

in the acylation of  $\text{CO}_2$  since various acylating agents  $\text{CH}_3\text{C}(\text{O})\text{X}$  ( $\text{X} = \text{Cl}, \text{OC}_2\text{H}_5, \text{SC}(\text{O})\text{CH}_3, \text{OC}(\text{O})\text{CH}_3$ ) did not give  $\text{CH}_3\text{C}(\text{O})\text{COO}^-$  under the similar electrolysis conditions. The present  $\text{CO}_2$  fixation, which is essentially identical with that of pyruvate synthase, may therefore give a clue to elucidate the reaction mechanism of eq 1 as the key steps in the reductive carboxylic acid cycle.

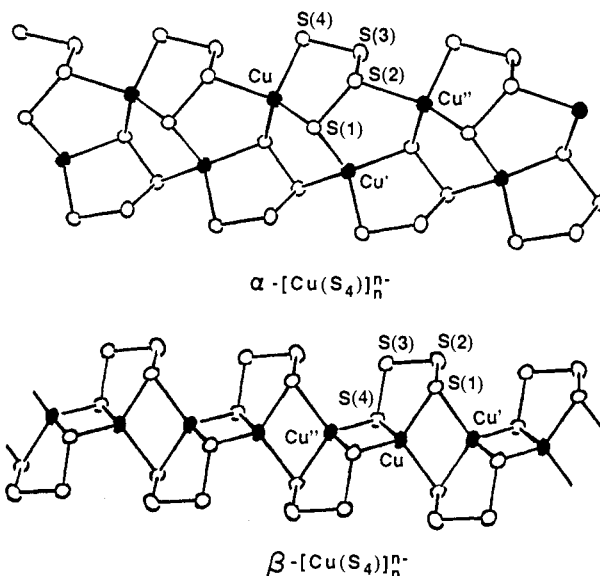
(31) Pyruvate was also produced catalytically when  $\text{CH}_3\text{C}(\text{O})\text{SC}_2\text{H}_5$  was used in place of  $\text{CH}_3\text{C}(\text{O})\text{SC}_2\text{H}_5$ .

### Polychalcogenide Synthesis in Molten Salts. Novel One-Dimensional Compounds in the K/Cu/S System Containing Exclusively $\text{S}_4^{2-}$ Ligands

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Thus far, the great majority of synthetic metal/chalcogenide chemistry has been carried out either in solution<sup>1</sup> at (or near) room temperature or in the solid state at high (>350 °C) temperatures.<sup>2</sup> The compounds obtained at low temperatures are soluble, discrete molecular species containing a diverse repertoire of  $\text{Q}_x^{2-}$  ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ ) ligands with  $x$  ranging from 1 (e.g.,  $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-3}$ ) to 9 (e.g.,  $[\text{Au}(\text{S}_9)]^{1-4}$ ). By far, among the discrete polychalcogenides, the  $\text{Q}_4^{2-}$  ligands are the most frequently occurring. The high-temperature compounds tend to be extended, three-dimensional, solid-state structures containing either  $\text{Q}^{2-}$  or  $\text{Q}_2^{2-}$  ligands. The higher  $\text{Q}_x^{2-}$  ligands are too thermally sensitive to be stabilized in solid-state compounds from high temperatures.<sup>5</sup> They dissociate to lower polychalcogenides and sulfur. In general, the low-temperature compounds can be viewed as metastable and thus capable of transforming to their high-temperature solid-state counterparts via interesting and perhaps isolable low-dimensional intermediates. These could occur in the intermediate temperature range (ca. 150–350 °C). Increasing interest in metastable low-dimensional polychalcogenides derives not only from the catalytic<sup>6</sup> and electronic properties of these materials<sup>7</sup> but also because they offer a bridge between molecular and solid-state chemistry. To date, a very limited effort has been invested in the systematic



