

CXXXIV.—*Thiocarbamide as a Solvent for Gold.*

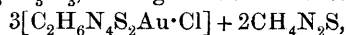
By JAMES MOIR, M.A., D.Sc.

It has been recently shown (Proc., 1906, 22, 105) that gold slowly dissolves in acid solutions of thiocarbamide, and that solution takes place with remarkable rapidity in the presence of suitable oxidising agents.

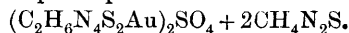
Since then, two new complex gold salts have been isolated from these solutions, and an attempt has been made to ascertain their constitution.

The new sulphate and chloride were obtained by dissolving precipitated gold in solutions of thiocarbamide acidified with sulphuric or hydrochloric acid respectively, the action being accelerated by the addition of hydrogen peroxide. They have approximately the composition of addition-compounds of thiocarbamide with aurous salts, namely, $\text{Au}_2\text{SO}_4 + 6\text{CH}_4\text{N}_2\text{S}$ and $\text{AuCl} + 2\frac{2}{3}\text{CH}_4\text{N}_2\text{S}$; in this respect they are analogous to the series of double-salts of the heavy metals, such as $\text{CuCl} + 3\text{CH}_4\text{N}_2\text{S}$, described by Emerson Reynolds and others.

The author considers, however, that the chloride has in reality the formula $\text{C}_8\text{H}_{26}\text{N}_{16}\text{S}_8\text{Au}_3\text{Cl}_3$, having some such constitution as

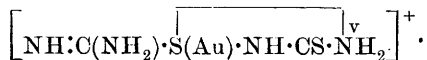


and infers that the sulphate possesses a similar formula, namely,



In the latter case, however, the analytical evidence is incomplete, owing to the difficulty of preparing the substance, and the formula must be taken as only tentative. In the case of the chloride, on the

other hand, the evidence is clear that there is a smaller proportion of hydrogen in the compound than is required by the supposition that it is merely an addition-compound of AuCl and $\text{CH}_4\text{N}_2\text{S}$. It is probable that the cation $\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au}$ has the constitution



The complex chloride can also be obtained from the product of the reaction between potassium aurichloride and thiocarbamide, a fact which supports the formula which is proposed for it, as the following equation shows:



It is converted, by boiling with strong hydrochloric acid, into the compound $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, first described by Emerson Reynolds (*Annalen*, 1869, 150, 255).

These three complex gold salts behave so differently from ordinary aurous compounds that one is compelled to assume the existence in them of a complex cation such as $\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au}$, an assumption supported by analogy, since the properties of such salts as cuprous thiocarbamide carbonate and sulphate (*Ber.*, 1884, 17, 300, for example, $\text{Cu}_2\text{SO}_4 + 5\text{CH}_4\text{N}_2\text{S} + 2\text{H}_2\text{O}$ *) show that copper, at least, does not react in the usual way when combined with thiocarbamide. The author is inclined to suspect that most of these so-called addition-compounds of thiocarbamide and salts of the heavy metals are constituted similarly to his new gold compound, and thus contain less hydrogen than is indicated by the accepted formulæ.

The action of *s*-diphenyl- and diacetyl-thiocarbamide on gold was tried, but the results were negative. Hence it is probable that the activity of thiocarbamide itself depends on its isomerisation to



the hydrogen of the $-\text{SH}$ group being replaceable by gold, just as in the recently-discovered gold mercaptides (*Ber.*, 1905, 38, 2813).

EXPERIMENTAL.

(a) Preparation of Gold-thiocarbamide Sulphate.

Finely-divided gold, prepared from auric chloride and ferrous sulphate, was added to a strong solution of thiocarbamide acidified with sulphuric acid. The action was accelerated by occasional addition of hydrogen peroxide and warming to 50° . The filtered solution was allowed to evaporate spontaneously, when opaque, white rosettes of the complex sulphate crystallised. These were recrystallised for

* Beilstein (I, 1317) formulates this substance incorrectly as $\text{Cu}_2(\text{SO}_4)_2$, &c.

analysis, and dried for several hours at the temperature of boiling water (94.5°), thereby losing water of crystallisation, which was not determined. The substance then melted without decomposition at 161° .

