

The Relation of Alkaloidal Chemistry to Inorganic, and the Use of Bromauric Acid as a Reagent for Inorganic Microcrystal Tests*

By Charles C. Fulton†

RELATIONSHIPS

The so-called "alkaloidal reagents" are really amine precipitants, and precipitate other complex amines as readily as the alkaloids. Simple amines are precipitated by the more general of these reagents. Ammonium, even, is precipitated by some of them.

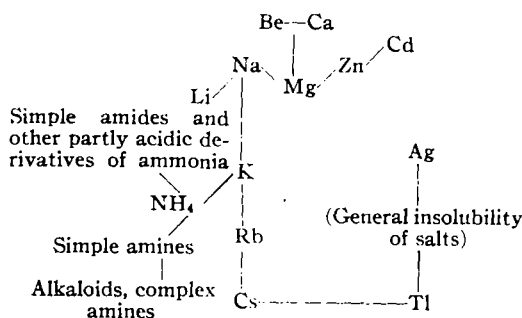
On the inorganic side, ammonium is very closely related to potassium, the latter showing almost the same solubilities of salts. Potassium in turn is related to the heavier alkali metals, rubidium and caesium, and to the lighter, sodium and lithium. Rubidium is precipitated by about a third or more of the "alkaloidal reagents"—some 200 formulas, utilizing at least 75 different compounds as precipitating agents—and caesium is precipitated by most of them. Thallium (univalent) is related to caesium and is also precipitated by these reagents, but here we get into a general insolubility of most salts, as with silver.

Although sodium is closely related to potassium in most respects, there is quite a gap between them in the properties we are now considering. In fact, practically speaking, sodium is not precipitated by any of the "alkaloidal reagents" from aqueous solutions. However, the writer (1) has previously shown that the amine compounds reach an extreme insolubility in syrupy phosphoric acid; and this is true also of the inorganic precipitates. In a test drop of this acid, not only sodium, but also lithium, magnesium, zinc and cadmium are precipitated in a few compounds, and in particular as bromaurates. (Paradoxically, lithium is even more readily precipitated as bromaurate than sodium, and magnesium more readily than zinc or cadmium.) With a high

concentration of the precipitating compound, bromaurate crystals can also sometimes be obtained with calcium and beryllium.

Not all the elements or metals have been investigated, by any means, but apparently the further we get away from the heavy alkali metals the more difficult it is to get bromaurates or any of the other insoluble compounds characteristic of "alkaloidal" precipitation.

The relationships mentioned above are indicated in the accompanying diagram:



BROMAURIC ACID

Bromauric acid, or "gold bromide," HAuBr_4 , is very sensitive to most alkaloids, but is not as general a precipitant in aqueous solution as the complex oxygen acids and some other reagents. It does not precipitate ammonium from water. In syrupy phosphoric acid, however, it becomes virtually a reagent for basic nitrogen, even in compounds predominately acidic. The acid acts not only to decrease the solubility of the compounds formed, but also to suppress any acidic characteristics in the substances tested. The greatest value of such a reagent is, naturally, not with alkaloids which can be precipitated by a host of other reagents, but with the simpler amines, and amine derivatives that are partly acidic; *e. g.*, amides, amino acids and other organic acids which contain nitrogen with some residual basic properties.

* From the Alcohol Tax Unit Laboratory, U. S. Treasury Department, Saint Paul, Minn.

† Present Address: Alcohol Tax Unit Laboratory, U. S. Treasury Department, 727 Post Office Building, Chicago, Ill.

Likewise in inorganic chemistry the value of HAuBr_4 in H_3PO_4 is greatest in the micro-crystal tests it gives for lithium, sodium, magnesium and zinc. Common as sodium and magnesium are, good tests for them are not plentiful, so the value of this reagent is all the greater.

For the more easily precipitated alkali metals, and ammonium, diluted phosphoric or sulfuric acid can be used as solvents for HAuBr_4 , giving reagents with different properties.