**Figure 1.** Top: View of the  $\alpha\text{-}[\text{Cu}(\text{S}_4)]_n^{n-}$  infinite chain (four unit cells) with labeling scheme. Selected distances are as follows: Cu–S(1) 2.299 (3), Cu–S(4) 2.298 (4), Cu'–S(1) 2.324 (3), Cu''–S(2) 2.432 (4), S(1)–S(2) 2.089 (5), S(2)–S(3) 2.093 (4), S(3)–S(4) 2.056 (6) Å. Selected angles are as follows: Cu–S(1)–Cu' 102.0 (1), S(1)–Cu–S(4), 103.3 (1)°. Cu' and Cu'' are crystallographically equivalent to Cu. Bottom: View of the  $\beta\text{-}[\text{Cu}(\text{S}_4)]_n^{n-}$  infinite chain (four unit cells) with labeling scheme. Selected distances are as follows: Cu–S(1) 2.368 (2), Cu–S(4) 2.360 (2), Cu'–S(1) 2.372 (2), Cu''–S(4) 2.378 (2), S(1)–S(2) 2.078 (2), S(2)–S(3) 2.060 (3), S(3)–S(4) 2.079 (3) Å. Selected angles are as follows: S(1)–Cu–S(4) 110.33 (8), Cu–S(1)–Cu' 66.7 (7), Cu–S(4)–Cu'' 68.4 (6), S(1)–Cu–S(1)' 113.3 (1), S(4)–Cu–S(4)' 111.6 (1), Cu''–Cu–Cu' 173.5°. Cu, Cu', and Cu'' atoms are crystallographically equivalent.

synthesis of inorganic and particularly chalcogen-rich compounds at intermediate temperatures. This is primarily because of the lack of suitable solvents.<sup>8</sup> A sensible approach would be to employ molten salt systems as solvents. Despite the considerable knowledge accumulated about molten salts and eutectics,<sup>9</sup> little chalcogenide synthesis has been reported. Alkali metal polychalcogenide systems are appropriate and have been previously used, at high temperatures, to prepare and/or recrystallize simple mostly binary metal sulfides.<sup>10</sup> Ibers and co-workers were successful in applying such synthetic approach at 340–375 °C to isolate the very interesting  $\text{K}_4\text{Ti}_3\text{S}_{14}$  and  $\text{Na}_2\text{Ti}_2\text{Se}_8$  which possess unusual one-dimensional structures featuring  $\text{Q}_2^{2-}$  ligands.<sup>11</sup> Recently we reported<sup>12</sup> on the new, metastable, one-dimensional  $[\text{Ag}(\text{Se}_4)]_n^{n-}$ , containing  $\text{Se}_4^{2-}$  ligands, and we have been investigating other coinage metals for similar behavior. It should be noted that the only other solid-state compound containing a  $\text{Q}_4^{2-}$  ligand is the  $(\text{NH}_4)\text{CuS}_4$ <sup>13</sup> which was prepared at room temperature. In this report we wish to contribute two novel one-dimensional compounds, in the K/Cu/S system, containing only  $\text{S}_4^{2-}$  ligands and prepared in molten alkali metal polysulfide solvents, at 215–250 °C.

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(5) There are only two examples of higher polychalcogenides,  $\text{S}_3^{2-}$  and  $\text{Se}_3^{2-}$ , which occur in the compounds  $\text{P}_2\text{Nb}_4\text{S}_{21}$  and  $\text{Nb}_2\text{Se}_8$ , respectively. These compounds are prepared at high temperatures (ca. 600 °C). The assignment of charge in the Se species however is ambiguous, and the trisulfide is not bonded to a metal center. (a)  $\text{P}_2\text{Nb}_4\text{S}_{21}$ : Brec, R.; Evain, M.; Grenouilleau, P.; Rouxel, J. *Rev. Chim. Miner.* **1983**, *20*, 283–294. (b)  $\text{Nb}_2\text{Se}_8$ : Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* **1979**, *B35*, 1747–1750.

