

are brought together, no reaction takes place even at elevated temperatures or under strong pressure. Several tubes containing these substances were allowed to stand for a year but at the end of this time no reaction had taken place. The two when heated together in tubes of very heavy glass, which had been obtained for work of this character, would not react, all of the tubes exploding when the temperature was sufficiently raised, but without previously showing any signs of change in the contents. After numerous attempts to bring the two to react the dioxide of selenium was vaporized from a porcelain boat in a glass tube in the vapor of sulphuryl chloride, and was condensed in a cooler portion of the tube. Analysis of the sublimed dioxide showed it to be chlorine-free, thus showing that it is possible to sublime selenium dioxide in the vapor of sulphuryl chloride without any reaction taking place.

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## ON THE MERCURY NITROGEN COMPOUNDS

(THE MERCURIAMMONIUM SALTS AND BASES)

EDWARD C. FRANKLIN

Received Nov. 23, 1906

Notwithstanding the considerable attention which has been given to the study of the mercury nitrogen compounds, widely diverse views are still held concerning their constitution as will be evident from consultation of the dictionaries of chemistry, scarcely any two of which agree in their methods of formulating these compounds. Most frequently, however, they are assumed to be substituted ammonium bases and salts. According to the view of Rammelsberg, which has been followed by Fehling<sup>1</sup> and by Dammer<sup>2</sup> in their classification of the mercury nitrogen compounds, and which in recent years has been defended especially by Pesci<sup>3</sup> and his pupils, and also by Rây,<sup>4</sup> all the mercury ammonia compounds are referred to the one type of mercuriammonium compounds in which the four ammonium hydrogen atoms of an ammonium salt are substituted by two atoms of mercury as indicated, for example, by the formulas,  $\text{Hg}_2\text{NOH}$  and  $\text{Hg}_2\text{NCl}$ , for dimercuriammonium hydroxide and chloride respectively. According to Pesci the salts of dimecuriammonium are especially prone to the formation of hydrates, and to union with ammonium and mercuric compounds to form double and complex salts. In accordance with this theory the well known fusible white precipitate is given the formula,  $\text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl}$ ; the infusible precipitate, the formula,  $\text{Hg}_2\text{NCl} \cdot \text{NH}_4\text{Cl}$ ; the chloride of Millon's base, the

<sup>1</sup> Handwörterb. Chem. (1890) 5, 1091.

<sup>2</sup> Handb. anorg. Chem. (1894) 2.2, 896 and (1903) 4, 630.

<sup>3</sup> Z. anorg. Chem. 21, 361.

<sup>4</sup> Ibid. 33, 193 and J. Chem. Soc. 81, 645.

formula,  $\text{Hg}_2\text{NCl}\cdot\text{H}_2\text{O}$ ; the ammoniated mercuric chloride,  $\text{HgCl}_2\cdot\text{NH}_3$ , the formula,  $\text{Hg}_2\text{NCl}\cdot 2\text{HgCl}_2\cdot 3\text{NH}_4\text{Cl}$ ; and Kane's salt, the formula,  $\text{Hg}_2\text{NNO}_3\cdot 2\text{NH}_4\text{NO}_3\cdot 2\text{H}_2\text{O}$ ; to illustrate by a few of the best known compounds.

According to other views all the mercury nitrogen compounds are formulated as substituted ammonium salts and bases, but differ from the Rammelsberg-Pesci theory in that a considerable number of types is assumed to exist. For example, the above enumerated compounds are in other places<sup>1</sup> found formulated respectively as mercuridiammonium chloride,  $\text{Hg}(\text{NH}_2\text{Cl})_2$ ; as mercuriammonium chloride,  $\text{HgNH}_2\text{Cl}$ ; as oxydimercuriammonium chloride,  $\text{NH}_2(\text{HgOHg})\text{Cl}$ ; as a double salt of mercuridiammonium chloride and mercuric chloride,  $\text{Hg}_2\text{N}_2\text{H}_6\text{Cl}_2\cdot\text{HgCl}_2$ ; and as a hydrated double salt of oxydimercuriammonium nitrate and ammonium nitrate,  $\text{NH}_2(\text{HgOHg})\text{NO}_3\cdot 2\text{NH}_4\text{NO}_3\cdot\text{H}_2\text{O}$ .

According to still other views<sup>2</sup> the compounds of the type of the fusible and infusible white precipitates are removed from the category of substituted ammonium salts and are formulated respectively as mercury amines and amidomercuric compounds, leaving the salts of Millon's base and related compounds to be formulated in accordance with the theory that they are substituted ammonium salts.

