

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

ADDITION COMPOUNDS OF GOLD HALIDES WITH BENZYL SULFIDE

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Previous Work.—In studying the action of organic sulfides upon gold chloride, in 1905, F. Herrmann¹ made the following observations. Upon mixing 2 mols of benzyl sulfide and 1 mol of gold chloride, in ethereal or alcoholic solution, there was gradually formed in the initially clear liquid a voluminous orange-colored precipitate, consisting of spheroidal growths of small needles, of the composition² $\text{AuCl}_2\text{S}(\text{Bz})_2$. After the mixture had stood for 8 days this precipitate changed into a compact, colorless, crystalline powder; and upon mixing alcoholic gold chloride solution with a large excess of benzyl sulfide, at 50° , there was no intermediate precipitation of the orange compound, but a direct separation of long colorless needles from the solution. In both cases, the white substance corresponded to the formula $\text{AuCl}\cdot\text{S}(\text{Bz})_2$. Under no conditions was it possible to obtain a compound containing more than one molecule of benzyl sulfide to each gold atom.

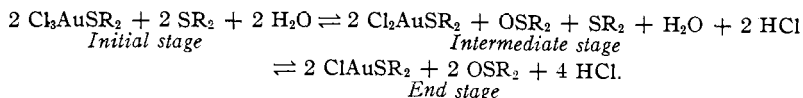
Upon solution in hot chloroform, the white compound nearly always deposited metallic gold, though only in traces; the presence of a slight excess of benzyl sulfide always prevented this decomposition. In chloroform solution, the white compound gave with hydrogen sulfide a brownish precipitate of aurous sulfide, and with mercaptans a white precipitate of AuSR ; Herrmann therefore considered it to be "auro-dibenzyl sulfine chloride."

The orange-colored compound was best prepared in ether, from 3 mols of benzyl sulfide and 2 mols of gold chloride. Recrystallized from chloroform, it separated in fine silky needles of a fiery, orange color. When heated with alcohol, it was reduced to the colorless compound $\text{AuCl}\cdot\text{S}(\text{Bz})_2$. In chloroform solution, by means of the boiling-point method, Herrmann found for the orange-colored compound the molecular weight 604–608 (calc. for $\text{AuCl}_2\text{S}(\text{Bz})_2$: 482.2). Notwithstanding the excellent agreement of the values for several concentrations, Herrmann considered the result unsatisfactory; he remarked, however, that it came out nearer to the single than to the double formula, and he concluded that the substance was neither an auric, nor an auro-auric compound. He named it "dichlorauri-dibenzyl sulfide," assigned the formula $[\text{Au}, \text{Cl}_2, \text{S}(\text{C}_7\text{H}_7)_2]$, and left the constitution unsettled.

¹ Herrmann, *Ber.*, **38**, 2813 (1905).

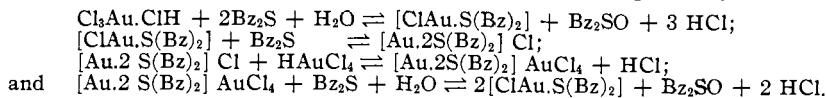
² In this paper, $\text{S}(\text{Bz})_2$, or Bz_2S , is adopted as an abbreviation for $\text{S}(\text{C}_7\text{H}_7)_2$.

In discussing the formation of the two compounds Herrmann assumed the initial formation of Cl_3AuSR_2 , followed by the reactions



He was able to separate and identify the dibenzyl sulfoxide produced, and also to show that, in chloroform solution, with a mixture corresponding in composition to the end stage, the action could be driven backwards by means of hydrogen chloride.

Investigation of the Addition Compounds Containing Chlorine.—The following scheme, in which the gold addition products are assumed to be analogous to those of platinum, more recently studied by Tschugaeff and his students,³ appeared to the writer to offer a more complete explanation of the experimental data than the scheme originally proposed by Herrmann.



Furthermore, the existence of the compound $[\text{Au.2S(Bz)}_2] \text{AuCl}_4$, partially ionized in solution, would account in a very satisfactory manner for the intermediate molecular-weight values observed by Herrmann, which fell between those for $\text{Cl}_2\text{Au.S(Bz)}_2$ and the double formula.

