

Summary

1. It is pointed out that anhydrous auric chloride reacts rapidly, at ordinary temperatures, with aromatic compounds except nitrobenzene, with the liberation of hydrogen chloride and the formation of compounds RAuCl_2 .

2. It is shown that anhydrous auric chloride reacts with most oxygen-containing substances, forming complexes.

3. Nitrobenzene is shown to be the only solvent, thus far discovered, which dissolves gold chloride without undergoing a reaction with that reagent.

4. The effect of substituents in the benzene ring on the speed of reaction of the compounds with gold chloride is discussed.

5. The behavior of aryl gold dichlorides toward reducing reagents is discussed.

6. It is shown that the aryl gold dichlorides, while insoluble in water, dissolve in sodium chloride solution probably forming complexes of the chloroaurate type.

7. The effect of gold chloride as a halogen carrier is discussed from the standpoint of the intermediate compounds that have been isolated, and the further reaction of those substances and chlorine.

8. The preparation and properties of the following aryl gold dichlorides are described: phenyl auric dichloride, tolyl auric dichloride, diphenyl auric dichloride, methyl salicylate auric dichloride and *o*-nitroanisole auric dichloride.

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THE CHEMISTRY OF ORGANIC GOLD COMPOUNDS. IV. GOLD IMIDE COMPOUNDS¹

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Introduction

The elements of the first sub-group in the periodic system, *i. e.*, copper, silver and gold, form two distinct classes of imide salts. Thus, copper in alkaline solution gives the well-known "biuret"² reaction with biuret and reacts readily also with other compounds which contain an imide group. Specifically, with succinimide, a complex salt,³ $\text{K}_2\text{Cu}(\text{C}_2\text{H}_2\text{O}_2\text{N})_4$

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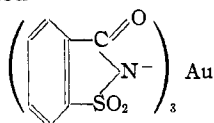
² Schiff, *Ber.*, 29, 298 (1896); *Ann.*, 352, 73 (1907); Rising and Johnson, *J. Biol. Chem.*, 80, 709 (1928); Rising, Hicks and Moerke, *ibid.*, 89, 1 (1930).

³ Tschugaeff, *J. Russ. Phys.-Chem. Soc.*, 7, 1083 (1906); *Ber.*, 40, 1973 (1907).

is formed. However, silver forms a normal salt with succinimide ($\text{Ag}(\text{C}_2\text{H}_4\text{O}_2\text{N})$).⁴

The tendency of gold to form compounds of the chloroaurate type⁵ is clearly shown by a new class of gold imide compounds which we have prepared.

Previous Work.—There are no gold carbonyl imides described in the literature. The sulfinimides, which are more acidic, form metallic salts more readily and a process has been described for the preparation of gold sulfinimides.⁶ The method consists in treating the alkali salt of the sulfinimide with auric hydroxide. In the case of saccharin a compound of the following type is claimed



According to the disclosure in the patents, these gold sulfinimides give "the well-known gold reactions with stannous chloride or oxalic acid." Obviously these gold sulfinimides furnish an appreciable concentration of auric ions in solution. The patents further state that "the formation of these compounds is surprising, since by the use of aromatic carbonyl imides as for example, phthalimide, this reaction does not take place."

Our experience differs fundamentally from that of the above authors in the following respects: (1) we have been able to prepare gold carbonyl imide complexes. (2) The structures of the gold imide complexes are different from those assumed in the German patents. (3) The stability of our gold imide complexes is very great, for they do not give, at ordinary temperatures, tests for gold when treated with such reagents as stannous chloride or oxalic acid.

Properties of Imido-auric Acids.—The compounds of gold imides which we have prepared may be represented by the general formula $\text{H}^+[\text{Au}(\text{imide})_4]^-$. We have designated them as imido-auric acids because their structures are similar to the structure of chloroauric acid. They give colorless solutions which are characterized by great stability toward both heat and reducing agents. Thus, neutral solutions of these compounds may be warmed without reduction with hydroquinone, stannous chloride or other powerful reducing agents, while strongly acid or alkaline solutions of the substances are only reduced upon warming. This great stability of the gold compounds toward reducing agents indicates that they do not ionize to give an appreciable quantity of gold ions.