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The reaction of 0.10 g (1.57 mmol) of Cu and 0.97 g (4.71 mmol) of  $K_2S_4$  in a vacuum-sealed Pyrex tube in a 1:3 ratio at 215 and 250 °C for 4 days afforded orange-red needle-shaped crystals of  $\alpha$ - $KCuS_4$  and  $\beta$ - $KCuS_4$ , respectively,<sup>14</sup> in quantitative yield. The reaction occurs in molten  $K_2S_x$ , and the products crystallize upon slow cooling (2 °C per h). This is a redox reaction in which Cu metal is oxidized and some  $K_2S_4$  is reduced probably to  $K_2S$  and/or  $K_2S_2$ . The resulting  $K_2S_x$  ( $x = 1-3$ ) and the remaining  $K_2S_4$  form a eutectic mixture acting as a solvent for the reaction. The products were isolated by removing the excess  $K_2S_4$  with water. These compounds are insoluble in all common organic solvents and stable with regard to hydrolysis and air oxidation. The nature of these materials was established by single-crystal X-ray diffraction studies.<sup>15</sup> Due to the complexity of polysulfide melts<sup>10</sup> no effort was made to identify the produced  $K_2S_x$  phases.

Both compounds possess one-dimensional structures, shown in Figure 1. The  $\alpha$ - $KCuS_4$  is isostructural with the known  $(NH_4)CuS_4$ <sup>13</sup> and contains tetrasulfide ligands chelating Cu atoms. It consists of infinite noncentrosymmetric chains running parallel to the  $a$  axis. The chains are composed of condensed  $CuS_4$  five-membered rings related to each other by a crystallographic 2-fold screw axis, parallel to the chain direction. The whole  $\alpha$ - $[Cu(S_4)]_n^{n-}$  chain can be viewed as an array of fused  $CuS_4$  and  $Cu_2S_3$  five-membered rings. Each copper atom features a distorted tetrahedral geometry. The  $S_4^{2-}$  ligand is in a unique, asymmetric bridging mode bound to three  $Cu^+$  centers with no precedence in molecular polysulfides.<sup>16</sup> The Cu-Cu distance is 3.592 (2) Å and compares favorably with that found in  $(NH_4)CuS_4$ <sup>13</sup> at 3.589 (2) Å. The shortest K-S distance is K-S(3) at 3.223 (4) Å.

The structure of  $\beta$ - $KCuS_4$  is composed of centrosymmetric one-dimensional chains (running parallel to the  $a$  axis) in which an almost linear array (Cu-Cu-Cu angle is 173.5°) of Cu atoms are bridged by  $S_4^{2-}$  ligands. This bridging occurs via the terminal sulfur atoms of the chelating tetrasulfide unit and is distinct from that in the  $\alpha$ -polymorph, resulting in an entirely new structural motif for a low-dimensional material. It is the first example of a single tetrasulfide ligand holding on to three almost colinear metal centers. The  $\beta$ - $[Cu(S_4)]_n^{n-}$  chain can be viewed as being composed of fused five-membered  $CuS_4$  and four-membered  $Cu_2S_2$  rings. The center of symmetry in the  $\beta$ - $[Cu(S_4)]_n^{n-}$  chain lies at the center of the  $Cu_2S_2$  rhombus. Each copper atom is tetrahedrally coordinated by sulfur atoms. The average Cu-S distance is 2.369 (6) Å. There are two very short Cu-Cu distances at 2.607 (1) and 2.661 (1) Å, respectively. The presence of sulfide bridging ligands complicates any attempts to characterize these short distances as bonding, although they may be viewed as  $d^{10}$ - $d^{10}$  "attractive interactions".<sup>17</sup> Short Cu-Cu contacts are not un-

common in either discrete<sup>18</sup> or solid-state structures, some examples of which include  $KCu_3S_2$ ,<sup>19a</sup>  $K_3Cu_8S_6$ ,<sup>19b</sup> and  $KCuS$ .<sup>19c</sup> Selected bonds and angles for both compounds are given in Figure 1. The shortest K-S distance is K-S(2) at 3.237 (4) Å. Both  $\alpha$ - and  $\beta$ - $[Cu(S_4)]_n^{n-}$  are structurally distinct from the recently reported<sup>12</sup> one-dimensional  $[Ag(Se_4)]_n^{n-}$  in which the  $Ag^+$  atoms feature a trigonal-planar coordination and the bridging mode of the  $Se_4^{2-}$  ligands is different from those of  $S_4^{2-}$  ligands found here.