In order to test this point in a preliminary manner, the following experiments were performed.

(1) 0.5055 g. (2 mols) of $\text{Cl}_2\text{Au.S(Bz)}_2$ and 0.2527 g. (3 mols) of Bz_2S were dissolved in 40 cc. of chloroform, a few drops of water were added, and the mixture was allowed to stand overnight, when it entirely lost its color. It was allowed to evaporate somewhat, and was then tested, as follows.

Several volumes of ether were added to one portion, with the formation of a white precipitate of crystalline needles. Of these, 0.1054 g. gave on ignition 0.0459 g. of gold, or 43.55% (calc. for $[\text{Au.2S(Bz)}_2] \text{Cl}$: 29.82; and for ClAu.S(Bz)_2 : 44.12).

The second portion was treated with ethereal chloro-auric acid solution. Precipitation began in less than 1 minute, and was complete in about 5 minutes; 0.0503 g. of the orange-colored precipitate gave on ignition 0.0205 g. of gold, or 40.75% (calc. for $[\text{Au.2S(Bz)}_2] \text{AuCl}_4$: 40.80).

(2) 0.1722 g. (2 mols) of $\text{Cl}_2\text{Au.S(Bz)}_2$ and 0.0383 g. (1 mol.) of Bz_2S were dissolved in 35 cc. of chloroform, treated with 5 drops of water, and allowed to stand. The lemon-yellow solution became colorless overnight, showing the reaction to be quantitative. Owing to the absence of an excess of benzyl sulfide, however, minute traces of gold were observed on the test-tube walls.

(3) In chloroform solution, ClAu.S(Bz)_2 was found to give with hydrogen sulfide a brownish-yellow precipitate of aurous sulfide, as stated by Herrmann; but, in the presence of a large excess of benzyl sulfide, hydrogen sulfide failed to produce a precipitate in the solution. Upon corking the test-tube, however, and allowing the mixture to stand overnight, a small quantity of aurous sulfide was deposited even in this case.

³ Tschugaeff with Benewolensky, *Z. anorg. Chem.*, **82**, 420 (1913); with Kobljanski, *ibid.*, **83**, 8 (1913); with Chlopin, *ibid.*, **86**, 241 (1914).

(4) Upon treating $\text{Cl}_2\text{Au.S(Bz)}_2$ in chloroform solution with hydrogen sulfide, the gold was quantitatively precipitated as flocculent black disulfide, Au_2S_2 . Assuming the existence of $[\text{Au}_2\text{S(Bz)}_2]\text{AuCl}_4$, this reaction might be considered in the light of the equation, $[\text{Au}_2\text{S(Bz)}_2]\text{AuCl}_4 + 2 \text{H}_2\text{S} = \text{Au}_2\text{S}_2 + 2 \text{Bz}_2\text{S} + 4 \text{HCl}$.

Although these data may be interpreted in terms of the mechanism suggested by the writer, they nevertheless do not necessarily indicate the existence of $[\text{Au}_2\text{S(Bz)}_2]\text{Cl}$. The formation of this compound would account for the stabilizing effect of benzyl sulfide upon ClAu.S(Bz)_2 , but this same effect might very well be due only to mass action; in the latter case, as actually happens, even a small excess of benzyl sulfide should tend to counteract the dissociation, $\text{ClAu.S(Bz)}_2 = \text{AuCl} + \text{Bz}_2\text{S}$. In order to test this point rigidly, conductivity measurements were carried out in a cell provided with gold electrodes, as outlined in Table I. The measurements were made at 25° , in the regular manner, with the use of a Wheatstone bridge.

Since it was sufficient to know only the relative conductances of the solutions, no attempt was made to ascertain the capacity of the cell employed. The resistances observed ranged from about 15,000 to 52,000 ohms, in the different solutions. Measurements were first attempted with chloroform solutions, but the resistances were so high that it was considered advisable to change to alcohol.