⁴ Bunge, *Ann. Suppl.*, 7, 119 (1870); Ley and Werner, *Ber.*, 38, 2199 (1905); 40, 705 (1907).

⁵ This tendency has been stressed in our previous papers, *THIS JOURNAL*, 53, 2701 (1931); 53, 3053 (1931).

⁶ German Patents 347,139 and 348,070.

These complex salts of gold imides are also very stable toward mineral acids at ordinary temperatures. The addition of a mineral acid to a salt of the gold imides usually leads to the separation of the imido-auric acids. This behavior of the salts of gold imides is in striking contrast to the behavior of the salts of copper imides, which are decomposed instantly even by such weak acids as acetic.

The imido-auric acids are definitely acidic, forming well-characterized salts and reacting acid to indicators. In particular succinimido-auric acid is a relatively strong acid. It decomposes carbonates and turns Congo red blue. Even more remarkable is the fact that ammonium succinimido-aurate may be crystallized from hot glacial acetic acid without decomposition. The acid properties of this succinimido-auric acid cannot be attributed to succinimide, for the latter is a very weak acid.

The alkali and alkaline earth salts of the imido-auric acids are extremely soluble in water, but insoluble in alcohol. On the other hand, ammonium succinimido-aurate is crystalline and difficultly soluble in water but more soluble in alcohol than the corresponding alkali salts. The presence of other salts, particularly salts of halides, such as sodium chloride, produces a great change in the solubility of some of these compounds. Thus, the difficultly soluble ammonium succinimido-aurate dissolves easily in dilute aqueous salt solutions of chlorides and bromides. The desirability of avoiding the presence of large quantities of salts in the preparation and crystallization of these compounds is obvious.

Some of the free acids are very soluble in water, for example succinimido-auric acid; others are difficultly soluble, such as the phthalimido-auric acid.

The Preparation of Imido-auric Acids.—The imido-auric acids are best prepared by the direct combination of gold hydroxide and the desired imide. In some cases the reaction takes place by simply heating an aqueous mixture of auric hydroxide and the imide. Usually, however, the reaction takes place more readily in the presence of a small quantity of a halogen salt or a mineral acid. The halogen salt or acid serves as a means of obtaining an appreciable quantity of auric ions in solution. This is particularly desirable since auric hydroxide is practically insoluble in water. In general, any substance which increases the concentration of auric ions in solution would increase the rate at which the imido-auric acids are formed. An excess of auric hydroxide is also employed and serves as a buffer to regulate the acidity. In some cases, due to the insolubility of the imide, it is necessary to use other solvents besides water, *i. e.*, a mixture of alcohol and water. A soluble salt of the imide may be used, but this increases the difficulty in the separation of the products of the reaction.

The Structure of Ammonium Succinimido-aurate.—Since the reaction

between auric hydroxide and imides takes place slowly, the solution must be kept warm for a considerable period. This long heating may result in the hydrolysis of a portion of the imide, liberating ammonia, which may lead to the production of the ammonium salt of the imido-auric acid. Its formation in the presence of succinic acid indicates that the imido-auric acid is a relatively strong acid; otherwise it would not deprive succinic acid of the ammonium radical.

In order to establish the structure of ammonium succinimido-aurate, it was converted into the corresponding barium salt. This was accomplished by heating a solution of the ammonium salt with barium hydroxide, when ammonia was liberated and upon concentration of the solvent pure barium succinimido-aurate separated. Subsequently the barium salt was decomposed with the calculated quantity of sulfuric acid and the crystalline free acid was obtained. This crystalline free acid was then changed back into the ammonium salt by treating it with ammonium hydroxide. Furthermore, succinimide was recovered, practically quantitatively, by the reduction of ammonium succinimido-aurate with zinc.

Experimental Part

1. **Ammonium Succinimido-aurate**, $\text{NH}_4\text{Au}(\text{C}_4\text{H}_4\text{O}_2\text{N})_4 \cdot 4\text{H}_2\text{O}$.—To 117 g. of succinimide and one gram of auric chloride dissolved in 500 cc. of water, moist auric hydroxide (equivalent to 40 g. of auric oxide) was added. The mixture was warmed on the steam-bath for forty-eight hours. Most of the auric hydroxide dissolved and a colorless product formed. Sufficient boiling water was then added to dissolve the crystals which had formed and the hot solution filtered. Upon cooling the filtrate, colorless crystals of ammonium succinimido-aurate separated. Sixty-six grams of solid was thus obtained. The product was crystallized from hot water and subsequently air dried at room temperature.