It has been proposed by the writer<sup>3</sup> to reject the substituted ammonium theory entirely as applied to the so-called mercuriammonium compounds and to substitute therefor a modified and extended form of Kane's old amide theory. Accordingly the attempt is made here to show that many of these substances are, in fact, compounds related to ammonia as the ordinary basic salts are related to water, they are ammonobasic salts; others are compounds which are basic at the same time to both ammonia and water, they are mixed ammonobasic-hydrobasic salts; while still others are simply mercuric salts with ammonia of crystallization.

#### THE AMMONIA SYSTEM OF ACIDS, BASES AND SALTS.

In earlier papers Franklin and Kraus<sup>4</sup> have called attention to the striking properties of liquid ammonia as a solvent. Next to water, it has been found to possess the widest solvent power of any liquid so far investigated. In its tendency to unite with salts and other compounds, it probably exceeds water, since salts with ammonia of crystallization are, perhaps, even more numerous recorded in the literature than are salts with water of crystallization. It is conspicuous for the facility with which

<sup>1</sup> Gmelin-Kraut: Handb. anorg. Chem. (1875) 3, 818-840. Watts: Dict. Chem. (1892) 3, 206-212. Ladenburg; Handwörterb. Chem. (1892) 10, 148-164.

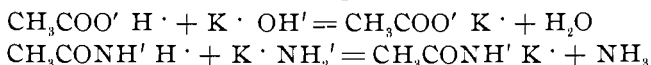
<sup>2</sup> Abegg: Handb. anorg. Chem. 2.2, 666. Cf. Gmelin-Kraut: Watts: Ladenburg: l. c.

<sup>3</sup> This Journal, 27, 827.

<sup>4</sup> Am. Chem. J. 20, 820; 21, 8; 23, 277; and this Journal, 27, 191.

many of its solutions carry the electric current, and especially to be noted is the fact that in its general, chemical and physical properties it shows a striking resemblance to water.

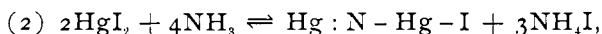
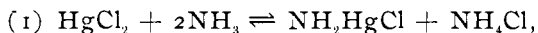
*Ammono acids, Ammono bases and Ammono salts.* Following up the analogies between water and ammonia indicated in the papers above cited, Franklin and Stafford<sup>1</sup> were able to show that the acid amides and the metallic amides, which are formally related to ammonia, as the ordinary acids and bases, respectively, are related to water, as a matter of fact act toward each other, in solution in liquid ammonia, in a manner strictly analogous to the familiar interaction of acids and bases in aqueous solutions. This relation is shown in the equations,



for the water and ammonia systems, respectively.

In a later paper by the writer,<sup>2</sup> the ammonia system of acids, bases and salts was further elaborated, and the proposal was made to refer to the acids, bases and salts of the ammonia system, that is, to the acid amides, the metallic amides, and to the metallic derivatives of the acid amides respectively, as *ammono acids*, *ammono bases* and *ammono salts*.

*Ammonobasic Salts.* In the paper last cited, the writer has shown that ammonia acts upon certain metallic salts in a manner analogous to the familiar hydrolytic action of water. The compounds thus formed are related to ammonia exactly as the ordinary or "hydrobasic" salts are related to water, for which reason the writer has ventured to refer to such compounds as *ammonobasic salts*, and to use the adjective *ammonolytic* to describe the action whereby they are produced. It has been shown, for example, that the reversible equations,



represent what takes place when the salts indicated are treated with liquid ammonia. The salts are ammonolyzed by the solvent, giving insoluble ammonobasic salts and setting free the respective halogen acids in the form of their ammonium salts.

*Ammonobasic Mercuric Salts.* Now it happens that most ammono bases, ammono salts and ammonobasic salts, for example potassium amide,  $\text{KNH}_2$ , magnesium acetamide,  $(\text{CH}_3\text{CONH})_2\text{Mg} \cdot 4\text{NH}_3$ , and the ammonobasic lead iodide,  $\text{NH}_2\text{PbNH}_2\text{PbI}$ , are completely hydrolyzed in the presence of water, from which it follows that such compounds, in general, can be formed only from ammonia solutions, or in any event, only

<sup>1</sup> Am. Chem. J. 28, 83.

<sup>2</sup> This Journal, 27, 820.

in the presence of solvents other than water. The compounds formed by the action of ammonia on mercuric oxide or on the salts of mercury, are, however, an exception to this rule. They are capable of existence in the presence of water, and, as a consequence, many ammonobasic mercuric compounds have been made in the past and are found described in the literature under various names, for the most part, however, as mercuri-ammonium compounds.