On careful ignition, 0.1327 gave 0.0550 Au. Au = 41.45.

$\text{Au}_2\text{SO}_4 + 6\text{CH}_4\text{N}_2\text{S}$ requires Au = 41.64.

$(\text{C}_2\text{H}_6\text{N}_4\text{S}_2\text{Au})_2\text{SO}_4 + 2\text{CH}_4\text{N}_2\text{S}$ requires Au = 41.82 per cent.

(b) *Preparation of Gold-thiocarbamide Chloride.*

(1) *From Gold.*—Exactly the same method as the above was employed, using hydrochloric instead of sulphuric acid. The product formed large, colourless, six-sided plates or lozenges possessing a waxy lustre and striated parallel to the longer diagonal, which is also the direction of extinction of polarised light.

It melts at 190° without decomposition, which, however, begins at about 210° (see p. 1349). It is alkaline to litmus, as is Reynolds compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, and contains chlorine, but no cyanogen or sulphocyanogen.

After drying in the steam-bath :

0.14775 gave 0.0671 Au. Au = 45.42 per cent.

(2) *From Gold Chloride.*—To a strong solution of thiocarbamide at 50° , a solution of gold potassium chloride was added until the red precipitate ceased to redissolve. The resulting pale yellow solution was warmed for an hour, when it became nearly colourless; a little sulphur was deposited and was separated. On standing overnight, a good yield of the hexahedral compound was obtained, identical with that prepared by the former method. As this method is simple, it was possible to prepare a fair quantity of the substance for exhaustive analysis. It should be noted, however, that it is essential to use gold potassium chloride and not chloroauric acid, since the latter gives Reynolds' compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, instead of the hexahedral compound.

0.1322 gave 0.0600 Au. Au = 45.39.

0.0474 „ 0.0216 Au. Au = 45.50.

0.3370 „ 0.1532 Au. Au = 45.46.

Average, allowing for difference of quantity used, Au = 45.44 per cent.

0.2125 gave 0.0690 AgCl. Cl = 8.03.

0.2125 „ 0.2178 BaSO_4 . Soluble S = 14.08.

0.2135 „ 0.3106 BaSO_4 . Total S = 19.97 per cent.

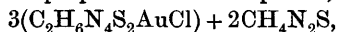
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Total sulphur was determined by digesting with aqua regia and precipitating as BaSO_4 .

From these figures, the atomic ratio $\text{Au} : \text{Cl} = 1 : 0.983$, that is, 1 : 1. The ratio $\text{Au} : \text{total S} = 1 : 2.703$, which is most probably 3 : 8.

The simplest formula for this substance would be $3\text{AuCl} + 8\text{CH}_4\text{N}_2\text{S}$, which requires $\text{Au} = 45.26$ per cent., but an error of even so little as 0.2 per cent. in excess is nearly impossible in the mean of four estimations of gold by ignition.

The formula which I propose for the compound, namely,



requires $\text{Au} = 45.47$; $\text{Cl} = 8.17$; $\text{S} = 19.72$ per cent.

It is just possible, however, that the discrepancy is due to an error in the accepted atomic weight of gold, and that the substance really possesses the formula $3\text{AuCl} + 8\text{CH}_4\text{N}_2\text{S}$.

(c) *Conversion of the Hexahedral Chloride into Reynolds' Compound.*

On boiling the hexahedral compound for a minute with strong hydrochloric acid and separating from a little sulphur, lustrous, opaque, white needles, agreeing exactly with Reynolds' compound, were obtained on cooling. After being recrystallised and dried in the steam oven, 0.0534 gave 0.0273 Au. $\text{Au} = 51.2$; $\text{C}_2\text{H}_8\text{N}_4\text{ClS}_2\text{Au}$ requires $\text{Au} = 51.24$ per cent.