TABLE I⁴CONDUCTIVITY OF Cl Au.S(Bz)_2 AS INFLUENCED BY THE PRESENCE OF Bz_2S

Stock Solutions: (A) 187.5 mg. of ClAu.S(Bz)_2 dissolved in 125 cc. of absolute alcohol; (B) 90.0 mg. of Bz_2S dissolved in 50 cc. of absolute alcohol. 25 cc. of Solution A was used in each experiment.

Mixture Employed		Composition of the Solution Mols Bz_2S per mol ClAu.S(Bz)_2	Relative Conductivity
Solution B Cc.	Abs. Alcohol Cc.		
0.0	25.0	0.0	1.000
5.0	20.0	0.5	0.474
10.0	15.0	1.0	0.304
15.0	10.0	1.5	0.296
20.0	5.0	2.0	0.289

The results of these measurements are very different from those obtained by Tschugaeff and Kobljanski³ in the case of the platinum complexes. They found that in methyl alcohol the conductivity of $[\text{Cl}_2\text{Pt.2-SR}_2]$ became increasingly greater, the larger the quantity of R_2S that was added to the solution, this being due to the formation of the ionogen, $[\text{Pt.4 SR}_2]\text{Cl}_2$. In the present case, the results indicate the non-formation of a substance of the type $[\text{Au}_2\text{S(Bz)}_2]\text{Cl}$, and hence do not bear out the

⁴ Since alcohol is not without action upon $\text{Cl}_2\text{Au.S(Bz)}_2$, the orange-colored compound was not investigated in these experiments. It is worthy of note, however, that in the earlier series a solution of 0.2251 g. of $\text{Cl}_2\text{Au.S(Bz)}_2$ in 25.0 cc. of chloroform was found to be a non-conductor of the order of conductivity water.

assumed existence of $\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2$ as $[\text{Au} \cdot 2 \text{S}(\text{Bz})_2]^1 \text{AuCl}_4$; therefore, the high molecular weight observed by Herrmann for the orange-colored compound cannot be accounted for on the basis of its presence in chloroform as partially ionized $[\text{Au} \cdot 2 \text{S}(\text{Bz})_2] \text{AuCl}_4$. For the latter phenomenon, however, there is another explanation possible.

Accepting $\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2$ as the structure of the orange-colored compound, with a molecular weight of 482.4, this if combined with 1 molecule of the solvent chloroform⁵ would give a solvate of the molecular weight 601.8, a value in excellent agreement with those observed. Experiments made with crystals obtained from chloroform at various temperatures, from the boiling point of the saturated solution to as low as -10° , in order if possible to obtain the solvate in crystalline form, were negative in their results.

For example, clear, orange-colored needles, freshly crystallized at the ordinary temperature and quickly freed from chloroform between filter papers, were found to weigh 0.3049 g. After 30 minutes on the balance, this weight was still unchanged. Heated at 95° for 15 minutes, and weighed after cooling, the loss was only 0.4 mg.; the crystals were still clear and unchanged in appearance. Upon ignition, they yielded 0.1240 g. of gold, or 40.66% (calc. for $\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2$: 40.80; for $\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2 \cdot \text{CHCl}_3$: 32.77).

Although it was not possible to obtain the solvate in solid form, this simply indicates that, if present in the chloroform solution, its solubility is not exceeded as soon as that of the unsolvated compound; it offers no proof that the solvate is not the form mainly present at the boiling temperature in dil. chloroform solutions. On the other hand, the excellent agreement between the molecular weight as observed by Herrmann⁶ at several low concentrations, and the theoretical molecular weight of the solvate containing one molecule of chloroform, as well as the known existence of the chloroform solvate of $\text{Cl}_2\text{Pt} \cdot 2\text{S}(\text{Bz})_2$ previously referred to in Ref. 5, would seem to justify the conclusion that this solvate actually predominates in the boiling chloroform solution.