*Mixed Ammonobasic-Hydrobasic Mercuric Salts.* In addition to their undergoing ammonolysis, mercuric salts, generally speaking, are also susceptible to hydrolysis. The halogen salts, excepting the fluoride, and the ammono salts are but slightly hydrolyzed, while the hydro salts are highly hydrolyzed in aqueous solution. In a mixture of water and ammonia, in addition to the ammonolytic action of the ammonia, the normal hydrolytic action of the water is accentuated by the increased concentration of the hydroxyl ions, due to the presence of ammonium hydroxide. We might therefore expect the formation of products which are at the same time basic both to water and ammonia, and as a matter of fact this class of compounds is very numerous among the known mercury nitrogen compounds.

#### THE PRECIPITATES AND THE CHLORIDE OF MILLON'S BASE.

The fusible white precipitate is mercuric chloride with ammonia of crystallization,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ ; the infusible precipitate is an ammonobasic mercuric chloride,  $\text{NH}_2\text{-Hg-Cl}$ ; and the chloride of Millon's base is a mixed hydrobasic-ammonobasic mercuric chloride,  $\text{HO-Hg-NH-Cl}$ , or  $\text{NH}_2\text{-Hg-O-Hg-Cl}$ .

These formulas are in accord with the ideas held over sixty years ago by Kane,<sup>1</sup> concerning the constitution of the compounds under consideration, for he clearly points out the fact that the fusible white precipitate is one of a large number of compounds, in which ammonia plays a part analogous to that of water in salts containing water of crystallization; he recognized that the infusible white precipitate is a compound, related to ammonia as an ordinary basic salt is related to water, and he also observed that the yellow salts, later known as salts of Millon's base, are compounds resembling basic salts.

Although for many years Kane's theories have been entirely ignored, his method of formulating the white precipitates has nevertheless been followed to a greater or less extent since the promulgation of his views. Especially has his formula for the infusible white precipitate been emphasized in recent years by Hofmann and Marburg<sup>2</sup> and by Fürth<sup>3</sup> who

<sup>1</sup> Ann. chim. phys. 72, 337.

<sup>2</sup> Ann. 305, 194; Z. anorg. Chem. 23, 126.

<sup>3</sup> Monatsh. 23, 1147.

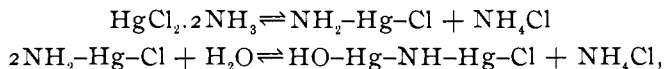
give conclusive evidence of the correctness of Kane's formula and of the inadequacy of the Rammelsberg-Pesci formula.<sup>1</sup>

The writer's view of the constitution of the white precipitates and the chloride of Millon's base is certainly justified by their methods of preparation, by their general properties, and by the manner in which they are mutually converted into each other.

The fusible white precipitate is formed by the direct addition of ammonia to mercuric chloride when the latter is treated with liquid ammonia. In the presence of an excess of the liquid, ammonolysis takes place resulting in the conversion of a small portion of the salt into the infusible precipitate, the quantity of which may be increased at pleasure by the addition of an alkaline amide. Inversely the infusible precipitate is converted into the normal salt by the action of a liquid ammonia solution of ammonium chloride.<sup>2</sup>

Entirely similar changes take place in aqueous ammonia solutions, excepting that here, as the concentration of the ammonium chloride becomes very small, the hydrolytic action of the water is superimposed upon the ammonolytic action of the ammonia. Various investigators have repeatedly observed that the fusible white precipitate is stable only in the presence of a considerable concentration of ammonium chloride, that when it is washed with water it is converted first into the infusible white precipitate and finally, after long washing, into the chloride of Millon's base. Contrarywise, by digestion with ammonium chloride solution the latter compound is changed first into the infusible white precipitate and then into the fusible precipitate.

The action of water on the white precipitates, and the inverse action of ammonium chloride solution on the chloride of Millon's base and on the infusible precipitate, which are represented by the equations,



are therefore phenomena which are very like the formation of ordinary basic salts by the action of water on normal salts, and the reconversion of the former into the latter by an excess of acid.<sup>3</sup>

<sup>1</sup> Cf. however, Pesci: *Z. anorg. Chem.* 21, 361.

<sup>2</sup> Franklin: *This Journal* 27, 841.

<sup>3</sup> It has been shown that in liquid ammonia solutions ammonium salts exhibit a behavior which in many respects is very similar to the action of acids in aqueous solution. (Franklin: *this Journal*, 27, 822.) It is not surprising therefore that in certain cases a similar action should take place in aqueous solutions. In addition to the above described reactions, the well known solubility of zinc and magnesium and of certain metallic hydroxides in aqueous solutions of ammonium salts, the hydroxides of magnesium and calcium, for example, may be mentioned as illustrative of the acid properties of such solutions.

