

# Synthesis of $\text{Au}_2\text{S}$ and $\text{Au}_2\text{S}_3$ Using $\text{H}_2\text{S}$ , Short-Chain and Ring-Structured Sulfur as Sulfur Sources

F. E. Senftle<sup>+</sup> and D. B. Wright\*

U. S. Geological Survey, Reston, Va. 22092, USA

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To determine which of the two known gold sulfides (containing either mono- or trivalent gold) are formed by reacting trivalent gold with different allotropes of sulfur, experiments were made using three different sources of sulfur. When trivalent gold in the form of  $\text{Au}_2(\text{SO}_4)_3$  in concentrated acid is reacted with electrolytically formed short-chain sulfur, monovalent gold sulfide ( $\text{Au}_2\text{S}$ ) is formed. If hydrogen sulfide gas reacts with the same solution, trivalent gold sulfide ( $\text{Au}_2\text{S}_3$ ) is produced. Alternatively, if ordinary  $\alpha$ -sulfur (ring structure) is used, a 50/50 mixture of  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_3$  is formed. The synthesis procedure for the two gold sulfides is substantially simpler than previously reported methods of preparation.

## Introduction

In the reported methods [1–3] to synthesize the monovalent and trivalent gold sulfides,  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_3$ , only  $\text{H}_2\text{S}$  has been used as the source of the  $\text{S}^{2-}$  ion. Examination of the literature reveals no instance where any solid form of sulfur has been used to carry out the synthesis. Solid sulfur exists in many allotropic forms such as multiple-atom rings of sulfur or open chains of sulfur atoms containing an indeterminate number of atoms. The reactivity of an element is affected by its allotropic form, and thus one would expect that trivalent gold will react differently with different allotropic forms of sulfur. In this investigation,  $\text{H}_2\text{S}$ , the ordinary eight-atom ring form of sulfur ( $\alpha$ -sulfur), and chain sulfur ( $\omega$ - or catenapolysulfur) are compared as sulfur sources in the synthesis of  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_3$  using trivalent gold.

The known methods of preparation of monovalent and trivalent gold sulfide use gold complexes having the appropriate valence state of gold. Hirsch *et al.* [4] formed  $\text{Au}_2\text{S}$ , a brownish-black precipitate, by bubbling  $\text{H}_2\text{S}$  through an acidified solution of  $\text{K}[\text{Au}(\text{CN})_2]$ . After drying, the  $\text{Au}_2\text{S}$  is very slightly soluble in water, insoluble in mineral acids or  $\text{KOH}$ , but is soluble in aqua regia and sodium cyanide solutions. No diffraction pattern has been indexed by the International Center for Diffraction Data [5].

Early attempts to synthesize the trivalent sulfide,  $\text{Au}_2\text{S}_3$ , from aqueous solutions failed primarily be-

cause water causes the formation of auric oxide or hydroxide. To circumvent this problem, Antony and Lucchesi [6] passed  $\text{H}_2\text{S}$  over dry lithium tetrachloraurate and then washed with alcohol,  $\text{CS}_2$ , and ether to purify the  $\text{Au}_2\text{S}_3$ . Gutbier and Dürrwächter [7] passed  $\text{H}_2\text{S}$  through an acidified solution of  $\text{H}(\text{AuCl}_4)$  in absolute ether and precipitated a copious quantity of  $\text{Au}_2\text{S}_3$  with a small amount of metallic gold. Hoffmann and Höchtlen [8] used a similar preparation except they used  $\text{AuCl}_3$ .  $\text{Au}_2\text{S}_3$  is a black precipitate that reacts vigorously with nitric acid and is insoluble in the other mineral acids. It is soluble in sodium cyanide and concentrated sodium sulfide solutions. The material appears to be amorphous and has no reported X-ray diffraction pattern.

In this work we use trivalent gold in the form of  $\text{Au}_2(\text{SO}_4)_3$  in concentrated  $\text{H}_2\text{SO}_4$  to synthesize both forms of gold sulfide. The strong acid solution of trivalent gold is reacted with short-chain sulfur, ring sulfur ( $\alpha$ -sulfur) and  $\text{H}_2\text{S}$ , each of which gives a different product. The synthesis of both  $\text{Au}_2\text{S}$  and  $\text{Au}_2\text{S}_3$  is significantly easier than the previously reported methods.

## Experimental

Before discussing the synthesis experiments it is pertinent to explain the source of the trivalent gold and the chain sulfur solutions. Both the  $\text{Au}_2(\text{SO}_4)_3$  and a chain form of sulfur are prepared by electrolyzing concentrated  $\text{H}_2\text{SO}_4$  (97 percent) in a U-tube with gold electrodes [9]. A  $1.5 \times 3 \times 20$  mm gold bar of 99.99 percent purity was used as an anode and a  $1.5 \times 3 \times 10$  mm gold bar cut from the same stock was used for the cathode. After electrolysis at 5 V and about 100 mA for an hour or two, the anolyte con-

<sup>+</sup> Reprint requests to Dr. F. E. Senftle.