The tests of this article are made by adding a drop of the reagent directly to a little of some powdered salt of the metal or base to be identified. A cover glass is applied and examination made under the microscope. The bromaurates are easily distinguished by their colors from any particles of the original salt remaining undissolved, or other crystals that may possibly form. In most cases the characteristic crystals form quickly.

The acid radical with which the base is combined has considerable effect on the result. Trials have been made chiefly on the chlorides, sulfates and primary phosphates. In general the sulfates may be considered to give "normal" precipitation. Phosphate as the acidic constituent of the salt will increase the sensitivity of the test, while chloride will make it considerably less sensitive. Acetate also decreases the sensitivity of the test. Bromides are similar to chlorides. Salts such as iodides, which react at once with the reagent, cannot be used. Nitrates soon react with the reagent made with syrupy H_3PO_4 , but can be used at least with the weaker reagents. Bisulfates and secondary and tertiary phosphates can be used. The lesser sensitivity of chlorides and bromides as compared to sulfates and phosphates is not a disadvantage in all cases, for if precipitation is still obtained the crystals are usually larger.

For organic identifications over the whole field of compounds of basic nitrogen, a series of "gold bromide" reagents is very desirable, in fact essential. HAuBr_4 in H_3PO_4 has the greatest precipitating power, but is chiefly useful with compounds rather difficult to precipitate. Bromaurates of easily precipitated substances, such as the alkaloids, are usually

too insoluble in H_3PO_4 for good results, do not crystallize readily enough or crystals are too minute. HAuBr_4 in concentrated HCl will probably provide more good micro-crystal tests than any other reagent known. The various "gold bromide" reagents, utilizing H_3PO_4 , diluted H_2SO_4 , HBr , HCl , water and acetic acid, differ not merely in the solubilities of the bromaurates in the test solution, and in the readiness with which crystallization occurs, but also in the actual forms and kinds of crystals produced. The crystals form so readily, with so many different substances, and are so highly characteristic, that a series of 8 or 10 different HAuBr_4 reagents used both on dry substances and on aqueous solutions will probably provide more good microcrystal tests for all kinds of compounds of basic nitrogen than any equal number of other reagents, utilizing other precipitating compounds.

A series of different "gold bromide" reagents can be used in inorganic chemistry also, as described below. However, HAuBr_4 in syrupy H_3PO_4 is the outstanding reagent. The reagents can be applied to aqueous solutions for inorganic chemistry also, and the heavier alkali metals and ammonium can be so precipitated, but not the lighter metals. The latter require strong phosphoric acid for the test drop. In some cases the compound might first be dissolved in syrupy phosphoric acid and the reagent applied; but a fairly high concentration of both base and HAuBr_4 is required, and is best obtained in localized spots by applying the reagent to a little of the dry salt.

The tests have a limited applicability to mixtures. A reactive base can be identified in the presence of material with which the reagent does not react. If two reactive bases are present a reagent can often be chosen which will affect only the one more easily precipitated.

Most of the tests are fairly sensitive, but they are intended for identification, not for the detection of minute amounts. They belong to that class of tests covered by Chamot and Mason in their "Handbook of Chemical Microscopy" (2), except that the large majority of current tests depend on the mixing of two aqueous solutions.

BROMAURIC ACID IN SYRUPY PHOSPHORIC ACID
(HAuBr_4 IN H_3PO_4)

Gold chloride crystals ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)	1 Gm.
HBr (40%)	1.5 cc.
Water	1.0 cc.
Syrupy (85%) H_3PO_4	To make 20 cc.

The formula for this reagent was originally given (1) without the 1 cc. of water. It is then saturated with HAuBr_4 , with some undissolved crystals, as this compound itself is not highly soluble in syrupy H_3PO_4 . It has been found much better to use just enough water to hold all the HAuBr_4 in solution. The reagent can be made with $\text{AuBr}_3 + \text{HBr}$, or with HAuBr_4 crystals, both of which are commercially obtainable; but since "gold chloride" (chlorauric acid) is the most commonly used gold salt, and seems to work just as well, it is used to make the reagent.