Under the conditions employed, the  $\beta$ - $[Cu(S_4)]_n^{n-}$  polymorph<sup>20</sup> or perhaps its (thus far unidentified) solution precursor is thermodynamically more stable than the corresponding species associated with the  $\alpha$ -polymorph. It is reproducibly obtained from a slightly higher temperature (250 °C) than that required (215 °C) for the  $\alpha$ -polymorph. The  $\alpha$ - to  $\beta$ -transformation is not reversible and only happens when in molten  $K_2S_x$  ( $x = 4-5$ ). Upon cooling from 250 °C to room temperature, no  $\beta$ - to  $\alpha$ -transition was observed. It should be noted that slow cooling of the molten reaction mixture is essential for the isolation and crystallization of these phases. Direct quenching experiments from the maximum reaction temperature did not result in the formation of either  $\alpha$ - or  $\beta$ - $KCuS_4$ . Heating crystals of  $\alpha$ - $KCuS_4$  under vacuum at 250 °C, in the absence of  $K_2S_4$  resulted in decomposition to  $CuS^{21}$  and  $K_2S_x$ .

Synthesis at this temperature range (150–300 °C) can provide an avenue to metastable materials that possess both molecular and solid-state attributes. Such materials raise the possibility of exploiting the reactivity characteristics of  $Q_4^{2-}$  ligands (which have been explored to some degree in molecular species<sup>22,23</sup>), in the solid state. They should display a variety of interesting properties (e.g., reactivity of the  $Q_4^{2-}$  ligands with small molecules, reversible reduction of the S-S bonds) of potential value to heterogeneous catalysis, such as hydrodesulfurization<sup>6,24,25</sup> or reversible battery cathode materials operating by a topotactic ion intercalation process.<sup>26</sup> We demonstrate here that the structural diversity of  $Q_x^{2-}$  ligands with  $x > 2$ , which is pervasive in molecular species, is maintained at intermediate temperatures and can be stabilized in extended solid-state structures.

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(14) When the reactions are carried out at  $T > 250$  °C, pure CuS and  $KCu_4S_5$  were isolated depending on the exact temperature: Park, Y.; Kanatzidis, M. G., to be submitted for publication.

(15) (a) Crystals of  $\alpha$ - $KCuS_4$  are orthorhombic  $P2_12_12_1$  with  $a = 5.245$  (1) Å,  $b = 8.338$  (3) Å,  $c = 12.539$  (3) Å,  $V = 548.4$  (4) Å<sup>3</sup>,  $Z = 4$ .  $D_{\text{calcd}} = 2.80$  g/cm<sup>3</sup>,  $\mu = 60.6$  cm<sup>-1</sup>,  $2\theta_{\text{max}} = 49$ . Data with  $F_o^2 > 3\sigma(F_o^2)$ : 670. Unique data: 719. Complete anisotropic refinement (55 variables) resulted in a final  $R = 0.052$ ,  $R_w = 0.057$ . (b) Crystals of  $\beta$ - $KCuS_4$  are monoclinic  $P2_1/c$  with  $a = 5.260$  (2) Å,  $b = 16.771$  (6) Å,  $c = 6.928$  (5) Å,  $\beta = 113.52$  (1)°,  $V = 560$  (1) Å<sup>3</sup>,  $Z = 4$ .  $D_{\text{calcd}} = 2.74$  g/cm<sup>3</sup>,  $\mu = 59.30$  cm<sup>-1</sup>,  $2\theta_{\text{max}} = 46$ °. Data with  $F_o^2 > 3\sigma(F_o^2)$ : 711. Unique data: 823. Complete anisotropic refinement (55 variables) resulted in a final  $R = 0.034$ ,  $R_w = 0.042$ . Single-crystal X-ray diffraction data were collected at 23 °C on a Nicolet P3 four-circle diffractometer (Mo  $K\alpha$  radiation) using a  $\theta/2\theta$  scan mode. An empirical absorption correction was applied to all data.