A study of the above equations in accordance with the principles of the Phase Rule, as first suggested for the identification of ordinary basic salts, by Miller and Kenrick,<sup>1</sup> and applied by Allen<sup>2</sup> and by Cox,<sup>3</sup> was begun in this laboratory but unfortunately has been interrupted for the time being by the recent earthquake. The work so far has shown that the two compounds  $\text{HgCl}_2 \cdot 2\text{NH}_3$  and  $\text{NH}_2\text{-Hg-Cl}$  are mutually in equilibrium with a 0.49 normal aqueous solution of ammonium chloride. All that can be said at the present time concerning the concentration of ammonium chloride in the second equation is that it is very much lower than in the first equation.

Among the characteristic properties of ordinary basic salts are their insolubility, their generally amorphous character, and their tendency to form mixtures of indefinite composition.

Similarly the infusible white precipitate, the chloride of Millon's base, and the mercury nitrogen preparations classified in the later pages of this paper have been obtained generally as insoluble, amorphous precipitates, while in the manner in which various obviously complex mixtures of the mercury nitrogen compounds have been reported as chemical individuals, the analogy between the latter and the ordinary basic salts is further exemplified.

#### MILLON'S BASE AND ITS DEHYDRATION PRODUCTS

The so-called Millon's base,  $\text{Hg}_2\text{NH}_5\text{O}_2$ , has been prepared and studied by numerous investigators,<sup>4</sup> and has been represented by no less than seven different formulas<sup>5</sup> depending upon the view intended to be expressed concerning its constitution. Generally, however, the base and its dehydration products have been formulated as substituted ammonium hydroxides.

In accordance with the view of the writer Millon's base and its dehydration products are best accounted for by assuming them to be mixed ammonia water bases; that is they are compounds which are basic at the same time to both ammonia and water. The amorphous character of these bases and their insolubility are in harmony with this assumption concerning their constitution as is also their behavior toward acids. As dilute acids convert certain of the hydro bases into hydrobasic salts while more concentrated acid solutions change them into neutral salts, so also do acids<sup>6</sup> or ammonium salts, depending upon the concentration,

<sup>1</sup> J. phys. Chem. 7, 259.

<sup>2</sup> Am. Chem. J. 25, 307.

<sup>3</sup> Z. anorg. Chem. 40, 146.

<sup>4</sup> Gmelin-Kraut: Handb. anorg. Chem. (1875) 3, 875; Hofmann and Marburg: Ann. 305, 240.

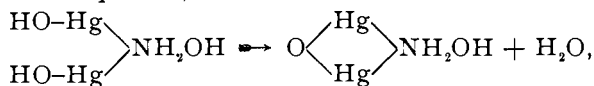
<sup>5</sup> Ladenburg: Handwörterb. Chem. (1892) 10, 156; Hofmann and Marburg: loc. cit. Fürth: Monatsh. 23, 1147.

<sup>6</sup> Nitric acid and sulphuric acid dissolve the salts of Millon's base only in the presence of a small quantity of ammonium chloride. (Pesci: Z. anorg. Chem. 21, 368.)

convert these bases into mixed ammonobasic-hydrobasic salts, into ammonobasic salts or into neutral salts.

As is well known, Millon's base is formed by the action of ammonia on mercuric oxide. It seems worth while to emphasize here the view that the action of ammonia on mercuric oxide is analogous to the ordinary hydration of a metallic oxide to form an hydroxide, and is due in the present instance to the well known tendency of mercury to replace hydrogen in many of the derivatives of ammonia. Just as water, for example, reacts with calcium oxide to form calcium hydroxide, so ammonia, in the absence of water, unites with mercuric oxide to form, not as might perhaps be expected, the mixed hydro ammono base, HO-Hg-NH<sub>2</sub>, but the deammoniated product of this compound, HO-Hg-NH-Hg-OH. In the presence of water a product is formed containing an additional molecule of water, namely, Millon's base. Millon's base is therefore better represented by the formula, HO-Hg-NH-Hg-OH.H<sub>2</sub>O, or perhaps rather by the formula of Hofmann and Marburg, (HOHg)<sub>2</sub>NH<sub>2</sub>OH, or of Fürth, HO-Hg-O-Hg-NH<sub>2</sub>OH, than by any others which have so far been suggested.