Uses.—Identifying magnesium, zinc, cadmium, sodium, lithium, potassium, ammonium, rubidium, caesium and innumerable organic compounds of nitrogen of slight basic properties.

CRYSTALS

Magnesium.—Beautiful crystals, orange to deep red hexagonal plates, are obtained from the chloride, either $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or dried MgCl_2 , and from the phosphate, $\text{MgH}_2(\text{PO}_4)_2$ (Fig. 1). Good crystals are

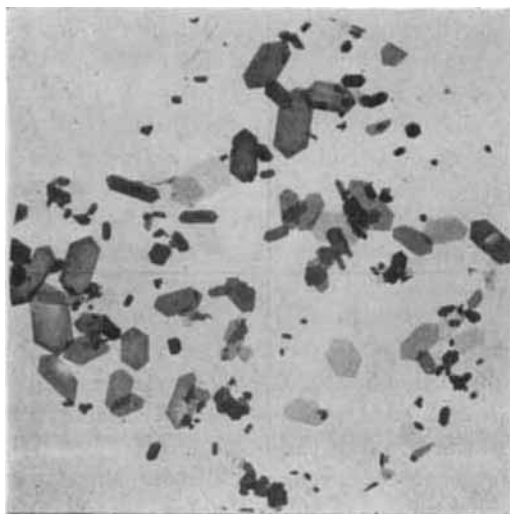


Fig. 1.—Magnesium bromaurate (magnesium gold bromide). Obtained with HAuBr_4 in syrupy H_3PO_4 , and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Photomicrograph by John B. Dalton, Police Department, St. Paul, Minn.

also obtained from the nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, before decomposition sets in. The sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, yields smaller and more numerous crystals.

Zinc.—The sulfate gives crystals related to those of magnesium, but lighter, more yellow-orange in color and mostly diamond-shaped, rather than hexagonal, when first formed. The crystals from the phosphate are very small, minute orange grains, or diamond-shaped or hexagonal platelets. They are better if the H_3PO_4 is a little diluted with water. The chloride and acetate cannot be depended on to yield any crystals.

Cadmium.—The sulfate and phosphate yield small brown-red plates, on or very close to the undissolved particles.

Sodium.—The sulfate, Na_2SO_4 , and the phosphate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, yield crystals readily, orange splinters or thin rods at first, tending to become thin brownish yellow prisms (Fig. 2). These crystals have a fairly well-marked dichroism with polarized light. They are just obtained from the bromide or acetate, and cannot be obtained at all from the chloride with this strength of reagent, but one more concentrated in HAuBr_4 will give them.

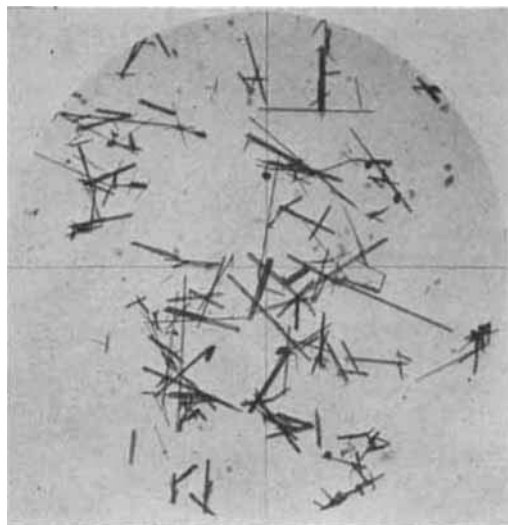


Fig. 2.—Sodium bromaurate (sodium gold bromide). Obtained with HAuBr_4 in syrupy H_3PO_4 , and Na_2SO_4 . Photomicrograph by John B. Dalton, Police Department, St. Paul, Minn.

Lithium.—The crystals are similar to those of sodium, but are best obtained from the chloride. The sulfate and phosphate do

not dissolve readily in the reagent, but the crystals soon form around the undissolved material.

Potassium.—There are several different forms of crystals, but the precipitate is characterized by small, deep red, rectangular grains. The crystals are somewhat larger with the chloride than with the sulfate or phosphate, but any convenient salt can be used.