(16) It should be noted that, there are several molecular Cu/polysulfides all of which are characterized by a relatively high degree of aggregation and a variety of  $S_x^{2-}$  ligands in diverse bridging modes. This, coupled with the ability of  $Cu^+$  centers to adopt linear, trigonal-planar, and tetrahedral geometries, results in an abounding collection of unusual cluster structures. (a) Muller, A.; Romer, M.; Bogge, H.; Krickemayer, E.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *85*, L39-L41. (b) Muller, A.; Romer, M.; Bogge, H.; Krickemayer, E.; Bergmann, D. *J. Chem. Soc., Chem. Commun.* **1984**, 348-349. (c) Muller, A.; Schimansky, U. *Inorg. Chim. Acta* **1983**, *77*, L187-L188. (d) Betz, P.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 311-312. (e) Muller, A.; Krickemayer, E.; Sprafke, A.; Schladerbeck, N. H. *Chimia* **1988**, *42*(2), 68-69.

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**Supplementary Material Available:** Tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles of all atoms (8 pages); listings of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

## Isolation and Molecular Structure of the First Bicyclo[2.2.0]hexastannane

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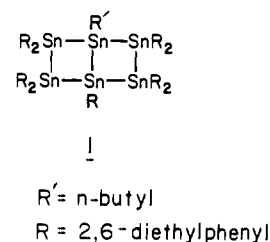
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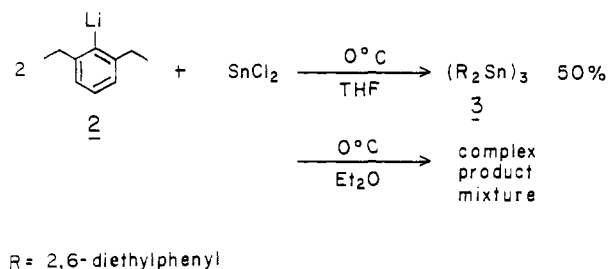
Recent advances in the area of group IVB polymetallanes has led to the isolation and characterization of a wide range of structurally unique polycyclic frameworks. These compounds represent not only challenging synthetic<sup>1</sup> and theoretical<sup>2</sup> "benchmarks" but also serve to provide insight for the design of new solid-state materials. With regard to polystannanes, linear<sup>3</sup> and cyclic<sup>4</sup> structures have been known for some time; however, report of a polycyclic polystannane has not yet been documented. Herein, we describe the isolation and molecular structure of the first bicyclo[2.2.0]hexastannane derivative, **1** (Scheme I).

Inherent in the quest for the synthesis of ring-strained polymetallanes is the judicious choice of an exocyclic ligand which can kinetically stabilize the final desired product as well as the proper selection of reaction conditions. For example, we find that slow addition of a solution of the aryllithium reagent, **2** [prepared from 10 g (47 mmol) of 1-bromo-2,6-diethylbenzene and 29 mL of *n*-butyllithium (1.8 M in hexane) in 50 mL of diethyl ether], to a solution of 3.65 g (24 mmol) of tin dichloride in 50 mL of tetrahydrofuran (THF) at 0 °C provides the known cyclotristannane **3**<sup>4a</sup> in 50–55% yield after the usual workup and purification (Scheme II). By performing the same reaction with a suspension of SnCl<sub>2</sub> in diethyl ether at 0 °C, however, a deep red crude oil is obtained.<sup>5</sup> From this mixture, compound **1** was

Scheme I



Scheme II



isolated in 1.5% yield in the form of orange-red single crystals by slow crystallization from a concentrated pentane solution at –20 °C.