Hofmann and Marburg<sup>1</sup> formulate the dehydration of Millon's base in accordance with the equation,

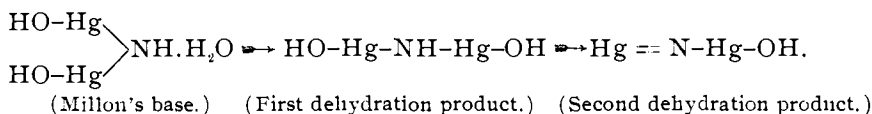


and express the opinion that the basic properties of the compound are due to the ammonium hydroxyl. The writer on the contrary believes that the formula for the dehydration product is rather HO-Hg-NH-Hg-OH, and that in both compounds the basic properties are due, not to the ammonium hydroxyl, but to hydroxyl in combination with mercury. It is a well known fact that the hydroxyl group attached to mercury exhibits strong basic properties while so far as the present writer knows, there is no certainty of the existence of metallic derivatives of ammonium hydroxide from which conclusions can be drawn concerning the strength of such bases. Furthermore in view of the slight ionization of the mercury halogen compounds and the consequent marked tendency of halogen ions to unite with mercury ions, it is difficult to believe that a compound of the formula,  $\text{O} \left\langle \begin{array}{c} \text{Hg} \\ \text{Hg} \end{array} \right\rangle \text{NH}_2\text{Cl}$ , as required by Hofmann and Marburg, rather than one of the formula, HO-Hg-NH-Hg-Cl, would be formed when the base is treated with dilute hydrochloric acid.<sup>2</sup>

<sup>1</sup> Ann. 305, 204.

<sup>2</sup> It must be admitted that the formula, (HOHg)<sub>2</sub>NH<sub>2</sub>OH, while in harmony with the above considerations, nevertheless represents the base as a substituted ammonium hydroxide. Its properties as such, however, are entirely inconspicuous and are subordinate to its properties as a mercury base.

As a mercury base the second dehydration product of Millon's base, which has usually been formulated as dimercuriammonium hydroxide,  $\text{Hg}_2\text{N-OH}$ , can scarcely be otherwise represented than by the formula,  $\text{Hg:N-Hg-OH}$ , while the formulas of either Hofmann and Marburg,  $(\text{HOHg})_2\text{NH}_2\text{OH}$ , or of Fürth,  $\text{HO-Hg-O-Hg-NH}_2\text{OH}$ , for Millon's base and either  $\text{HO-Hg-NH-Hg-OH}$ , or  $\text{HO-Hg-O-Hg-NH}_2$  for the first dehydration product, seem equally applicable. The adoption of the formula,  $\text{Hg:N-Hg-OH}$ , for the second dehydration product, however, permits a choice to be made between the formulas for the other two compounds, from the fact that the mechanism of the dehydration is the more readily explained if the formulas,  $(\text{HOHg})_2\text{NH}_2\text{OH}$  and  $\text{HO-Hg-NH-Hg-OH}$ , are used. The dehydration of Millon's base is therefore represented as follows,



#### MERCURY DERIVATIVES OF THE SUBSTITUTED AMMONIAS.

Hofmann and Marburg<sup>1</sup> have already called attention to the fact that the mercury derivatives of the alkylamines cannot be formulated in accordance with the theory of Rammelsberg and Pesci, and that since such compounds as  $\text{HgCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$  and  $\text{C}_2\text{H}_5\text{NH-Hg-Cl}$ , are obviously the ethylamine analogues of the fusible and infusible white precipitates respectively, it follows that the formulas,  $\text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl}$  and  $\text{Hg}_2\text{NCl} \cdot \text{NH}_4\text{Cl}$ , for the latter compounds must be abandoned. It becomes a matter of importance therefore to enquire whether the properties of the known mercury derivatives of the substituted ammonias, and the methods by which they are prepared are in harmony with the theory made use of in this paper for the systematization of the mercury ammonia compounds. It may be said at once that such is in fact the case. The ethylamine analogue of the fusible white precipitate has been made by the action of ethylamine on a solution of mercuric chloride containing hydrochloric acid<sup>2</sup>; the analogue of the infusible precipitate, by the action of ethylamine on a solution of mercuric chloride in the absence of any excess of hydrochloric acid; while the ethylamine analogue of the chloride of Millon's base has been prepared by adding ethylamine to a solution of mercuric chloride and boiling the precipitate formed with a large excess of water.<sup>3</sup> The conditions necessary for the formation of these three compounds are thus seen to be identical with those which give the three corresponding ammonia derivatives. Below a certain concentration of

<sup>1</sup> Ann. 305, 201.

<sup>2</sup> Hofmann and Marburg: Ann. 305, 202.