Anal. Subs., 0.1022: Au, 0.0296. Calcd. for $\text{AuC}_{18}\text{H}_{20}\text{O}_8\text{N}_4 \cdot 4\text{H}_2\text{O}$: Au, 29.02. Found: Au, 28.96.

Crystalline ammonium succinimido-aurate became anhydrous after drying for several months *in vacuo* over phosphoric anhydride. Samples were also dehydrated by drying for eight hours at 80° *in vacuo*.

Anal. Subs., 0.3624: Au, 0.1373; N, 29.5 cc. of *N*/10 acid. Calcd. for $\text{AuC}_{16}\text{H}_{20}\text{O}_8\text{N}_4$: Au, 32.47; N, 11.51. Found: Au, 32.51; N, 11.40.

The salt separates from water in transparent prismatic crystals, frequently in the form of almost regular hexagons but sometimes elongated; when viewed from the ends they are rectangular and from the sides trapezoidal.

An 0.1-g. quantity of the substance heated in a crucible, detonated violently. In a melting point tube, it decomposed at 270 to 280° , gradually turning purple and finally black, without melting.

The compound is difficultly soluble in water or dilute alcohol, insoluble in ether, benzene, chloroform and most organic solvents. It is fairly soluble in hot glacial acetic acid, crystallizing upon cooling. It gives colorless solutions in concentrated sulfuric acid which decompose when heated, with the precipitation of metallic gold. It is soluble in sodium carbonate solution or in alkalis, forming the corresponding alkali salts.

Two grams of ammonium succinimido-aurate was dissolved in 50 cc. of hot glacial acetic acid. Upon cooling the filtrate 1.3 g. of crystalline ammonium succinimido-aurate separated. This was washed with ether and dried at 70° *in vacuo*.

Anal. Subs., 0.1062; Au, 0.0345. Calcd. for $\text{AuC}_{16}\text{H}_{20}\text{O}_8\text{N}_6$: Au, 32.47; Found: Au, 32.49.

A second lot of crystalline succinimido-aurate was obtained by the addition of ether to the mother liquor. The crystals weighed 0.6 g.

Barium Succinimido-aurate, $\text{Ba}[\text{Au}(\text{C}_4\text{H}_4\text{O}_2\text{N})_4]_2$.—Two grams of ammonium succinimido-aurate was dissolved in 29 cc. of cold *N/10* barium hydroxide. After solution the odor of ammonia was observed. The solution was concentrated *in vacuo* to about 5 cc., when a small quantity of unchanged ammonium succinimido-aurate had separated. The clear filtrate was diluted with methyl alcohol until it turned slightly turbid, when crystallization of the substance occurred. After several hours the crystals were collected on a filter. It was crystallized from a mixture of alcohol and water. The pure product was dried at 70° *in vacuo* to the constant weight of 0.7514 g.

Anal. Subs., 0.0712: Au, 0.0212; BaSO_4 , 0.0126. Calcd. for $\text{BaAu}_2\text{C}_{32}\text{H}_{32}\text{O}_{16}\text{N}_8$: Au, 29.97; Ba, 10.44. Found: Au, 29.93; Ba, 10.40.

The crystals separated from dilute alcohol or water in long slender needles which formed in fan-like clusters. They were very soluble in water but insoluble in organic solvents. In a melting point tube the compound decomposed at 268 – 270° . A water solution was not reduced by aqueous solutions of hydroquinone or stannous chloride.

Succinimido-auric Acid, $\text{HAu}(\text{C}_4\text{H}_4\text{O}_2\text{N})_4$.—To 0.5 g. of barium succinimido-aurate dissolved in 15 cc. of water, 7.6 cc. of *N/10* sulfuric acid was added slowly while the solution was shaken vigorously. The barium sulfate which precipitated was collected on a filter. The clear filtrate was evaporated *in vacuo* to a sirup, which was brought to crystallization by the addition of a small quantity of alcohol. The crystals were collected on a filter, washed with alcohol, followed by ether, and finally dried at 80° *in vacuo*. The weight of material was 0.35 g.

