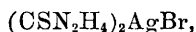


XX.—*Some Silver Compounds of Thiourea.*

By J. EMERSON REYNOLDS, M.D., D.Sc., F.R.S.

AT the conclusion of a paper on some derivatives of thiourea, published in 1888 (Trans., **53**, 857), I pointed out that a definite crystalline compound of silver bromide with thiourea,



was obtained by the interaction of silver nitrate with  $(\text{CSN}_2\text{H}_4)_4\text{NBr}$  in equal molecular proportions.

It was further stated that analogous compounds with other silver salts had been obtained by the same method, as well as by direct union with thiourea, and that the examination of these compounds in some detail had cleared up certain obscure facts which were simply recorded in my earlier papers on thiourea.

I did not intend to publish details of the examination of these silver compounds of thiourea until a similar examination could be made of the more interesting gold and platinum derivatives. But the recent appearance of a paper by Kurnakow (*Ber.*, **24**, 3956) on the silver compounds of thiourea renders further delay undesirable,

as the Russian chemist refers only to the paper in which I described thiourea 22 years ago, and not to any later ones on the subject. Hence in the following pages will be found the details of the work on silver compounds referred to in 1888.

Kurnakow's communication being almost exclusively concerned with the products of the action of silver nitrate on thiourea, I shall first give the notes of my results in that direction.

*Compounds of Silver Nitrate with Thiourea.*

The white precipitates which can be obtained on mixing aqueous solutions of silver nitrate and thiourea vary in composition with the proportions of the reagents used, and gradually decompose when washed with water. If, however, alcohol be substituted for water, a perfectly definite crystalline compound can be prepared, containing three mols. of thiourea to one of silver nitrate.

17 grams of silver nitrate were dissolved in alcohol, and added to a hot alcoholic solution of 30.4 grams of thiourea (1—4 mols.). The solution soon deposited a large quantity of beautiful silky crystals, which when collected, washed with cold alcohol, and recrystallised from hot, strong alcohol, afforded a pure product, which melted sharply at 141°. The fused product began to decompose at about 150°, sulphide of silver separating.

Analysis of the pure crystals gave the following data:—

- I. 0.4934 gram gave 0.178 of AgCl.  
 II. 0.3758 „ „ 0.683 of BaSO<sub>4</sub>.  
 III. 0.3633 „ „ 0.646 of BaSO<sub>4</sub>.  
 IV. 0.3384 „ „ 67.2 c.c. of N at 7° and 760.5 mm.

The results agree closely with the formula (CSN<sub>2</sub>H<sub>4</sub>)<sub>2</sub>AgNO<sub>3</sub>.

		Experiment.			
		I.	II.	III.	IV.
Ag .....	Theory. 27.13	27.15	—	—	—
S.....	24.24	—	24.98	24.44	—
N.....	24.52	—	—	—	24.2

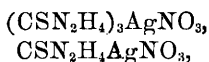
If the above pure compound be boiled with strong alcohol for some time or be recrystallised from 50 per cent. alcohol, decomposition occurs, and a substance is obtained which is richer in silver, and approximates to the formula (CSN<sub>2</sub>H<sub>4</sub>)<sub>2</sub>AgNO<sub>3</sub>, but I have not obtained a pure compound of that composition.

On the other hand, when aqueous solutions of equimolecular proportions of silver nitrate and thiourea were mixed, a precipitate was obtained, which, when slightly washed, pressed, and dried, gave

43·16 per cent. of Ag, as against 43·9 per cent. of Ag required for the compound  $\text{CSN}_2\text{H}_4\text{AgNO}_3$ . And this product, after free washing, was found to contain 46·3 per cent. of silver, indicating decomposition by the continued action of water. I, therefore, long since arrived at the conclusion that the silver precipitate mentioned in my paper of 1869 was a product of decomposition of the too carefully washed lower compound of silver nitrate and thiourea just referred to.

Kurnakow's more recent work (*loc. cit.*) has led him to substantially the same result respecting the silver precipitate I first described, and he has isolated and more fully analysed the compound  $\text{CSN}_2\text{H}_4\text{AgNO}_3$ , whose existence was indicated by my silver determination cited above. Moreover, by dissolving the 1 : 1-compound in aqueous solution of thiourea he produced the 1 : 3-substance which I formed more simply of direct union in alcoholic solution, and examined more fully than he has done.

The general result of both lines of work is therefore the complete identification of the compounds



whilst some evidence of the existence of the intermediate substance  $(\text{CSN}_2\text{H}_4)_2\text{AgNO}_3$  has been obtained.

#### *Silver Bromide and Thiourea.*

It has been shown in a former paper, as already mentioned, that the cautious addition of silver nitrate in alcoholic solution to an equimolecular proportion of  $(\text{CSN}_2\text{H}_6)_4\text{NBr}$ , affords a liquid from which the compound  $(\text{CSN}_2\text{H}_4)_2\text{AgBr}$  separates out in crystalline form.

A considerable quantity was also obtained in the following manner:—17 grams of silver nitrate were precipitated by potassium bromide; the resulting AgBr was thoroughly washed with water and lastly with rectified spirit. A hot solution of 30·4 grams of thiourea (4 mols.) in 300 c.c. of alcohol was gradually added to the moist silver bromide. The addition of 75 c.c. (= 1 mol.) of thiourea sufficed to completely change the pale yellow of the bromide to white, and solution only commenced when this point was passed, and was not complete until the whole of the thiourea was added, and the mixture was gently warmed. On standing over night, a crop of fine crystals separated, consisting of beautiful, prismatic needles. These were collected, washed with cold alcohol, in which they are almost insoluble, pressed, and dried for analysis. The pure crystals melt at 120—121° to a clear liquid, but on heating to 180—183° gas is evolved, and at 190° blackening occurs.

