(9) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133−138.
(10) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417−419.
(11) Pyykkö, P.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3*, 1458−1465.
(12) Sunshine, S. A.; Kang, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 6202−6204.
(13) Klepp, K. O.; Weithaler, C. *J. Alloys Compd.* **1996**, *243*, 1−5.
(14) Klepp, K. O.; Weithaler, C. *J. Alloys Compd.* **1996**, *243*, 12−18.
(15) Axtell, E. A., III; Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, *37*, 5583−5587.
(16) Le Page, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264−269.
(17) Sheldrick, G. M. *SHELXTL* DOS/Windows/NT Version 5.10; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 1997.
(18) *SMART* Version 5.054 Data Collection and *SAINT-Plus* Version 6.02A Data Processing Software for the SMART System; Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2000.
(19) Sheldrick, G. M. *SHELXTL* PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

10.1021/ic001275i CCC: $20.00

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for LiAuS and Li_3AuS_2

atom	*x*	*y*	*z*	U_{eq} (Å^2)^a
		LiAuS		
Li	1/8	1/8	0.478(2)	0.017(5)
Au	0	0	0	0.0132(3)
S	1/8	0.4122(5)	1/8	0.0103(7)
		Li_3AuS_2		
Li1	0	0.230(2)	1/4	0.021(6)
Li2	1/2	0	1/4	0.015(7)
Au	0	0	0	0.0090(3)
S	0.2929(4)	0.14073(17)	0	0.0103(6)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for LiAuS and Li_3AuS_2

LiAuS		Li_3AuS_2	
Li−S ×2	2.52(2)	Li1−S ×2	2.450(15)
Li−S ×2	2.53(1)	Li1−S ×2	2.517(11)
Au−S ×2	2.307(3)	Li2−S ×4	2.5311(16)
Au···Au ×2	3.1632(4)	Au−S ×2	2.317(2)
S−Au−S	180	Au···Au ×2	3.1383(6)
		S−Au−S	180

matrix (0 1 0, −1 0 0, 1 0 2), and the new coordinates are related to the old ones by the transformation matrix (0 1 0, −1 0 $^1/_2$, 0 0 $^1/_2$). The relation between these cells is shown in Figure 1.

Results and Discussion

The unit cell of LiAuS is shown in Figure 1. LiAuS contains infinite zigzag one-dimensional $^{1}_{\infty}[\mathrm{AuS}^-]$ chains that run along [101] and $[10\bar{1}]$. Each Li atom is tetrahedrally coordinated to four S atoms in four individual chains. The present metrical data do not differ significantly from those determined previously.[15] The Li−S distances of 2.52(2) and 2.53(1) Å are comparable to those of 2.29(7)−2.59(7) Å in $LiGaS_2$.[20] Each Au atom in LiAuS is linearly coordinated to two S atoms by an Au−S distance of 2.307(3) Å, to be compared with that of 2.32(1) Å in $CsAu_3S_2$.[13] Each Au atom in the chain has two very close Au neighbors at a $Au^+\cdots Au^+$ distance of 3.1632(4) Å. Similar short $Au^+\cdots Au^+$ interactions have been found in other A/Au/Q compounds, for example 3.096(1) Å in $CsAu_3S_2$,[13] 3.1405(5) Å in $CsAu_3Se_2$,[13] and 3.402(2) and 3.013(2) Å in $Cs_4Au_6S_5$.[14]

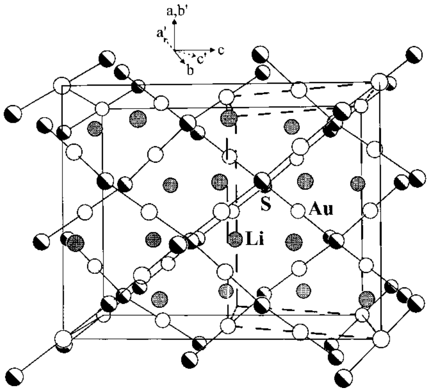

Figure 1. Unit cell of LiAuS along [010] showing the correct cell in solid lines and the incorrect cell in dashed lines.

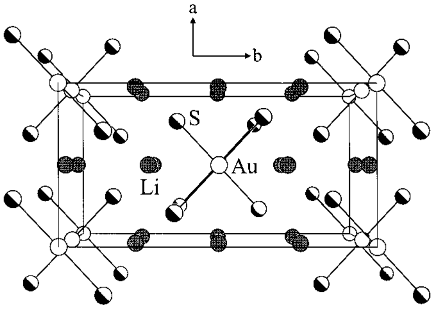

Figure 2. Unit cell of Li_3AuS_2 along [001] showing the Au···Au interactions.

The structure of the compound Li_3AuS_2, which is isostructural with that of Na_3AgS_2,[21] is shown in Figure 2. It consists of isolated linear S−Au−S units. These isolated $[\mathrm{AuS_2}^{3-}]$ units are linked together by short $Au^+\cdots Au^+$ interactions of 3.1383(6) Å (Table 3) to form chains along [001]. The chains are separated by Li atoms, which are tetrahedrally coordinated to four S atoms in four individual units. Bond distances (Table 3) in Li_3AuS_2 are normal.

No Li/Au/Se or Li/Au/Te structures have been reported. The two known Li/Au/O structures are Li_3AuO_3[22] and Li_5AuO_4,[22] both compounds with four-coordinated Au^{3+}.

Acknowledgment. This research was supported by the U.S. National Science Foundation under Grant DMR 97-09351. This work made use of Central Facilities supported by the MRSEC program of the National Science Foundation (DMR-9632472) at the Materials Research Center of Northwestern University.

Supporting Information Available: Crystallographic data in CIF format for LiAuS and Li_3AuS_2. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001275I

---

(20) Leal-Gonzalez, J.; Melibary, S. S.; Smith, A. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 2017−2019.

(21) Klepp, K. O.; Bronger, W. *J. Less-Common Met.* **1985**, *106*, 95−101.

(22) Wasel-Nielen, H. D.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1970**, *375*, 43−54.