

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CHEMICAL DEPARTMENT OF THE CITY OF CHICAGO, MUNICIPAL, TUBERCULOSIS SANITARIUM]

NEW METHODS FOR THE PREPARATION OF SODIUM AUROTHIOSULFATE

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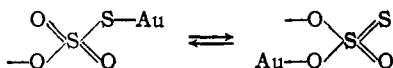
Sodium aurothiosulfate was prepared first by Fordos and Gélis¹ in 1845 on the addition of an aqueous solution of auric chloride to sodium thiosulfate dissolved in water. This method gives a mixture of different substances and the yield of the pure compound is low. Recently Mollgaard² who became interested in the synthesis of this compound in connection with chemotherapeutic studies in tuberculosis reports the preparation of sodium aurothiosulfate with a 90–95% yield by a method quite different from that of Fordos and Gélis. The product thus synthesized has been registered by him under the name of "Sanocrysin." Since Mollgaard's procedure was not available, it became necessary to develop a better method for the preparation of sodium aurothiosulfate than that of Fordos and Gélis, when studies on sanocrysin were begun in this Laboratory.

Mollgaard,² after chemical investigation of this compound, concluded that the gold in sodium aurothiosulfate, $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$, is attached to the oxygen as Au^{+++} , and that the sodium gold thiosulfate can be prepared only by the use of gold in the trivalent form.

It is evident that the gold in sodium aurothiosulfate is monovalent and not trivalent from the fact that sodium gold thiosulfate can be synthesized from both the aurous and the auric salts as shown in the following methods of preparation. It is significant that when sodium gold thiosulfate is prepared from sodium thiosulfate and an aurous salt, two molecular equivalents of thiosulfate are sufficient for one of the aurous salt, whereas if an auric salt is used, four molecular equivalents of thiosulfate are required for one of auric salt. If a less quantity of thiosulfate is used a brown substance is formed. Two molecular equivalents of the thiosulfate are necessary for the reduction of the auric gold to the aurous condition.

The following equations may represent the reactions that take place: (1) $\text{CsAuCl}_4 + 4\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 + \text{Na}_2\text{S}_4\text{O}_6 + 3\text{NaCl} + \text{CsCl}$; (2) $\text{NaAuCl}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 + 2\text{NaCl}$.

Whether the gold is attached to the oxygen or to the sulfur in the molecule cannot be definitely established but probably it exists in solution in a state of tautomeric equilibrium.



¹ Fordos and Gélis, *Ann. chim. phys.*, **13**, 394 (1845).

² Mollgaard, "Chemotherapy of Tuberculosis," *Nyt Nordisk Forlag*, 1924.

This evidence confirms the opinion of Fordos and Gélis that the sodium gold thiosulfate contains gold in the monovalent condition.

Experimental Part

Preparation of Sodium Aurothiosulfate from Cesium Auric Chloride

Cesium Auric Chloride.—Twenty-one and five-tenths g. of 24-carat granulated gold was treated with small portions of aqua regia and heated on the water-bath until reaction ceased. The gold solution was separated by filtration from a small amount of impurity. To the chloro-auric acid solution was added 22.35 g. of cesium nitrate (5% excess) dissolved in 45 cc. of hot water. The precipitated mass was cooled to 0° and the cesium auric chloride collected upon a filter, washed with ice water, alcohol and ether. The yield is practically that calculated. Cesium auric chloride is a golden-yellow crystalline substance, with a solubility of 0.8 g. in 100 g. of water solution at 20° and is slightly unstable in light.

Anal. Subs., 0.3211: Au, 0.1323. Calcd. for CsAuCl_4 : Au, 41.79. Found: 41.21.

Sodium Aurothiosulfate. I.—To a solution of 119.5 g. (4 molecular equivalents plus 10% excess) of hydrated sodium thiosulfate in 380 cc. of water was added 51.6 g. of cesium auric chloride in small portions while the mixture was constantly stirred. The reaction took place immediately, giving a colorless solution. A second portion of the cesium salt was not added until the previous one had reacted completely. This addition requires about 45 minutes. To the filtered solution 3 volumes of 95% alcohol were added and the precipitated white crystalline sodium aurothiosulfate consisting of 51.1 g. was collected. An analysis of this crude product gave 33.1% of gold, which represents a purity of 90%. A second yield of 15 g. of crystals was obtained by the addition of 2 volumes of 95% alcohol to the alcoholic filtrate. An analysis of this crude product gave 24.0% of gold which represents a purity of 63%; thus the total recovery of the gold employed in the synthesis was 96%.

For purification the substance was first dissolved in twice its weight of water. At this point the solution is turbid due to the presence of a small amount of colloidal sulfur and other impurities which are easily removed by the addition of a small amount of alcohol, just to the point of beginning precipitation. The mixture was filtered and to the clear filtrate 3 volumes of 95% alcohol were added and the precipitated sodium aurothiosulfate was collected upon a filter. The substance was recrystallized in the same manner, washed with alcohol and ether, dried in a vacuum in the dark over sulfuric acid and analyzed.