\* Graduate student, Howard University, Washington, D. C. 20059.

taining Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is yellow-orange in color and the catholyte has a milky appearance due to finely divided colloidal sulfur (white) formed by the reduction of H<sub>2</sub>SO<sub>4</sub>. The catholyte and anolyte are easily removed from the U-tube for further experiments.

The colloidal electrolytically-formed sulfur, unlike ordinary  $\alpha$ -sulfur, is white and insoluble in CS<sub>2</sub>, and in this respect resembles “flowers of sulfur” or  $\omega$ -sulfur [10, 11, 12] which are forms of catenapolysulfur with chains of indeterminate length. If the colloidal acid solution is diluted with water, the sulfur coagulates and immediately reverts to the normal yellow  $\alpha$ -sulfur. As long as the sulfur remains as a colloid in the concentrated acid, it is stable for weeks at room temperature. However, if it is brought down and concentrated by centrifuging, some of the sulfur reverts to the  $\alpha$  form of sulfur. Catenapolysulfur has an electron on each of the terminal sulfur atoms and therefore has characteristics of a free radical [13, 14]. The relatively high concentration of H<sub>3</sub>SO<sub>4</sub><sup>+</sup> ions in concentrated sulfuric acid is conducive to a loose association at the terminal sulfur atoms of the chain, and is probably the cause of the chain’s stability in the concentrated acid. When the acid is diluted with water the autoprotection process in H<sub>2</sub>SO<sub>4</sub> is repressed, leaving the terminal sulfur atoms “exposed”. The chain subsequently breaks into the more stable eight atom sections and joins forming S<sub>8</sub> rings. Gillespie and Ummat [15] found that at a somewhat higher temperature (70 °C), similar colloidal solutions of sulfur in concentrated H<sub>2</sub>SO<sub>4</sub> were stable for only about 12 hours. These properties are essentially the same as those formed for the fibrous or  $\omega$ -sulfur formed by cooling and stretching melted sulfur. Sulfur was identified by X-ray fluorescence but X-ray diffraction of the colloidal solutions yielded no pattern indicating extremely short chains of sulfur atoms compared with the usual much longer chains of  $\omega$ -sulfur. Short chains and the exceedingly fine particle size of the sulfur would account for the absence of a diffraction pattern for the electrolytically formed sulfur. The properties of the electrolytically formed sulfur are generally the same as those described by Donohue and Meyer [10] for  $\omega$ -sulfur; therefore it is believed that the colloidal solution is composed of a

catenapolysulfur allotrope of sulfur ( $\omega$ -sulfur), but with much shorter chains of sulfur atoms.

The following synthesis experiments were performed by reacting Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with  $\omega$ -sulfur,  $\alpha$ -sulfur and H<sub>2</sub>S.

#### *Gold sulfide from short-chain $\omega$ -sulfur*

When the anolyte containing Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and the catholyte containing the short-chain sulfur are separated in a U-tube during electrolysis, and subsequently reacted in a gas collecting bottle after the electrolysis is terminated, no gas is formed. Electrolysis of concentrated sulfuric acid was therefore carried out in an open 250 ml beaker at a potential of 5 V, and a current of 110–120 mA over a period of 3 to 5 h. Throughout the electrolysis the electrolyte was continuously mixed. Within a few minutes after initiation of electrolysis the electrolyte started to darken and eventually became a dense black color as the anolyte and catholyte reacted. Following electrolysis, the electrolyte and reaction product were removed, centrifuged, and the nearly clear supernatant acid was decanted. Care was taken not to wash the precipitate initially with water because it was found that, if water is added to a concentrated acid solution of Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, the gold precipitated as gold oxide and gold hydroxide which would contaminate the precipitate. Therefore the black precipitate was washed first with 100 ml of fresh concentrated sulfuric acid to remove any unreacted Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and then with some 500 ml of distilled water to dilute and wash out any residual acid. After centrifuging and decanting the water, the precipitate was finally washed in acetone and air-dried to a brownish-black powder. Some unreacted chain sulfur undoubtedly remained, but unlike  $\alpha$ -sulfur, chain sulfur is insoluble in CS<sub>2</sub> and, although the sample was washed in this solvent, it is doubtful if the residual chain sulfur was removed. X-ray diffraction showed the precipitate to be amorphous. It was only very slightly soluble in water, insoluble in mineral acids or KOH, but soluble in aqua regia and NaCN solutions.

To establish the compound formed, gravimetric analyses were made on the dried precipitate. Table I

Tab. I. Percentage gold and sulfur measured in samples of gold sulfide prepared from three different forms of sulfur.