Compounds Containing Bromine or Iodine.—In the course of the foregoing work, it seemed desirable to prepare and study the corresponding bromine and iodine compounds, which were at that time unknown. Although the new compounds obtained have thrown but little additional

⁵ Several compounds of this nature are described in the literature; such as $\text{Cl}_2\text{Pt} \cdot 2\text{S}(\text{Bz})_2 + \text{CHCl}_3$, Blomstrand, *J. prakt. Chem.*, [2] **38**, 521f (1888).

⁶ The following are the data obtained by Herrmann (Ref. 1).

Solvent G.	Subs. G.	B. p. elev. ° C.	Obs. mol. wt.	
21.83	0.1550	0.042	607	Calc. for $\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2$, 482.4; for
21.83	0.2544	0.069	608	$\text{Cl}_2\text{Au} \cdot \text{S}(\text{Bz})_2 \cdot \text{CHCl}_3$, 601.8.
21.83	0.4033	0.110	604	

It should be stated that 0.4033 g. of the solute would require only 0.1000 g. of chloroform to yield the solvate in question, so that it would be unnecessary to take account of this in calculating the molecular weight.

light on the subject, their description will nevertheless not be out of place at this point.

In the preparation of all these compounds, it was found most convenient to start with a solution of chloro-auric acid containing sufficient hydrochloric acid to prevent hydrolysis. This solution was prepared from metallic gold, and was made up to contain 50 mg. of gold per cubic centimeter. Upon shaking a definite volume of this solution with ether and the corresponding hydrogen halide, an ethereal solution of known gold content, of HAuCl_4 , HAuBr_4 , or HAuI_4 , was readily obtained; this could then be treated with the required quantity of benzyl sulfide, also dissolved in ether.⁷

1. $\text{Br}_2\text{Au.S(Bz)}_2$.—In the preparation of this compound, 20 cc. of the chloro-auric acid solution was shaken with 7 cc. of constant-boiling hydrobromic acid and, after 15 minutes, the solution was extracted with ether. In order to remove any residual chlorine, the extract was shaken with 10 cc. of water and 5 cc. of the hydrobromic acid, after which the ethereal solution was treated with 2.0 g. of benzyl sulfide. The dark reddish-brown liquid retained its color after the addition of the benzyl sulfide, and no precipitate was formed, even after 24 hours. It was, therefore, allowed to evaporate spontaneously, and, after draining on filter paper, the residue was dissolved in chloroform and the solution filtered. With the gradual evaporation of the solvent, the compound separated in the form of prismatic crystalline needles of a dark-maroon color.

Analyses. Subs., (I) 0.1029, (II) 0.2245, (III) 0.2183: Au, (I) 0.0343; AgBr, (II) 0.1483; BaSO_4 , (III) 0.0858. Calc. for $\text{Br}_2\text{Au.S(Bz)}_2$: Au, 34.52; Br, 27.98; S, 5.61. Found: Au, 33.33; Br, 28.11; S, 5.40.

As obtained from ether, this preparation had a strong odor resembling that of benzyl bromide; and upon the ignition of the recrystallized (odorless) substance there was a marked evolution of "tear gas." A sample of the raw product, when washed with alcohol, then with conc. hydrobromic acid and again with alcohol, and dried in air, was found under the microscope to consist of clusters of homogeneous maroon-colored, clean-cut needles. Upon ignition, they also yielded "tear gas," and were found to contain 34.2% of gold.

2. BrAu.S(Bz)_2 .—This compound could not be obtained by the reduction of the higher bromide by means of benzyl sulfide, even when the latter was employed in large excess. It was, however, successfully prepared by heating $\text{Br}_2\text{Au.S(Bz)}_2$ with alcohol, from which it crystallized in long, colorless, transparent needles. The substance is practically insoluble in ether; when dissolved in alcohol and poured into boiling water

⁷ Preparation of the Compounds Containing Chlorine.—Thirty cc. of the chloro-auric acid was treated with a little conc. hydrochloric acid, and the gold extracted with ether. (a) The ethereal extract was treated with 2.44 g. of benzyl sulfide, and, after 1 hour, the orange-red crystals were filtered off with suction, washed with ether, and dried between filter paper sheets; yield, 3.3 g. of $\text{Cl}_2\text{Au.S(Bz)}_2$. Or, (b) the ethereal extract was treated with 3.26 g. of benzyl sulfide. An orange-red precipitate was formed, but upon evaporating off the ether on the water-bath, and heating the residue with 60 cc. of alcohol, a white crystalline deposit was obtained from the solution upon evaporation. This was dissolved in a little hot chloroform, filtered, and precipitated by means of several volumes of ether. The crystals were filtered off, washed with ether and allowed to dry; yield, 2.7 g. of ClAu.S(Bz)_2 .

