Inorg. Chem. **2002**, *41*, 3605–3607

Inorganic Chemistry
Communication

Controlling Lewis Basicity in Polythioarsenate Fluxes: Stabilization of $KSnAsS_5$ and $K_2SnAs_2S_6$. Extended Chains and Slabs Based on Pyramidal β-$[AsS_4]^{3-}$ and $[AsS_3]^{3-}$ Units

Ratnasabapathy G. Iyer and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental Materials Research,
Michigan State University, East Lansing, Michigan 48824

Received February 1, 2002

Two low-dimensional compounds, $KSnAsS_5$ and $K_2SnAs_2S_6$, were prepared using liquid polythioarsenate salts, and the results differ from those obtained with the well studied thiophosphate flux. $KSnAsS_5$ crystallizes in the orthorhombic space group *Pbam* with cell parameters of $a = 8.136(2)$ Å, $b = 13.784(4)$ Å, $c = 7.428(2)$ Å. $KSnAsS_5$ features the unusual pyramidal species $[AsS_2(S_2)]^{3-}$. $K_2SnAs_2S_6$ crystallizes in the trigonal space group $P\bar{3}$ with cell parameters $a = 6.717(5)$ Å, $b = 7.204(8)$ Å, $\gamma = 120°$. The compounds were obtained by controlling the Lewis basicity of the $K_2S/As_2S_3/S$ flux. The optical, thermal, and spectroscopic properties of the compounds are reported.

In view of the considerable body of information now available on polychalcophosphate fluxes,[1] it is timely to ask how the corresponding *polychalcoarsenate* fluxes perform as synthetic tools and what type of phases are likely to form. Because P and As are members of the same group in the periodic table, one might expect simple analogues both in composition and structure. However, there seems to be a significant divide at the P−As boundary in terms of chemical and electronic behavior in these two elements. A marked difference in their ionization energies could give rise to different redox behavior. For example, whereas the most stable oxidation states of P as evidenced by the frequency of the $[P_2Q_6]^{4-}$ [2] and $[PQ_4]^{3-}$ [3] ($Q = S$, Se) anions in known phases are $+4$ and $+5$, this is not likely to be the case for As because of the greater stability of the $+3$ state and the extreme rarity of the $+4$ state. The corresponding ethane-like unit $[As_2Q_6]^{4-}$ (ubiquitous in P chemistry) does not exist; however, other anions such as $[As_2Q_5]$,$^{4-}$ [4] $[AsQ_3]$,$^{3-}$ [5] are known and might form in the melt. Conversely, in P chemistry, these species are unknown or are extremely rare. The only species common in both elements are the classical tetrahedral $[PQ_4]^{3-}$ and $[AsQ_4]^{3-}$ [6] anions. Therefore, we anticipate a sharp contrast between $[As_xQ_y]^{z-}$ and $[P_xQ_y]^{z-}$ chemistry.

Here, we report on the reactivity of Sn in thioarsenate melts of increasing Lewis basicity and the isolation of $KSnAsS_5$, a new structure type with infinite chains and the rare pyramidal β-$[AsS_4]^{3-}$ ligand, and the layered $K_2SnAs_2S_6$. $KSnAsS_5$ forms by dissolving Sn in liquid "$K_2As_2S_{14}$" at 500 °C.[7] The structure[8] contains extended chains oriented parallel to the *c*-axis and separated by K^+ ions, Figure 1a. The key unit in the chain is a centrosymmetric $[Sn(AsS_2(S_2))]_2$ dimeric core that propagates down the chain with bridging μ_2-S^{2-} ions. The pyramidal β-$[AsS_4]^{3-}$ anion features the As^{3+} ion and a disulfide unit, and it is very different from the well-known As^{5+} species *a*-$[AsS_4]^{3-}$.

All three terminal sulfur atoms are involved in binding the two Sn^{4+} ions. The terminal atom, S(1), of the disulfide

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* To whom correspondence should be addressed. E-mail: kanatzid@cem.msu.edu.