Sulfur sources	Percent gold [%]		Percent sulfur [%]		Total composition [%]
	average	theoretical	average	theoretical	
Short chain sulfur	90.16 ± 1.67	92.49 <sup>a</sup>	8.10 ± 0.22	7.51 <sup>a</sup>	98.27
Ring type sulfur	85.46 ± 1.59	86.02 <sup>b</sup>	13.58 ± 0.22	13.97 <sup>b</sup>	99.04
H <sub>2</sub> S gas	80.81 ± 1.7	80.41 <sup>c</sup>	19.8	19.59 <sup>c</sup>	100.61

<sup>a</sup> For Au<sub>2</sub>S; <sup>b</sup> for a 50:50 mixture of Au<sub>2</sub>S and Au<sub>2</sub>S<sub>3</sub>; <sup>c</sup> for Au<sub>2</sub>S<sub>3</sub>.

shows the gravimetric measurement of the average gold and sulfur concentrations in the specimens. Gold was measured by ashing each of the sample preparations at 500 °C, and sulfur was determined by standard chemical methods. Neither the experimental values of gold or sulfur correspond closely with the theoretical values for Au<sub>2</sub>S. This is not too surprising in view of our inability to wash out any residual chain sulfur with CS<sub>2</sub>. However, both the qualitative properties described above and the gravimetric analysis of the precipitate correspond sufficiently close to those of Au<sub>2</sub>S to identify the product as being primarily Au<sub>2</sub>S.

#### *Gold sulfide from α-sulfur*

Gold sulfide was also prepared from reagent α-sulfur reacted with a solution of Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in concentrated sulfuric acid prepared in the U-tube electrolysis cell as described above. The sacrificial gold anode was weighed prior to and again after the electrolysis to determine the amount of gold dissolved in the concentrated acid. After the gold sulfate solution was removed from the U-tube, a small amount of ordinary reagent grade α-sulfur was added to the solution. To ensure a complete reaction of all the gold present, the amount of sulfur added was slightly more than that necessary to completely react with the measured amount of gold present. A black precipitate was formed immediately with the evolution of SO<sub>2</sub> gas. After centrifuging, the residue was washed with fresh concentrated sulfuric acid to remove any excess gold sulfate. After washing with concentrated acid, the black precipitate was washed with water to remove all traces of acid, and then with acetone, and air dried. The dried black precipitate was finally extracted with CS<sub>2</sub> to remove any excess α-sulfur. Attempts to obtain an X-ray diffraction pattern were unsuccessful due to the amorphous state of the product. The gravimetric data in Table I using ring-type α-sulfur as a sulfur source do not correspond to either Au<sub>2</sub>S or Au<sub>2</sub>S<sub>3</sub>. However, the average values of gold and sulfur correspond approximately to 86.02, and 13.97 percent, respectively, the values expected for equal mixture of Au<sub>2</sub>S and Au<sub>2</sub>S<sub>3</sub>. The sulfate concentration of the sample was less than 0.3 percent.

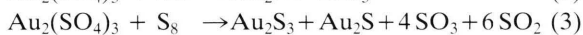
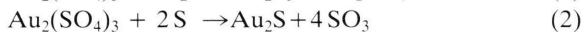
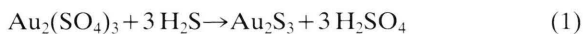
#### *Gold sulfide from H<sub>2</sub>S*

For comparison with the solid forms of sulfur, gold sulfide was also prepared by bubbling H<sub>2</sub>S through a concentrated sulfuric acid solution of Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> prepared electrolytically as described above. The black precipitate formed was washed with fresh concentrated sulfuric acid, water and acetone. After drying

to a black powder, it was found that the product reacted with nitric acid, but insoluble in other mineral acids. It was soluble in sodium cyanide and concentrated sodium sulfide solutions. The concentration of gold and sulfur was determined gravimetrically as shown in Table I. The sulfate concentration was determined to be less than 0.8 percent. The data correspond to Au<sub>2</sub>S<sub>3</sub> as the product of the reaction.

### **Results and Discussion**

When trivalent gold in the form of Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in concentrated sulfuric acid is reacted with allotropic forms of sulfur different reactions occur. Sulfur in the form of H<sub>2</sub>S, electrolytically formed short-chain sulfur, and ordinary yellow sulfur (ring structure) were reacted with Au<sup>3+</sup> as follows:



When H<sub>2</sub>O gas is allowed to pass through an acidic solution of Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (eq. (1)), there is sufficient ionization of H<sub>2</sub>S so that S<sup>2-</sup> ions react with Au<sup>3+</sup> to form the trivalent gold sulfide. If electrolytically formed chain sulfur is reacted with Au<sup>3+</sup> (eq. (2)), the monovalent sulfide is formed. The formation of these sulfides from Au<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is substantially easier and is a simpler method than the previously reported techniques using gold complexes.

When ordinary ring-structured yellow sulfur is used (eq. (3)), a mixture of the two sulfides are formed. The reasons for the two different products formed in eq. (2) and (3) are undoubtedly associated with the chain and ring structures of the two allotropic forms of sulfur. Although the mechanism is unknown, a possible explanation has been presented elsewhere [16]. The formation of different gold sulfides from the three forms of sulfur demonstrate Schmidt and Siebert's [17] insistence that the allotropic forms of sulfur are indeed different compounds of sulfur.

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