Numerous samples of both compounds were analyzed for gold, with results in excellent agreement with the formulas of Herrmann.

it yields a blue solution of colloidal gold. Like the higher bromide, it yields "tear gas" upon ignition.

Analyses. Subs., 0.0980: Au, 0.0391. Calc. for BrAu.S(Bz)_2 : Au, 40.14. Found: 39.90.

3. $\text{I}_2\text{Au.S(Bz)}_2$.—Twenty cc. of the chloro-auric acid solution was shaken with 10 cc. of constant-boiling hydriodic acid and after 15 minutes the mixture was extracted with ether. The extract was again shaken with 15 cc. of 1:2 hydriodic acid after which it was separated and treated with 2.0 g. of benzyl sulfide. The liquid remained very dark reddish-brown, almost black, and yielded no precipitate. The next day, after filtration, the liquid was allowed to evaporate slowly. There remained an oily, black liquid, which partially crystallized upon stirring. The mixture was washed twice with small portions of ether, after which the crystals were spread upon several thicknesses of filter paper, and allowed to dry.

Analyses. Subs., (I) 0.6432, (II) 0.5081, (III) 0.4235: Au (I) 0.1824; AgI (II) 0.3708; BaSO_4 , 0.1456. Calc. for $\text{I}_2\text{AuS(Bz)}_2$: Au, 29.64; I, 38.15; S, 4.82. Found: Au, 28.36; I, 39.45; S, 4.72.

Under the microscope this compound appeared to consist of thick, almost black needles. When treated with organic solvents, especially upon heating, it is decomposed into benzyl sulfide, iodine, and lemon-yellow aurous iodide, the latter remaining as an insoluble residue, though it may even be reduced to metallic gold. Like $\text{Br}_2\text{Au.S(Bz)}_2$, this substance is not reduced to the aurous compound by benzyl sulfide; in fact, it was successfully recrystallized from hot alcoholic solution in the presence of a very large excess of benzyl sulfide. Thus obtained, it consisted of black prismatic needles which were found to contain 29.67% of gold. All attempts to obtain the compound, IAu.S(Bz)_2 , met with failure.

4. ClIAu.S(Bz)_2 .—In describing the action of bromine upon $\text{Cl}_2\text{Au.S(Bz)}_2$, Herrmann referred to the isolation of a compound, ClBrAu.S(Bz)_2 , and in that connection the following is worthy of note. After the unsuccessful attempts which have already been described, to isolate a chloroform solvate of $\text{Cl}_2\text{Au.S(Bz)}_2$, it occurred to the writer that perhaps better success might be met with in the case of iodoform. The following experiment was therefore performed, but it led only to the discovery of the compound ClIAu.S(Bz)_2 ; this product resulted, probably, from the action of iodine upon $\text{Cl}_2\text{Au.S(Bz)}_2$, the iodine being set free from the dissolved iodoform.

An ethereal solution of 1.03 g. of $\text{HAuCl}_{4.4} \text{H}_2\text{O}$ was treated with 0.81 g. of Bz_2S and 0.84 g. of iodoform, both dissolved in ether. Precipitation took place, and the following fractions were separated: (1) precipitate formed in the first 15 minutes; (2) precipitate formed in the next 30 minutes; (3) precipitate formed upon evaporating the residual solution to 30 cc. on the water-bath; (4) solid obtained by allowing the filtrate from (3) to evaporate overnight, extracting the dry mass with ether, and filtering off the residue. All 4 samples were washed with ether, and allowed to dry.