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(7) $KSnAsS_5$ was synthesized from a 1:1:1:10 mixture of K_2S (0.033 g, 0.3 mmol), Sn (0.036 g, 0.3 mmol), As_2S_3 (0.074 g, 0.3 mmol), S (0.096 g, 3 mmol). The reactant mixture was sealed under vacuum ($\sim 10^{-5}$ mbar) in a fused silica tube and heated to 500 °C for 60 h followed by slow cooling to 250 °C at 5 °C/h and rapid cooling to room temperature. Reddish-brown, air and moisture stable, rectangular block-like crystals were isolated in >85% yield after dissolving the flux away using *N*,*N*-dimethylformamide (DMF). Semiquantitative microprobe (EDS) analysis on several of these crystals gave an average composition of $K_{1.0}Sn_{1.0}As_{1.0}S_{5.1}$. The Raman spectrum displays peaks at 137 (s), 154 (s), 167 (s), 187 (s), 219 (m), 254 (vs), 286 (vs), 319 (sh), 327 (vs), 342 (m), 377 (m), and 471 (w) cm^{-1}. These peaks can be attributed to either As−S or Sn−S vibration modes. However, the peak at 471 cm^{-1} is assigned to the S−S stretching of the disulfide unit. The electronic spectrum of $KSnAsS_5$ shows sharp optical absorption corresponding to a band gap of 2.11 eV which is consistent with its reddish-orange color.

10.1021/ic025523h CCC: $22.00

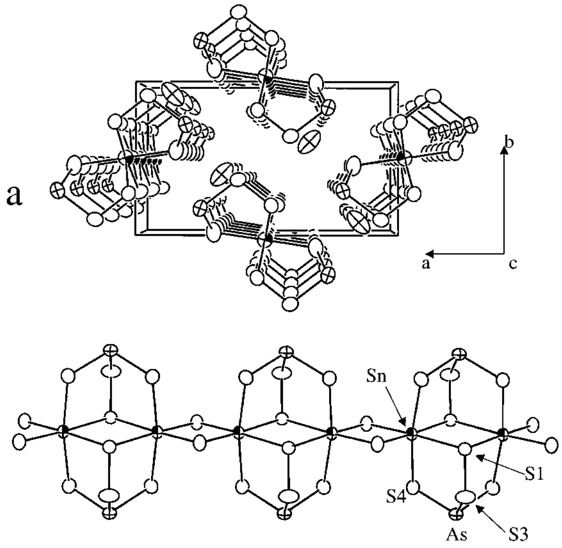


Figure 1. (a) ORTEP packing diagram of $KSnAsS_5$ looking down the *c* axis. The large ellipsoids with open quadrants are K^+ ions. S atoms are small open ellipsoids, As atoms are small ellipsoids with open quadrants, and Sn atoms are ellipsoids with a completely filled quadrant. (b) ORTEP representation and labeling of a single chain of $KSnAsS_5$. Selected bond distances (Å): Sn(1)−S(2), 2.4863(13); Sn(1)−S(4), 2.5540(14); Sn(1)−S(1), 2.6661; S(1)−S(3), 2.038(2); As(1)−S(4), 2.2172(14); As(1)−S(3), 2.2912(19). Selected bond angles (deg): S(2)−Sn(1)−S(4), 87.49; S(4)−Sn(1)−S(1), 84.65; S(4)−As(1)−S(3), 97.63; S(4)−As(1)−S(4), 104.52.

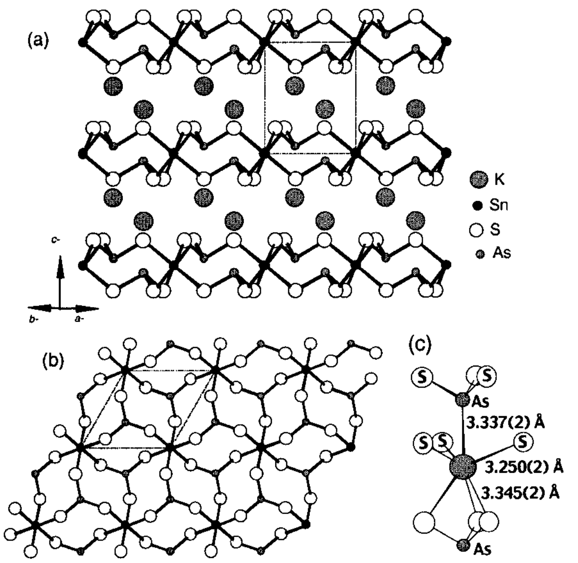
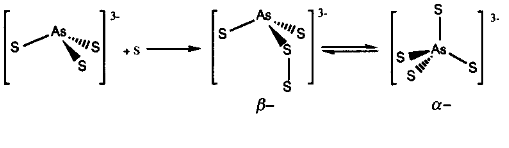