Anal. Subs., 0.2832: Au, 0.1063; BaSO_4 , 0.5022. Calcd. for $\text{Na}_2\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$: Au, 37.4; S, 24.36. Found: Au, 37.40; S, 24.37.

Sodium aurothiosulfate is a snow-white crystalline substance very soluble in water, and tastes sweet. It is somewhat unstable although it has remained undecomposed for months when covered with anhydrous ether

and kept in the dark in a refrigerator. The cesium chloride may be recovered by the method of Archibald and Hallett.³

The determinations of gold and sulfur in sodium aurothiosulfate were carried out in the following manner.

A weighed portion (0.25–0.35 g.) of the salt was dissolved in water and to the solution were added about 5 cc. of an approximately 30% solution of sodium hydroxide prepared from sodium, and 5 cc. of Perhydrol (30% hydrogen peroxide). The reaction mixture was warmed gently over a free flame until the gold was coagulated. The precipitated gold was collected upon an ashless filter, washed first with water, hydrochloric acid (1:4) and finally with water until the washings gave no test for chloride. The filter paper was ignited and the gold weighed. The filtrate from the precipitated gold was neutralized to the pink point of phenolphthalein and 0.3 cc. of concd. hydrochloric acid was added per 100 cc. of solution. The sulfate was precipitated as barium sulfate in the usual manner.

Preparation of Sodium Aurothiosulfate from Sodium Aurochloride

Sodium Aurothiosulfate. II.—Two cc. of a gold chloride solution (0.0382 g. of gold per cc.) with a Sørensen value (P_H) of approximately 6.6 was placed in a 50cc. beaker, and 3 cc. of a 4 *N* sodium chloride solution was added. Sulfurous acid with an oxygen equivalent of 0.001125 g. per cc. was run in from a buret during constant agitation until a colorless solution was obtained; the reaction required about 5 cc. The solution, according to Diemer,⁴ contains sodium aurous chloride. If small quantities of the gold chloride solution are reduced at a time, and if most of the acid is added quite rapidly, and an excess avoided at the end, the auric salt can be reduced to the aurous without any gold being precipitated or at most only a trace. The clear solution of the aurous salt was added in a small stream to 1.04 cc. of a 0.780 *M* sodium thiosulfate solution (2 molecular equivalents plus 5% excess) in which 0.5 g. of barium carbonate was suspended. Forty-six such titrations were made, the solutions collected and the barium sulfate and unused barium carbonate removed by means of filtration. Five to six volumes of 95% alcohol were added to the filtrate, and after the mixture had stood at 0° for some time the precipitated sodium aurothiosulfate was collected; yield, 7.5 g. After recrystallization from water and alcohol it was dried in a vacuum in the dark over sulfuric acid and analyzed.

Anal. Subs., 0.3737: Au, 0.1393. Calcd. for $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$: Au, 37.40. Found: 37.28.

The properties of this compound were identical with those of the sodium aurothiosulfate prepared from the cesium auric chloride.

Summary

1. New methods for the preparation of sodium aurothiosulfate have been developed.

³ Archibald and Hallett, *THIS JOURNAL*, 47, 1314 (1925).

⁴ Diemer, *ibid.*, 35, 555 (1913).

2. Evidence has been obtained that the gold in sodium aurothiosulfate is in the aurous condition.

3. A method for the preservation of the sodium aurothiosulfate is presented.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, MISSOURI SCHOOL OF MINES AND METALLURGY]

THE ELECTROMETRIC DETERMINATION OF TELLURIUM IN THE PRESENCE OF FERRIC IRON, SELENIUM AND COPPER

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The quantitative oxidation of tellurous acid to telluric acid by excess of potassium dichromate has been shown by Lenher and Wakefield¹ to be applicable to the volumetric determination of tellurium. The purpose of this investigation was to study the applicability of the electrometric method to this titration.

In converting Lenher and Wakefield's method, with slight modifications, to an electrometric titration, to avoid the use of a spot plate indicator, their results as a whole have been verified. The method is based on the following reaction: $3\text{TeO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 \rightarrow 3\text{H}_2\text{TeO}_4 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$, the excess of dichromate being titrated against ferrous sulfate. It was found that selenium dioxide is not affected by potassium dichromate under similar conditions.

Method and Materials.—Samples of pure tellurium dioxide or aliquot portions of a stock solution of the same material were used. The tellurium dioxide was dissolved in a very small amount of sodium hydroxide solution, and sufficient dilute acid added to bring the final acidity to the

TABLE I
TITRATION OF TELLURIUM DIOXIDE
10–20 cc. of H_2SO_4 (d. 1.84)

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken, g.	SeO_2 taken, g.	TeO_2 taken, g.	No. of analyses	Error of average, mg.	Av. deviation from av. mg.
Part 1					
0	0	0.2527	5	–0.14	0.18
0	0.1390	.2527	5	–.06	.10
Part 2					
0	.0556	.1015– .4023	7	–.06	.20
Part 3					
0	0	.2520	3	+ .13	.13
0.062–0.500	0	.2520	4	–.10	.10
.125	.0556	.2068	2	–.15	.15

¹ Lenher and Wakefield, THIS JOURNAL, 45, 1423 (1923).