Ammonium.—There are several different forms of crystals, the precipitate being characterized by orange spearhead and diamond-shaped plates. The chloride gives larger crystals than the sulfate or phosphate. Any convenient salt can be used.

Rubidium.—The crystals resemble those with ammonium.

Cæsium.—There is an opaque red precipitate, amorphous or too minutely crystalline for the shape of the crystals to be distinguished. Gradually fairly large, elongate, yellow-orange plates grow out from the amorphous masses. Also small to minute diamond-shaped plates, orange-yellow, form around the edges of the amorphous precipitate.

A SERIES OF "GOLD BROMIDE" REAGENTS

1. Concentrated HAuBr_4 in H_3PO_4 .

AuBr ₃	1 Gm.
HBr (40%)	0.4 cc.
Water	0.6 cc.
Syrupy H_3PO_4	
To make	7.5 cc.

See that the AuBr_3 is in solution before adding the H_3PO_4 . The water should be just enough to hold the HAuBr_4 in solution.

- HAuBr_4 in H_3PO_4 (see p. 179).
- HAuBr_4 in (3 + 1) H_3PO_4 .

HAuCl_4 crystals	1 Gm.
HBr (40%)	1.5 cc.
Diluted H_3PO_4	
(3 vols. syrupy H_3PO_4 to 1 vol. water)	
To make	20 cc.

4. HAuBr_4 in (1 + 1) H_3PO_4 . "Potassium reagent." Like the preceding, but using more dilute H_3PO_4 (equal vols. syrupy H_3PO_4 and water).

5. HAuBr_4 in (2 + 3) H_2SO_4 . "Ammonium reagent."

HAuCl_4 crystals	1 Gm.
HBr (40%)	1.5 cc.
Diluted H_2SO_4	
(2 vols. conc. H_2SO_4 to 3 vols. water)	
To make	25 cc.

6. HAuBr_4 in HBr. "Amine reagent."

HAuCl_4 crystals	1 Gm.
Water	2.65 cc.
HBr (40%)	24 cc.

If kept well stoppered these reagents are, so far as known, entirely permanent. The series might be extended even further for organic chemistry.

The first of the foregoing reagents gives the limit of the range of precipitation by HAuBr_4 . Thus in determining if there is any very slight tendency toward the formation of a bromaurate, it must sometimes be used instead of the usual HAuBr_4 in H_3PO_4 , No. 2. Its disadvantages, however, are greater cost and the much deeper color of the solution. The colors of the crystals, which are often very characteristic, are not easily seen when the reagent solution is so deeply colored. This reagent, No. 1, gives the sodium crystals with the chloride, and more readily than No. 2 with the bromide, acetate and nitrate. With the nitrate, good sodium bromaurate crystals are formed before decomposition begins; afterward bright red blades are formed in the solution around the outside of the area of decomposition. The zinc crystals with the sulfate are bright red hexagonal plates, resembling the magnesium crystals much more closely than with reagent No. 2. Zinc chloride gives orange splinter-plates, zinc acetate yields orange-red plates of intermediate type. These crystals are fairly soluble in the reagent as affected by chloride or acetate. Calcium chloride yields some deep red sticks or grains. They can be observed, with a high transmission of light, imbedded in the undissolved material. The bromaurate of beryllium is evidently just about as soluble as that of hydrogen, so that crystals can be obtained only with a high concentration, and then only if the room temperature is not too high. Long orange splinters were obtained with the sulfate. The phosphate of beryllium was not at hand for trial.

The crystals with reagent No. 2 have already been described.

No. 3 no longer gives crystals with magnesium chloride, zinc sulfate or cadmium sulfate or phosphate. The crystals with magnesium sulfate and zinc phosphate are, however, larger and better than with the preceding reagent. Potassium gives slender orange rods at first, gradually also deep red grains and prisms. Rubidium gives good crystals, orange diamond-shaped plates and dark orange sticks, many saw-edged or spear-headed with orange plates.