Figure 2. (a) View of $K_2SnAs_2S_6$ looking down the [110] direction. Large gray circles between the layers are K^+ ions. Small black circles are Sn atoms, small gray circles are As atoms, and open circles are sulfur atoms. (b) Single layer of $[SnAs_2S_6]^{2-}$ with the eight member −S−Sn−S−As−S−Sn−S−As− rings. Selected bond distances (Å): Sn−S, 2.572(4); As−S, 2.264(4). Selected bond angles (deg): S−As−S, 96.48(13); S−Sn−S, 84.15(12); S−Sn−S, 95.85(12); S−Sn−S, 180.0. (c) Local coordination environment of K ions with bond lengths. The apparent bonding interaction of the As atom with the K ion at 3.337(2) Å is shown.

group serves to bridge the Sn atoms in the core, Figure 1b. The formally Sn^{4+} centers possess a highly distorted octahedral coordination that is imposed by the ligation of the $[AsS_4]^{3-}$ anion. The S(4)−Sn−S(4) angle of 169.66(6)° deviates significantly from 180°. The Sn−S distances vary between 2.486(1) and 2.666(1) Å. The Sn−Sn distances within the core and between the cores are 3.967 and 3.461 Å, respectively. The adjacent chains are separated by hexacoordinated K^+ ions with a mean K−S distance of 3.342(2) Å.

This pyramidal unit is to be contrasted with the highly symmetrical tetrahedral α-$[AsS_4]^{3-}$ anion which is formally an As^{5+} species and isostructural to the more familiar $[PS_4]^{3-}$ anion. Therefore, we recognize here a radical departure of the thioarsenate flux chemistry from that of the thiophosphate which we attribute to the significant electronegativity difference in the two elements.



The β-$[AsS_4]^{3-}$ anion has been stabilized from a sulfur-rich flux, formally "$K_2As_2S_{14}$", which apparently is not oxidizing enough to produce As^{5+}. It is possible that the two isomers are in fact in equilibrium with each other. Presumably, this equilibrium would be sensitive to the basicity of the flux which to a large extent is controlled by the formal $K_2S/As_2S_3/S$ ratio, and by the nature of the alkali ion. Thus, by controlling such equilibria in the flux, one could favor different thioarsenate anions to produce different outcomes. The β-$[AsS_4]^{3-}$ ligand has been seen only in molecular $[Pt_3(AsS_4)_3]^{3-}$ and $[Pd_3(AsS_4)_3]^{3-}$.[9]

In KSnS(AsS_4), we discovered a glass forming property. The material melts at 400 °C and when cooled to room temperature forms a red glass. However, the melt slowly generates SnS_2 nanocrystals (confirmed by X-ray diffraction) which are found embedded in the glassy matrix.

The trigonal compound $K_2SnAs_2S_6$[10] formed in a mixture of $K_2S/Sn/As_2S_3/S$ at 500 °C using a 3/1/1/10 ratio (i.e., formally molten "$K_6As_2S_{16}$"). It is isomorphic to the rare mineral Ernigglite, $Tl_2SnAs_2S_6$,[11] and has $[SnAs_2S_6]^{2-}$ layers[12] consisting of SnS_6 octahedra and $[AsS_3]^{3-}$ pyramids,

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(8) Crystal data at 293(2) K: Siemens SMART Platform CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), orthorhombic, *Pbam*, $a = 8.136(2)$ Å, $b = 13.784(4)$ Å, $c = 7.428(2)$ Å, $V = 833.0(4)$ Å^3, $Z = 4$, $D_c = 3.134$ mg/m^3, crystal dimensions 0.174 × 0.017 × 0.048 mm^3, $\mu = 8.663$ mm^{-1}, $2\theta = 5.48-56.26°$, 7369 total reflections, 1034 unique reflections with $R(\text{int}) = 0.036$, refinement on F^2, GOF = 1.026, 45 parameters, R1 = 3.14%, wR2 = 7.85 for $I > 2\sigma(I)$. An empirical absorption correction was done using SADABS,[8a] and all atoms were refined anisotropically. Structure solution and refinement was performed using the SHELXTL[8a] package of crystallographic programs. (a) Bruker Analytical X-ray Instruments Inc., Madison, WI.