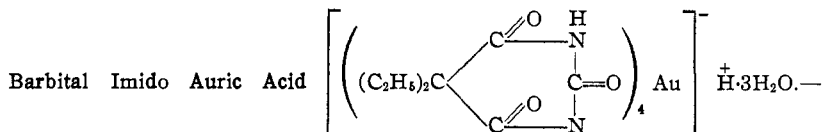
Anal. Subs., 0.0464: Au, 0.0154. Calcd. for $\text{HAuC}_{16}\text{H}_{16}\text{O}_8\text{N}_4$: Au, 33.19. Found: Au, 33.19.

When crystallized from dilute alcohol or water, succinimido-auric acid is obtained in the form of very fine needles. These needles are easily soluble in water, difficultly soluble in alcohol and insoluble in ether and ethyl acetate. In a melting point tube this compound decomposed at 210 – 240° , depending upon the rate of heating.

A water solution of succinimido-auric acid was neutralized with a solution of ammonium hydroxide. A precipitate of ammonium succinimido aurate formed immediately. The crystals were collected on a filter and dried *in vacuo*.

Anal. Subs., 0.1056: Au, 0.0342. Calcd. for $\text{NH}_4\text{AuC}_{16}\text{H}_{16}\text{O}_8\text{N}_4$: Au, 32.47. Found: Au, 32.38.

Separation of Succinimide from Ammonium Succinimido-aurate.—One gram of anhydrous ammonium succinimido-aurate, $(\text{NH}_4)\text{Au}(\text{C}_4\text{H}_4\text{O}_2\text{N})_4$, was partially dissolved at room temperature in 25 cc. of water which contained 0.2 g. of sodium chloride, and one gram of granulated zinc was added. The mixture was allowed to stand at room temperature. After twenty-four hours considerable gold had been deposited and the solution had become distinctly alkaline. Dilute acetic acid was then added until the solution was neutral. Then the mixture was set aside for another twenty-four hours, when the hydrogen-ion concentration was adjusted again. After standing for about ten days all the gold had been reduced to the metal. The succinimide was then isolated in the usual manner. The weight of material was 0.6 g. and the melting point 116° . After a single crystallization the melting point rose to 124° .



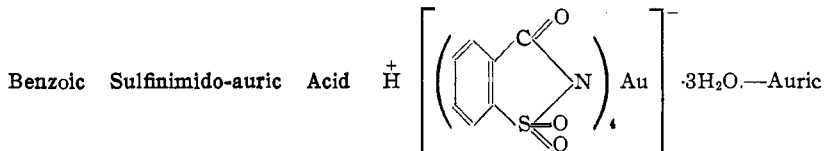
Barbital (di-ethylbarbituric acid) in water solution reacts with auric hydroxide very slowly to give a silky precipitate. A water solution of barbital on standing for two months with four grams of auric hydroxide formed less than 0.5 g. of this silky precipitate. Even on warming on a steam-bath the rate of formation was very slow. The addition of a small amount of auric chloride or a drop of hydrochloric acid, however, greatly accelerated the rate of formation; other chlorides had the same effect.

0.01 mole of auric hydroxide was mixed with 0.04 mole of barbital and 50 cc. of water and two drops of concentrated hydrochloric acid was added. After digestion on the steam-bath for forty-eight hours, practically all the gold hydroxide had been changed to a white silky precipitate. Upon crystallization from 50% alcohol a pure compound resulted.

Anal. Subs., 0.1122, 0.1164, 0.1449, 0.0466, 0.0916; Au, 0.0232, 0.0236, 0.0294, 0.0096, 0.0188. Calcd. for $\text{HAuC}_{22}\text{H}_{44}\text{O}_{12}\text{N}_8 \cdot 3\text{H}_2\text{O}$. Au, 20.41; N, 11.59. Found: Au, 20.68, 20.27, 20.29, 20.60, 20.52; average 20.47; N, 11.74, 11.42; average 11.57.

