

ART. XXIII.—*Some Complex Chlorides containing Gold.*

I. *Pollard's Ammonium-Silver-Auric Chloride*; by  
HORACE L. WELLS.

[Contribution from the Sheffield Chemical Laboratory of Yale University.]

Since numerous investigations upon double and triple salts have been carried out in this laboratory by the writer and his associates, attention was attracted to the description by William Branch Pollard<sup>1</sup> of a new triple chloride to which he gave the formula  $(\text{NH}_4)_8\text{Ag}_3\text{Au}_4\text{Cl}_{23}$ . Since this formula appeared to be a rather complex one, and because Pollard used apparently drastic methods in preparing the salt for analysis, including extracting it with ether and heating it sufficiently to volatilize ammonium chloride, a new investigation of it was undertaken.

The salt was readily obtained, by following Pollard's directions, from a solution of 25 g. of gold in 50 cc. of nitric and 150 cc. of hydrochloric acid, to which were added 30-35 g. of ammonium chloride and 3 g. of silver nitrate dissolved in 10 cc. of water. When a few more crystals of ammonium chloride were added the silver chloride precipitate that was present was gradually transformed into the dark triple salt. Then upon heating the salt with its mother-liquor there was a separation of silver chloride which, upon cooling, was replaced by the triple salt.

This method of preparing the salt for analysis did not appear to be very satisfactory on account of the concentrated condition of the solution and also on account of the possible danger of the entanglement of silver chloride in the product. It was found in the present investigation that when solutions somewhat similar to the one recommended by Pollard were diluted largely, perhaps with an equal volume or more of 1:1, or stronger, hydrochloric acid, it was easy to obtain clear, boiling solutions from which the triple salt could be obtained either by cooling or evaporation to crystallization on the steam-bath, and both methods of preparation, under wide variations of conditions, have been used in obtaining the products for analysis. The crops of crystals were usually washed to some extent by pouring off most of the mother-liquor, diluting the remainder rather largely with hydrochloric

<sup>1</sup> Jour. Chem. Soc., 117, 99, 1920.

acid, agitating and draining. In one case (analysis VI) where the crop had been deposited from a solution diluted to an unusual extent with concentrated hydrochloric acid no washing was done, for the sake of comparison. In all cases the products were rapidly pressed between smooth filter papers until the latter were no longer moistened by the operation and then they were dried in the air. There was practically no further loss in weight upon drying at 100°.

The crystals obtained were always very small, usually not over 1 or 2 mm. in diameter. The larger ones were very dark brownish-red in color, but evidently transparent, while the smaller ones were not so dark. Pollard has called the color purplish-brown. The crystals are beautiful and brilliant, and a description of their orthorhombic form is given in Pollard's article.

The salt is quickly decomposed by water, but it appears to be stable in the presence of strong hydrochloric acid, as was observed by Pollard.

The following analyses of separate crops were made:

|                    | Prepared by<br>hot evaporation |       | Prepared by<br>cooling |       |       |       | Calculated for<br>(NH <sub>4</sub> ) <sub>5</sub> Ag <sub>3</sub> Au <sub>3</sub> Cl <sub>17</sub> |
|--------------------|--------------------------------|-------|------------------------|-------|-------|-------|--|
|                    | I.                             | II.   | III.                   | IV.   | V.    | VI.   |  |
| NH <sub>4</sub> .. | 7.02 <sup>a</sup>              | ....  | 7.09 <sup>a</sup>      | ....  | ....  | ....  | 7.13   |
| Ag ...             | 14.31                          | 14.19 | 13.61                  | 14.03 | 14.47 | 14.16 | 14.21  |
| Au ...             | 38.89                          | 38.80 | 39.67                  | 38.84 | 38.54 | 38.62 | 38.96  |
| Cl ....            | 39.47                          | ....  | 39.82                  | ....  | ....  | ....  | 39.70  |
|                    | 99.69                          |       | 100.19                 |       |       |       | 100.00   |

<sup>a</sup> Calculated from the excess of chlorine.

|                       | Pollard found | Calculated for<br>(NH <sub>4</sub> ) <sub>5</sub> Ag <sub>3</sub> Au <sub>3</sub> Cl <sub>22</sub> | Pollard's formula<br>differs from new one |
|-----------------------|---------------|--|---|
| NH <sub>4</sub> ..... | 6.88          | 6.97   | — 0.16                                    |
| Ag .....              | 15.58         | 15.62  | + 1.41                                    |
| Au .....              | 37.99         | 38.06  | — 0.90                                    |
| Cl .....              | 39.44         | 39.35  | — 0.35                                    |
|                       | 99.89         | 100.00   |   |

The analyses in the present investigation were made by decomposing the salt with a liberal amount of water by the aid of heat, cooling, collecting the silver chloride in a Gooch crucible and weighing it, precipitating the gold in

the hot filtrate by means of ammonium oxalate, and, after hot digestion until the liquid was perfectly clear, collecting and weighing the gold in a Gooch crucible, then acidifying the last filtrate strongly with nitric acid, precipitating silver chloride by means of silver nitrate, and collecting and weighing the precipitate in the usual way. Of course the chlorine in the first precipitate of silver chloride was added to this.

From the evidence presented here it is believed that the new formula is the correct one. It is true that Pollard's results agree very closely with his formula, but he gives only one analysis, which may possibly represent selected results, while his method of preparing the salt for analysis, already alluded to, would probably not remove any silver chloride from the salt, but might remove small quantities of the other constituents. In fact, it was his object to remove any gold chloride and ammonium chloride that adhered to the crystals, so that his results may reasonably be expected to show too much silver chloride.

The new formula varies but slightly from Pollard's, and it has little advantage over his in regard to simplicity. The new investigation, therefore, confirms the fact that this ammonium-silver-auric chloride has a composition corresponding to a rather complex formula which appears without doubt to be  $(\text{NH}_4)_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$ .

In view of the frequent similarity of ammonium and potassium salts, an attempt was made to prepare a potassium-silver-auric chloride, but after many experiments under wide differences of conditions no evidence of the existence of such a triple salt was obtained.

When cesium chloride was used, however, a triple salt was easily obtained, and several other triple chlorides containing cesium and gold, as well as a new double salt of these two metals, have been prepared. This work will be described in subsequent articles in this Journal.

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