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(10) $K_2SnAs_2S_6$ was initially prepared in a low yield (5%) from a reaction of a 3:1:1:10 mixture of K_2S (0.099 g, 0.9 mmol), Sn (0.036 g, 0.3 mmol), As_2S_3 (0.148 g, 0.6 mmol), and S (0.096 g, 3 mmol) under vacuum in a silica tube at 500 °C for 60 h. A clean synthesis with yields of over 90% was achieved from a ratio of 4/1/3/10 of the same reactants. The product, consisting of air and moisture stable dark red hexagonal crystals, was isolated by washing the excess of flux, under nitrogen, with DMF and washed with ether. Microprobe analysis (EDS) gave an average composition of $K_{2.0}Sn_{1.0}As_{1.9}S_{6.0}$. The Raman spectrum displays three strong peaks at 318, 340, and 399 cm^{-1}. The far-IR spectrum of the compound shows three strong peaks at 350, 270, and 154 and medium to weak peaks at 404, 302, 247, and 228 cm^{-1}. The material melts at 490 °C and crystallizes at ~406 °C without apparent decomposition, as evidenced by the powder pattern taken after crystallization from the melt. The optical spectrum of $K_2SnAs_2S_6$ shows a sharp absorption corresponding to a band gap of 1.89 eV consistent with its red color.

Figure 2a,b. Topologically, the structure is TiS_2-type with Sn^{2+} cations in the octahedral Ti positions and $[AsS_3]^{3-}$ anions at the pyramidal S positions. However, the $[AsS_3]^{3-}$ pyramids are inverted in a way that the As^{3+} atoms of a $[AsS_3]^{3-}$ anion on the top side of a $[SnAs_2S_6]^{2-}$ slab lie toward the slab's interior so that the lone electron pair is directed to the bottom side, Figure 2a. This "expanded TiS_2" structure creates large rings in the layers that dominate the two-dimensional network. The Sn−S bond distances are all equal at 2.572(4) Å. The closest interlayer distance is 4.419 Å, and the closest Sn−Sn distances within the layer and between the layers are 6.717 and 7.204 Å. The layers are separated by seven coordinate K^+ ions. Noteworthy is the unusual and surprising interaction at 3.337(2) Å between K^+ ions in the layers and the As atom of a $[AsS_3]^{3-}$ ligand, which in fact lies on the opposite side of the $[SnAs_2S_6]^{2-}$ slab, Figure 2c. This is possible because of the inverted nature of the $[AsS_3]^{3-}$ anion as explained previously.

We have shown that by changing the Lewis basicity of the flux we can control the reactivity of Sn and outcome of the reaction. Namely, a relatively K_2S-poor/polysulfide-rich flux ("$K_2As_2S_{14}$") favors $KSnAsS_5$ with the disulfido β-$[AsS_4]^{3-}$ unit as the dominant species, whereas by increasing the fraction of K_2S (forming "$K_6As_2S_{16}$", the major constituents are $K_2Sn_2S_5$ and K_3AsS_4) the polysulfide anions break down as the Lewis basicity increases and $KSnAsS_5$ is destabilized in favor of $K_2SnAs_2S_6$ and the $[AsS_3]^{3-}$ anion. This chemistry has no direct counterpart in the corresponding Sn polythiophosphate systems.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-0127644) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Crystal data at 293(2) K: Siemens SMART Platform CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å), trigonal, $P\bar{3}$, $a = 6.7171(5)$ Å, $c = 7.204(8)$ Å, $V = 281.5(4)$ Å^3, $Z = 1$, $D_c = 3.18$ mg/m^3, crystal dimensions 0.074 × 0.049 × 0.013 mm^3, $\mu = 9.989$ mm^{-1}, $2\theta = 5.66-56.28°$, 1823 total reflections, 442 unique reflections with $R(\text{int}) = 0.065$, refinement on F^2, GOF = 1.157, 21 parameters, R1 = 5.54%, wR2 = 10.6 for $I > 2\sigma(I)$. An empirical absorption correction was done using SADABS,[8a] and all atoms were refined anisotropically. Structure solution and refinement was performed using SHELXTL[8a] package of crystallographic programs.