The compound is white and crystalline. It is soluble in dilute alcohol, very difficultly soluble in water and 95% alcohol, insoluble in ether, benzene and petroleum ether. It is not readily reduced by hydroquinone or sodium hydrosulfite. It decomposes at 200° to a black liquid.

Sodium Salt of Barbital Imido Auric Acid.—Barbital imido auric acid dissolves in sodium hydroxide solution forming a sodium salt which may be precipitated by the addition of alcohol. This salt is very soluble in water. It is very stable toward reducing agents. A water solution of this salt, after careful acidification with hydrochloric acid, gives a precipitate of barbital imido auric acid.

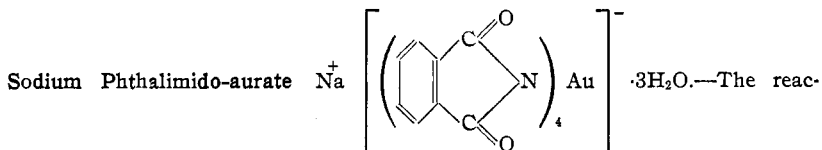


hydroxide reacts much more readily with saccharin than with any other compound which we tried, to form a complex imide. Due to the greater acidity of this group it is not necessary to add gold chloride or other substances in order to accelerate the reaction.

0.01 mole of auric hydroxide was digested with 0.04 mole of saccharin in water solution. A yellow crystalline compound resulted. After crystallization from 50% alcohol and drying for eighteen hours over phosphoric anhydride, the following analyses were obtained.

Anal. Calcd. for $\text{HAuC}_{26}\text{H}_{16}\text{O}_{12}\text{N}_4\text{S}_4 \cdot 3\text{H}_2\text{O}$. Au, 20.41; N, 5.69. Found: Au, 20.14; N, 5.41.

The compound is difficultly soluble in dilute alcohol, almost insoluble in water and 95% alcohol, insoluble in organic solvents, slightly soluble in salt solutions but soluble in alkalis. It decomposes gradually without melting at 135°.



tion with phthalimide proceeds slowly and the addition of gold chloride or other salts is necessary. The separation from the reaction product of any unchanged phthalimide is difficult, due to the low solubility of the latter.

The sodium salt was prepared by the reaction between sodium carbonate, auric hydroxide and phthalimide. It was crystallized several times from alcohol-water mixtures.

Anal. Subs., 0.0938: Au, 0.0220; Na_2SO_4 , 0.0094. Calcd. for $\text{NaAuC}_{32}\text{H}_{16}\text{O}_8\text{N}_4 \cdot 3\text{H}_2\text{O}$: Au, 22.95; Na, 2.70. Found: Au, 23.45; Na, 3.24.

The compound is difficultly soluble in water, insoluble in alcohol, acetone, ether and slightly soluble in dilute alcohol. It was not reduced by hydroquinone or sodium hydrosulfide. It begins to decompose at 185° , gradually becoming black as the temperature rises.

This product was not quite pure, and it probably contained a small amount of sodium phthalimide, which resulted in a high sodium content. However, there is no doubt as to the identity of this compound, as its physical and chemical properties indicate that the compound is sodium phthalimido-aurate.

The authors wish to acknowledge their indebtedness to Dr. Carl Voegtlin of the National Institute of Health of the United States Public Health Service for his interest and the encouragement he has given them throughout the work on gold compounds.

Summary

1. It is shown that gold hydroxide reacts with carbonylimides as well as with sulfinimides to give compounds of the chloro-aurate type. These compounds have been designated as imido-auric acids and are represented by the general formula $^+\text{H}[\text{Au}(\text{imide})_4]^-$.

2. The great stability of the imido auric acids, as well as their salts, toward powerful reducing agents is discussed.

3. The acid character of succinimido auric acid $^+\text{H}[\text{Au}(\text{succinimide})_4]^-$ is emphasized. It is shown that this acid is a stronger acid than carbonic acid.

4. The following representatives of a new class of gold carbonyl imides are described: succinimido-auric acid, ammonium succinimido-aurate, barium succinimido-aurate, barbitalimido-auric acid and sodium phthalimido-aurate.

5. A sulfinimide derivative, saccharinimido-auric acid, is described.

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