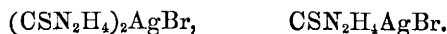
- I. 0.4013 gram gave 0.1279 of Ag.  
 II. 0.6845 „ 0.3785 of AgBr.  
 III. 0.6325 „ 0.8775 of BaSO<sub>4</sub>.  
 IV. 0.452 „ 63 c.c. of N at 9° and 762.5 mm.

These results agree with the formula (CSN<sub>2</sub>H<sub>4</sub>)<sub>2</sub>AgBr.

	Theory.	Experiment.
Ag .....	31.76	31.87
Br .....	23.52	23.53
S.....	18.82	19.07
N .....	16.47	16.72

This compound was partially decomposed by water, although it can be recrystallised from an aqueous solution of thiourea. By the action of much water, a white substance separated resembling the material formed when 1 mol. of thiourea was added to finely-divided silver bromide in the first instance. An estimation of silver in some of the latter, formed by digesting silver bromide with rather more than 1 mol. of thiourea, gave 42.45 per cent. of silver. The formula CSN<sub>2</sub>H<sub>4</sub>,AgBr requires 40.93; so that the whitening effect of thiourea on silver bromide, in the first instance, is probably due to the nearly complete formation of a 1 : 1-compound, which latter then dissolves in the urea solution with the formation of the 1 : 2 crystalline substance ultimately separated from the liquid.

There is, therefore, evidence that silver bromide forms the two compounds with thiourea:—



#### *Silver Chloride and Thiourea.*

14.3 grams of freshly precipitated and washed silver chloride were added to a hot alcoholic solution of 30.4 grams (4 mols.) of thiourea. Solution was nearly complete, and the filtered liquid, when cold, deposited a fine crop of colourless, needle-like crystals. These were washed thoroughly with cold alcohol, pressed, and dried for analysis.

The crystals melt at 170—171°, affording a clear liquid, but decomposition commences at 180°, much Ag<sub>2</sub>S separating.

The analytical data obtained were:—

- I. 0.251 gram gave 0.092 of Ag.  
 II. 0.3965 „ 0.1875 of AgCl.  
 III. 0.263 „ 0.4157 of BaSO<sub>4</sub>.

These numbers agree with the formula (CSN<sub>2</sub>H<sub>4</sub>)<sub>2</sub>AgCl.

	Theory.	Experiment.
Ag .....	36.54	36.65
Cl .....	12.01	11.69
S.....	21.65	21.73

This is identical with the substance obtained by Volhard (*J. pr. Chem.* [2], 9, 14).

No evidence was obtained of the formation of a 1 : 1-compound.

#### *Silver Iodide and Thiourea.*

Silver iodide is not nearly so soluble in hot alcoholic solution of thiourea as the bromide or chloride. The iodide is speedily whitened by thiourea, as in the case of the bromide, and forms a clotted mass, very little of which dissolves. Hence, in a large experiment, the iodide precipitated from 17 grams of nitrate was added gradually to a boiling alcoholic solution of 30.4 grams of thiourea. At first solution took place, but only an inconsiderable proportion of the iodide ultimately dissolved; the liquid was then filtered and allowed to stand for three days, when a white, crystalline precipitate was obtained, which was washed with alcohol and dried for analysis:—

- I. 0.5748 gram gave 0.4205 AgI for Ag.  
 II. 0.3947 „ „ 0.2875 AgI for I.  
 III. 0.409 „ „ 0.1362 Ag reduced by H.

These numbers indicated that the compound was  $\text{CSN}_2\text{H}_4\text{AgI}$  in a partially purified condition, but further washing led to decomposition.

	Theory.	Experiment.		
		I.	II.	III.
Ag.....	34.70	33.61	—	33.31
I .....	40.83	—	39.34	—

It may be that the compound  $(\text{CSN}_2\text{H}_4)_2\text{AgI}$  exists in the hot solution, but that decomposition takes place on cooling, resulting in the separation of the 1 : 1-product, retaining a small proportion of the compound richer in thiourea; but in none of the experiments has a substance been obtained which even approached the 1 : 2-compound in composition, though Mr. Werner, who rendered much assistance in this work, spared no trouble in attempts to prepare such a compound in the solid state.

#### *Silver Cyanide and Thiourea.*

Silver cyanide, recently precipitated from 17 grams of the nitrate, was treated, as in the other cases, with warm alcoholic solution of

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30.4 grams of thiourea. The cyanide dissolved completely, but the solution had to be cautiously evaporated at a low temperature before small crystals separated. The crop was collected, washed with alcohol, and dried at a low temperature, as they decomposed in the steam-bath. The perfectly dry crystals discolour at  $115^{\circ}$  and afford a black liquid at  $126^{\circ}$  (sharply).

0.7695 gram gave 0.29 of Ag.

0.4360 „ 0.717 of  $\text{BaSO}_4$ .

These data agree with the formula  $(\text{CSN}_2\text{H}_4)_2\text{AgCN}$ .

	Theory.	Experiment.
Ag .....	37.70	37.68
S .....	22.37	22.60

In this instance, as in that of silver chloride, a 1:1-compound has not been obtained.

All the foregoing substances agree in readily affording silver sulphide when heated to a few degrees beyond the respective melting points, or even before melting, as in the case of the silver cyanide compound just described. Moreover, treatment with weak alkalis tends to cause change in the same direction, just as the action of an alkali easily separates mercaptan from the compound of thiourea with ethyl bromide and iodide. In the latter, the alkyl group is attached to sulphur, and the silver haloid compounds of thiourea are probably similar in structure.

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