<sup>3</sup> Köhler: Ber 12, 2208-2321.



ethylamine hydrochloride the mercuric chloride with ethylamine of crystallization undergoes "aminolysis" to form an "aminobasic" salt, while at high dilution, that is by digestion with much water, simultaneous hydrolysis and "aminolysis" convert the "aminobasic" product into a mixed "hydrobasic-aminobasic" salt. The ethylamine analogues of the white precipitates and of the chloride of Millon's base may therefore be given the formulas,  $\text{HgCl}_2 \cdot 2\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{NH}-\text{Hg}-\text{Cl}$  and  $\text{HO}-\text{Hg}-\text{NC}_2\text{H}_5-\text{Hg}-\text{Cl}$  respectively.

Among other mercury derivatives of the substituted ammonias two of the benzylamine mercury compounds,<sup>1</sup> the sulphate,  $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}-\text{Hg})_2\text{SO}_4$ , and the acetate,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}-\text{Hg}-\text{C}_2\text{H}_3\text{O}_2$ , are especially interesting for the reason that they are oxygen acid salts of the type of the infusible white precipitate, a class which is unrepresented among the known ammonia derivatives.

Many mercuric salts with aniline of crystallization have been prepared as have also the aniline analogues of the infusible white precipitate,  $\text{C}_6\text{H}_5\text{NH}-\text{Hg}-\text{Cl}$ ,<sup>2</sup> and of the chloride of Millon's base,  $\text{HO}-\text{Hg}-\text{C}_6\text{H}_5\text{N}-\text{Hg}-\text{Cl}$ <sup>3</sup>.

The characteristic properties of ammonia and the amines in forming the various mercury compounds as discussed in the preceding pages are exhibited also by other nitrogen compounds. For example, pyridine and quinoline unite with mercury salts as pyridine and quinoline of crystallization<sup>4</sup> but do not form compounds corresponding to the ammonobasic salts; benzamide forms the "amidobasic"<sup>5</sup> iodide,  $\text{C}_6\text{H}_5\text{CONH}-\text{Hg}-\text{I}$ ;

succinimide forms the compound,<sup>6</sup>

$$\begin{array}{c} \text{CH}_2\text{CO} \\ \diagdown \quad \diagup \\ \text{N}-\text{Hg}-\text{Cl} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CO} \end{array}$$

formanilide and

form-*p*-toluide form compounds of the type,<sup>7</sup>

$$\begin{array}{c} \text{CHO} \\ \diagdown \quad \diagup \\ \text{Ar} \quad \text{N}-\text{Hg}-\text{Ac} \end{array}$$

while urea reacts with mercury salts<sup>8</sup> to give such compounds as  $\text{HgCl}_2 \cdot \text{CO}(\text{NH}_2)_2$ , mercuric chloride with urea of crystallization;

<sup>1</sup> Pesci: Z. anorg. Chem. 15, 224.

<sup>2</sup> Forster: Ann. 175, 25.

<sup>3</sup> Fürth: Monatsh. 23, 1157.

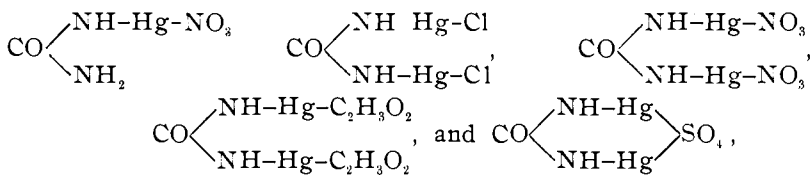
<sup>4</sup> Z. anorg. Chem. 15, 225.

<sup>5</sup> Tafel und Enoch: B. 23, 1554. Bruni and Manuelli, Z. elekt. Chem. 11, 554, have called attention to certain reactions for which they have proposed the name "amidolysis."

<sup>6</sup> Menschutkin: Ann. 162, 172; Ley und Schaefer: Z. physik. Chem. 42, 696.

<sup>7</sup> Wheeler and McFarland: Am. Chem. J. 18, 543.

<sup>8</sup> Ruspaggiari: Jsb. Chem. 1897, 1577; Pesci: Z. anorg. Chem. 15, 232. Ruspaggiari recognizes that these compounds are the urea analogues of the well known mercury ammonia compounds and assumes in accordance with the Rammelsberg-Pesci theory that they are salts of the divalent radical, mercuriurea,  $\text{CO}(\text{NHgH})_2$ .



urea analogues of the infusible white precipitate; and  $\text{CO} \begin{cases} \text{NH-Hg-OH} \\ \text{NH-Hg-OH} \end{cases}$  the urea analogue of Millon's base.