A mass spectrum of **1** (field desorption) reveals an isotope cluster pattern, M<sup>++</sup> *m/z* (1958–1980), which is consistent with the molecular formula of C<sub>94</sub>H<sub>126</sub>Sn<sub>6</sub>, and this implies that the organic ligands of **1** are comprised of one butyl (C<sub>4</sub>H<sub>9</sub>) and nine aryl (C<sub>90</sub>H<sub>117</sub>) groups.<sup>6,7</sup> However, interpretation of both the <sup>1</sup>H NMR (300 MHz, toluene-*d*<sub>6</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, toluene-*d*<sub>6</sub>) spectra is hampered by the number of resonances and complex multiplets (<sup>1</sup>H NMR) arising from the aryl substituents which experience different chemical environments and restricted rotation up to 100 °C.<sup>6</sup>

Determination of a bicyclic framework for **1** was provided by crystallographic analysis which reveals several interesting structural features.<sup>6</sup> As shown in Figure 1, the molecule is comprised of a cis fusion of two four-membered rings and overall possesses no axis or plane of symmetry. The angle between the mean planes formed by Sn<sub>1</sub>–Sn<sub>2</sub>–Sn<sub>3</sub>–Sn<sub>4</sub> and Sn<sub>1</sub>–Sn<sub>2</sub>–Sn<sub>5</sub>–Sn<sub>6</sub> is 131.9°, and each of the four-membered rings are puckered rather than planar as determined by the dihedral angle of 8.2° between the Sn<sub>1</sub>–Sn<sub>2</sub>–Sn<sub>3</sub> and Sn<sub>2</sub>–Sn<sub>3</sub>–Sn<sub>4</sub> planes and 4.5° between the Sn<sub>1</sub>–Sn<sub>2</sub>–Sn<sub>5</sub> and Sn<sub>2</sub>–Sn<sub>5</sub>–Sn<sub>6</sub> planes. The angles which construct the four-membered rings are in the range of 87.5–92.9° and are similar to those angles found for other cyclotetrastannanes.<sup>4c–e</sup> It is interesting to note that due to steric interactions among the exocyclic ligands, the butyl group at Sn<sub>1</sub> adopts a gauche conformation with a dihedral angle of 55.7° for C<sub>1a</sub>–C<sub>2a</sub>–C<sub>3a</sub>–C<sub>4a</sub>.

The tin–tin bond lengths of 2.818 (1)–2.931 (1) Å for the bicyclohexastannane fall in the range commonly found for small cyclopolystannanes possessing sterically hindered ligands.<sup>4</sup> Of particular interest, however, is that the shortest tin–tin bond length in the structure is between the central tin atoms (2.818 Å for Sn<sub>1</sub>–Sn<sub>2</sub>).<sup>8</sup> This undoubtedly arises from a decrease in steric interactions between the ligands on Sn<sub>1</sub> and Sn<sub>2</sub> vs the steric interactions for the bonds of Sn<sub>3</sub>–Sn<sub>4</sub> and Sn<sub>5</sub>–Sn<sub>6</sub>. Finally, all the tin–carbon bond lengths [2.214 (8)–2.230 (9) Å] are longer than normal and are indicative of strong steric interactions between the exocyclic ligands.

Compound **1**, which is surprisingly air-stable in crystalline form, exhibits unique optical properties, both in solution and in the solid

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(5) While efforts are in progress to characterize the main constituents of this reaction product, no cyclotristannane **3** is observed in freshly prepared material as determined by <sup>119</sup>Sn{<sup>1</sup>H} NMR (112 MHz).

(6) Detailed information is provided in the Supplementary Material.

(7) Mp 250 °C (dec), elemental Anal. Calcd for **1**: C, 57.34; H, 6.45. Found: C, 56.40; H, 6.23.

(8) In both the carbon and silicon analogues of **1**, the central bond of the ring is longer than the peripheral bonds, see: ref 1b and Andersen, B.; Srinivasan, R. *Acta Chem. Scand.* **1972**, *26*, 3468.