(d) *Action of Caustic Alkali on the Hexahedral Chloride.*

On adding sodium hydroxide to the aqueous solution of the compound, an orange, gelatinous precipitate is obtained, which on warming becomes denser and dark olive-green. This product is identical with that obtained by Rathke (*Ber.*, 1884, 17, 307) by the action of ammonia on Reynolds' compound, $\text{AuCl} + 2\text{CH}_4\text{N}_2\text{S}$, and amounted to 114 per cent. of the gold obtained by ignition (whereas Rathke's specimen amounted to 116 per cent.).* I find, with Rathke, that it seems to contain carbon and nitrogen as well as sulphur. The most probable constitution is $\text{Au}_2\text{S} + \text{CH}_3\text{N}_2\text{SAu}$, the theoretical amount of which is 118 per cent. of the contained gold.

The colourless filtrate contained the whole of the chlorine and the rest of the sulphur ; the chlorine was estimated by precipitating with silver nitrate, extracting the precipitate with ammonia, and reprecipitating with nitric acid. This procedure was necessitated by the

* Another specimen, made by the use of ammonia instead of sodium hydroxide, was analysed :

0.0611 gave 0.0521 Au. $\text{Au} = 85.27$.

$\text{CH}_3\text{N}_2\text{S}_2\text{Au}_3$ requires $\text{Au} = 84.67$ per cent.

fact that the original substance gives a complex precipitate with silver nitrate (see below). The residual silver sulphide was converted into barium sulphate, whereby the "soluble sulphur" of the analyses was determined. From the difference between "total" and "soluble" sulphur, the sulphur contained in the olive-green gold precipitate is calculated as 5.89 per cent. of the original, which is a little too high for that required by the formula suggested for the olive compound, but the determination of soluble sulphur by this circuitous process is probably inaccurate.

(e) *Effect of Heat on the Chloride.*

On heating in the air-bath at 210° to constant weight, the product was uniform and dark brown, and amounted to 148.6 per cent. of the gold obtained by ignition. It appears to be a single substance, and the only probable formula is $\text{Au}_3\text{S}_2 \cdot 3\text{CH}_3\text{N}_2\text{S}$, which corresponds to 148.7 per cent. of the contained gold.

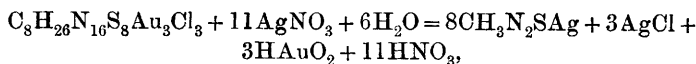
(f) *Action of Silver Nitrate.*

On adding silver nitrate in excess to a solution of the substance, an immediate brown precipitate of auric hydrate mixed with silver chloride is obtained, followed after a few seconds by a bulky mass of felted white needles of silver-thiocarbamide, whereby the whole is made to gelatinise. This operation was carried out quantitatively and the results agree with the complicated formula which I put forward for the gold thiocarbamide chloride.

The whole was diluted with very weak nitric acid, the precipitate filtered and dried at 60° for an hour, and finally left for a week over sulphuric acid in a vacuum. The filtrate contained a little dissolved silver thiocarbamide, the amount of which was determined by conversion into silver sulphide and this was added to the main quantity.

0.4280 gave 0.7543 mixed product and 0.0885 Ag_2S (= 0.0653 gram $\text{CH}_3\text{N}_2\text{SAg}$, or 1.08 mols.). Total $\text{Au} + \text{AgCl} + \text{CH}_3\text{N}_2\text{SAg}$ = 0.8196 gram, or 191.5 per cent. of the original.

The theoretical equation is :



whence 1301 grams should yield 8 mols. of silver thiocarbamide, 3 mols. of silver chloride, and 3 atoms of gold (on drying); total 191.2 per cent. of the original substance taken. This agreement between theory and experiment was confirmed by the subsequent

treatment of the precipitate, which was first ignited, then fully chlorinated and re-ignited, and finally reduced to gold-silver alloy.

Ignition: Theory for $3\text{Au} + 3\text{AgCl} + 6\cdot92$, $\text{Ag} = 0\cdot5811$ gram. Found $0\cdot5856$ gram.

Chlorination: Theory for $3\text{Au} + 9\cdot92$, $\text{AgCl} = 0\cdot6584$ gram. Found $0\cdot6410$ gram.

Alloy: Theory for $3\text{Au} + 9\cdot92$, $\text{Ag} = 0\cdot5466$ gram. Found $0\cdot5450$ gram.

I desire to thank Mr. H. Harding, B.Sc., for his kindness in supplying me with the necessary extracts from chemical literature inaccessible in this country.

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