Two other nitrogen compounds, hydroxylamine and hydrazine, unite with mercuric salts as hydroxylamine<sup>1</sup> and hydrazine<sup>2</sup> of crystallization respectively, while it has been observed that under the action of water the chloride of mercury with hydrazine of crystallization gives up hydrazine hydrochloride and is converted into the compound,  $\text{N}_2\text{H}_2\text{Hg}_2\text{Cl}_2$ . ( $\text{Cl-Hg-HNNH-Hg-Cl}$ ), in a manner analogous to the ammonolysis of the fusible white precipitate,  $\text{HgCl}_2 \cdot 2\text{NH}_3$ , to the infusible precipitate,  $\text{NH}_2\text{-Hg-Cl}$ .

#### MERCURY PHOSPHORUS AND MERCURY ARSENIC COMPOUNDS.

Finally certain mercuric phosphorus compounds<sup>3</sup> and mercuric arsenic compounds<sup>4</sup> may be formulated in accordance with the same principles. For example Aschan's compound,  $\text{Hg}_3\text{P}_2 \cdot \text{HgCl}_2$ , is the phosphorus analogue of the ammonobasic chloride,  $\text{Hg:N-Hg-Cl}$ ; and the two compounds,  $4\text{Hg}_3\text{P}_2 \cdot 5\text{HgCl}_2$  and  $3\text{Hg}_3\text{P}_2 \cdot 7\text{HgCl}_2$ , may be formulated respectively as mixtures,  $\text{P}(\text{HgCl})_3 \cdot 7\text{Hg} : \text{P-Hg-Cl}$  and  $\text{P}(\text{HgCl})_3 \cdot \text{Hg} : \text{P-Hg-Cl}$ , while Franceschi's compound,  $\text{AsH}(\text{HgCl})_2$  is the arsenic analogue of the ammonobasic salt,  $\text{NH}(\text{HgCl})_2$ .

#### CLASSIFICATION OF THE MERCURY NITROGEN COMPOUNDS.

In accordance with the theory above outlined the writer proposes in this paper to classify the mercury nitrogen compounds found described in the literature under the following groups and to give under each compound such brief data concerning its preparation and properties as are necessary to show that, without exception, all the compounds which have been prepared are readily to be brought into this scheme of classification.

- I. AMMONO BASES AND MIXED HYDRO AMMONO BASES
- II. MERCURIC SALTS WITH AMMONIA OF CRYSTALLIZATION AND WITH AMMONIA AND WATER OF CRYSTALLIZATION.
- III. AMMONOBASIC MERCURIC SALTS, which include the ammonobasic halogen salts, the ammonobasic hydro salts and the ammonobasic ammono salts.

<sup>1</sup> Adams: *Am. Chem. J.* 28, 198.

<sup>2</sup> Hofmann und Marburg: *Ber.* 30, 2019 and *Ann.* 305, 214.

<sup>3</sup> Aschan: *J. Chem. Soc.* 50, 423.

Partheil und Amort: *Ber.* 31, 594.

IV. MIXED AMMONOBASIC-HYDROBASIC MERCURIC SALTS, which may likewise be salts of either the hydro acids, the halogen acids or the ammono acids.

## MERCURY BASES

In the list of compounds indicated in the table which follows are given in the first column the purely empirical formulas. In the second column each compound is formulated as a basic mixture. The formulas given here are, as a matter of course, more or less arbitrary—the compound (4), for example, may be given any one of a half dozen or more possible formulas—but seem to be worth the space given them in view of their bearing on the theory of the writer concerning the constitution of these compounds. In the third column the structural formulation of the simpler compounds only is attempted for the reason, principally, that the more complicated formulas, in all probability, do not represent definite compounds.

TABLE I.

I.	II.	III.
1. $\text{Hg}_3\text{N}_2$		$\text{Hg:N-Hg-N:Hg}$
2. $\text{HgNH}_3\text{O}$	$\text{HgO.NH}_3$	$\text{HO-Hg-NH}_2$
3. $\text{Hg}_2\text{NHO}$	$\text{HgO.HgNH}$	$\text{Hg:N-Hg-OH}$
4. $\text{Hg}_2\text{NH}_3\text{O}_2$	$2\text{HgO.NH}_3$	$\text{HO-Hg-NH-Hg-OH}$
5. $\text{Hg}_2\text{NH}_5\text{O}_3$	$2\text{HgO.NH}_3.\text{H}_2\text{O}$	$(\text{HO-Hg})_2\text{NH.H}_2\text{O}$
6. $\text{Hg}_3\text{NHO}_2$	$2\text{HgO.HgNH}$	$\text{Hg:N-Hg-O-Hg-OH}$
7. $\text{Hg}_4\text{N}_2\text{O}$	$\text{HgO.Hg}_3\text{N}_2$	$(\text{Hg:N-Hg})_2\text{O}$
8. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_3$	$3\text{HgO.Hg}(\text{NH}_2)_2$	
9. $\text{Hg}_4\text{N}_2\text{H}_8\text{O}_3$	$4\text{HgO}.2\text{NH}_3.\text{H}_2\text{O}$	
10. $\text{Hg}_6\text{N}_3\text{H}_{10}\text{O}_8$	$6\text{HgO}.3\text{NH}_3.2\text{H}_2\text{O}$	