To the naked eye, Sample 4 was coarser, and distinctly darker in color than the first 3 samples; under the microscope, it could not be distinguished from a sample of pure, recrystallized $\text{Cl}_2\text{Au.S(Bz)}_2$, with which it was compared. Nevertheless, it was found on analysis to consist of fairly pure ClIAu.S(Bz)_2 .

Analyses. Subs., Sample I, 0.0387; Sample 2 (not analyzed); Sample 3, 0.1399; Sample 4a, 0.2552; Sample 4b, 0.1178: Au, (1) 0.0157 (40.57%), (3) 0.0567 (40.53%), (4a) 0.0886 (34.71%); Au(ClI), (4b) 0.0744 (27.12% Cl + I).

Sample 4, therefore, was ClIAu.S(Bz)_2 , for which the calculated values are gold, 34.36%, and halogens, 28.30%. The ethereal washings from Sample 4 (see above) were very dark, and appeared to contain some $\text{I}_2\text{Au.S(Bz)}_2$. Upon allowing them to evaporate and then extracting with chloroform, a small quantity of aurous iodide remained as a residue.

Summary

1. The two compounds which separate in the interaction of auric chloride and benzyl sulfide are addition compounds of gold monochloride and gold dichloride, respectively, with benzyl sulfide. They are conjugate compounds, probably constituted as shown in the formulas, $[\text{ClAu}\dots\text{S}(\text{Bz})_2]$ and $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Au}\dots\text{S}(\text{Bz})_2 \\ \diagup \\ \text{Cl} \end{array} \right]$.

2. Unlike the platinous chloride addition products, $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{Pt} \\ \diagup \\ \text{Cl} \end{array} \right] \cdot \begin{array}{c} \text{SR}_2 \\ \text{SR}_2 \end{array}$

which add additional molecules of the organic sulfides to form interpolation compounds, as $[\text{Pt}.4\text{SR}_2]\text{Cl}_2$, the conjugate compounds of benzyl sulfide with gold monochloride and gold dichloride appear to be incapable of yielding interpolation compounds by the further addition of benzyl sulfide.

3. Dichloro-gold-benzyl sulfide probably exists in chloroform solution as a solvate of the formula $\text{Cl}_2\text{Au}\cdot\text{S}(\text{Bz})_2\cdot\text{CHCl}_3$.

4. The following new compounds have been prepared and described: $[\text{Br}_2\text{Au}\cdot\text{S}(\text{Bz})_2]$, $[\text{BrAu}\cdot\text{S}(\text{Bz})_2]$, $[\text{I}_2\text{Au}\cdot\text{S}(\text{Bz})_2]$ and $\left[\begin{array}{c} \text{Cl} \\ \diagdown \\ \text{I} \\ \diagup \\ \text{Au}\cdot\text{S}(\text{Bz})_2 \end{array} \right]$.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY,
UNITED STATES DEPARTMENT OF AGRICULTURE, No. 61]

THE PREPARATION OF 6,6'-DI(ALPHA-HYDROXYISOPROPYL) INDIGO FROM PARA-CYMENE

By MAX PHILLIPS

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Since the elucidation of the constitutional formula of indigo by Adolf Baeyer, a number of investigators have been engaged in the preparation of alkyl and other derivatives¹ of this substance. The method usually followed consists in making use of one of the several syntheses of indigo and substituting for the usual indigo-yielding intermediate, one that already contains the particular group or groups that it is desired to introduce in the indigo molecule. From a study of the literature, it became apparent that no indigo derivative containing the *isopropyl* group had hitherto been prepared, and inasmuch as this laboratory has for some time been engaged in carrying on some investigations on *p*-cymene, the chief constituent of so-called spruce turpentine, the possibility of preparing an indigoid dye from this hydrocarbon suggested itself. The method followed in the synthesis of this dye may be represented as follows.

¹ *Ber.*, 16, 817, 2201 (1883); 23, 59 (1890); 24, 693 (1891); 25, Ref. 488 (1892); 45, 2074 (1912). *Ger. pat.*, 61,171. *Am. Chem. J.*, 27, 1 (1902).