No. 4, "potassium reagent," is intended to precipitate potassium but not sodium. The distinction is not quite absolute, as in order to leave the reagent sensitive enough to precipitate potassium as chloride, we have to allow for a slight effect on sodium as phosphate. If considerable sodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) is used, some sodium crystals may be found among the undissolved particles. They tend to dissolve in the solution. Na_2SO_4 gives no crystals. The potassium crystals are slender orange rods or rod-plates, and are obtained with the bromide, acetate and nitrate, as well as the chloride, sulfate and phosphate. This reagent no longer yields crystals with magnesium sulfate or lithium chloride or sulfate, or zinc sulfate. It does, however, yield the bromaurates of magnesium and lithium from their phosphates.

No. 5, "ammonium reagent," is intended to precipitate ammonium but not potassium. The chloride and sulfate of potassium give nothing. The phosphate, KH_2PO_4 , gives nothing immediately, even when used in large amount, but on standing for some time orange-red prisms form, mostly small and closely associated with the undissolved particles. Ammonium gives a dimorphous precipitate. With the phosphate and sulfate there are small orange grain-plates, and also larger dark, irregular stick-crystals. With the chloride the crystals are larger, the grain-plates redder and tending to the diamond shape. The precipitate with NH_4Cl is shown in Fig. 3. This reagent is a little more sensitive to magnesium and zinc than the preceding one, and gives crystals with their

phosphates. Sodium and lithium are barely precipitated from their phosphates.

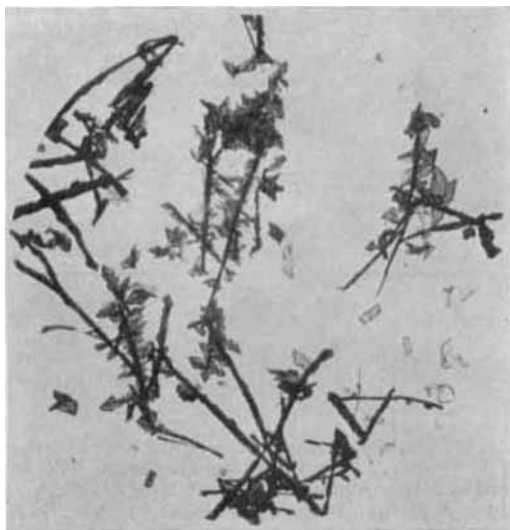


Fig. 3.—Ammonium bromaurate (ammonium gold bromide). Obtained with HAuBr_4 in (2 + 3) H_2SO_4 , and NH_4Cl . Photomicrograph by John B. Dalton, Police Department, St. Paul, Minn.

No. 6, "amine reagent," precipitates methylamine and ethylamine, and all more complex, fully basic amines, but not ammonium, as the chloride. Ammonium sulfate or phosphate will yield a few crystals, orange needles, splinters or rods, near the undissolved material. These tend to dissolve in the solution. Potassium phosphate likewise yields a few orange-red rods or splinters among the undissolved particles. Sodium, lithium, magnesium and zinc yield no crystals. Rubidium gives a characteristic precipitate of small crystals, orange to red: grains, rods, prisms and diamond-shaped plates. Cæsium gives a black precipitate of minute grains or little sticks, sometimes in star formation. The crystals with methylamine and ethylamine are shown in Figs. 4 and 5. Those with methylamine are brown plates, usually square. Crystals in the same field differ markedly in depth of color, although they show no dichroism with polarized light. Those with ethylamine are of two kinds. First are large orange-red, square-cut plates. On standing there develop also large thick grain-plates, mostly hexagonal or coffin-shaped, deep red to nearly black.

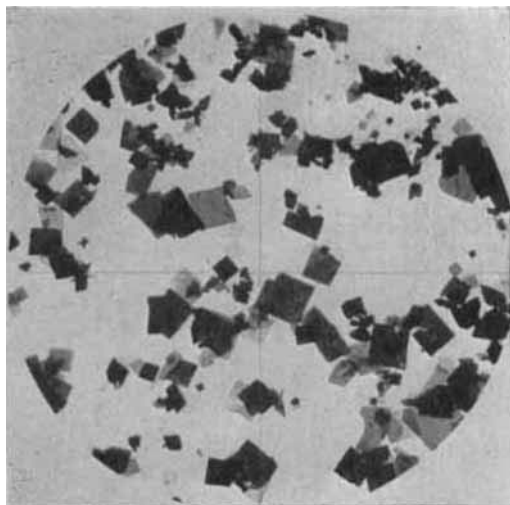


Fig. 4.—Methylamine bromaurate (methylamine gold bromide). Obtained with HAuBr_4 in HBr , and methylamine hydrochloride. Photomicrograph by John B. Dalton, Police Department, St. Paul, Minn.

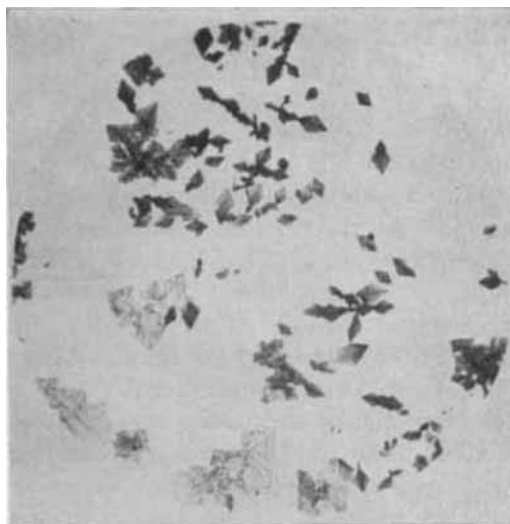


Fig. 5.—Ethylamine bromaurate (ethylamine gold bromide). Obtained with HAuBr_4 in HBr , and ethylamine hydrochloride. Photomicrograph by John B. Dalton, Police Department, St. Paul, Minn. (Note: This photograph was taken with only half the magnification used for the others, in order to get both kinds of ethylamine crystals in the field.)

CONCLUSIONS

1. The chemistry of the alkaloids, as regards precipitation and microcrystal tests,

is closely related to that of rubidium and caesium. Some of the "alkaloidal reagents" also precipitate ammonium and potassium. A few newer reagents, which extend the field covered in organic chemistry to even the simplest and most feebly basic amine derivatives, will precipitate even sodium, lithium, magnesium, zinc and cadmium, at least from syrupy phosphoric acid.

2. Bromauric acid in syrupy phosphoric acid, the most valuable reagent for simple, feebly basic amine derivatives, is also useful in inorganic chemistry for identifying magnesium, zinc, cadmium, sodium, lithium, potassium, ammonium, rubidium and caesium by microcrystal tests. It is applied directly to a little dry salt of the metal, or of ammonium, and is particularly valuable for magnesium and sodium (Figs. 1 and 2).

3. A series of "gold bromide" reagents is of great value for organic chemistry, and may be used for inorganic. HAuBr_4 in $(1 + 1) \text{H}_3\text{PO}_4$ precipitates potassium, but not sodium, except for a few crystals when considerable phosphate is used for the test. Similarly HAuBr_4 in $(2 + 3) \text{H}_2\text{SO}_4$, of the formula given, is a reagent for ammonium but not potassium (Fig. 3). HAuBr_4 in HBr , of the formula given, precipitates rubidium and caesium, and methylamine, ethylamine and all more complex, fully basic amines, but not ammonium from its chloride (Figs. 4 and 5).

4. These tests are intended for identification, not for detection of minute amounts. Broadly speaking, they belong to the class of tests covered by Chamot and Mason in their "Handbook of Chemical Microscopy," Vol. II.

REFERENCES

- (1) Fulton, Charles C., *Am. J. Pharm.*, 112 (1940), 51, 134.
- (2) Chamot, Émile Monnin, and Mason, Clyde Walter, "Handbook of Chemical Microscopy. Volume II, Chemical Methods and Inorganic Qualitative Analysis," John Wiley & Sons, Inc., New York, N. Y., 1931.