1.  $\text{Hg}_3\text{N}_2$ . Neither of the theoretically possible ammono bases, mercuric amide,  $\text{Hg}(\text{NH}_2)_2$ , nor mercuric imide,  $\text{HgNH}$ , is known.<sup>1</sup> The reactions which might be expected to give one or the other of them, namely the action of potassium amide on a mercuric salt in liquid ammonia, gives as a matter of fact the final deammoniated product,  $\text{Hg}_3\text{N}_2$ .<sup>2</sup>

2.  $\text{HgNH}_3\text{O}$ . Watts' Dictionary<sup>3</sup> is in error in giving a compound of the formula,  $\text{HO-Hg-NH}_2$ , as a product of the action of ammonia on mercuric oxide. Compounds of this type are however known, as for example, the urea derivative,  $\text{NH}_2\text{CONH-Hg-OH}$ ,<sup>4</sup> and Pesci's so-called mercuribenzylammonium hydroxide,<sup>5</sup>  $\text{C}_6\text{H}_5\text{CH}_2\text{NH-Hg-OH}$ .

<sup>1</sup> The aniline compound  $(\text{C}_6\text{H}_5\text{NH})_2\text{Hg}$ , corresponding to mercuric amide has been prepared. Pesci: Z. anorg. Chem. 15, 213.

<sup>2</sup> Franklin: This Journal 28, 835. The doubts expressed by Hofmann and Marburg (Ann. 305, 193 and 210) and repeated by Ley (Abeg. Handb. anorg. Chem. 2, 2, 675) concerning the existence of this compound are therefore removed.

<sup>3</sup> Ed. 1892, 3, 207. Cf. Ann. chim. phys. 72, 225.

<sup>4</sup> Beilstein: Handb. organ. Chem. (1893) I, 1295.

<sup>5</sup> Z. anorg. Chem. 15, 224.

3.  $\text{Hg}_2\text{NHO}$ . This compound is obtained as an explosive, brown powder by heating Millon's base in an atmosphere of ammonia.<sup>1</sup> It is usually formulated as dimercuriammonium hydroxide,  $\text{Hg}_2\text{NOH}$  or

$(\text{Hg}_2\text{N})_2\text{O}\cdot\text{H}_2\text{O}$ . Fürth<sup>2</sup> has proposed the formula,  $\text{O} \begin{array}{c} \diagup \text{Hg} \\ \diagdown \text{Hg} \end{array} \text{NH}$ , and

Rammelsberg<sup>3</sup> the formula,  $\begin{array}{c} \text{Hg} \\ | \\ \text{Hg} \end{array} \text{N} - \text{OH}$ .

4.  $\text{Hg}_2\text{NH}_3\text{O}_2$ . A brown, amorphous powder of this composition has been obtained by various investigators, most recently by Hofmann and Marburg,<sup>4</sup> by drying Millon's base in an atmosphere of ammonia. Weyl<sup>5</sup> obtained a yellow compound of the same composition by treating yellow mercuric oxide with dry gaseous ammonia or with alcoholic ammonia. In the dictionaries of chemistry this compound is found formulated as a hydrated dimercuriammonium hydroxide,  $\text{Hg}_2\text{NOH}\cdot\text{H}_2\text{O}$ , or  $(\text{Hg}_2\text{N})_2\text{O}\cdot 3\text{H}_2\text{O}$ , or as oxydimercuriammonium hydroxide,  $(\text{HgOHg})\text{NH}_2\text{OH}$ . Fürth gives it the formula,  $\text{NH}_2\text{HgOHgOH}$

and Rammelsberg the very unlikely formula,  $\begin{array}{c} \text{HOHg} \\ \diagdown \\ \text{HHg} \end{array} \text{NOH}$ .

5.  $\text{Hg}_2\text{NH}_3\text{O}_3$ . This is the well known Millon's base which is obtained most readily by the action of aqua ammonia on freshly precipitated mercuric oxide.<sup>6</sup> Fürth<sup>7</sup> has recently shown that Millon's base is also formed by the action of ammonia on an aqueous solution of mercuric acetamide. The constitution of Millon's base has already been discussed.

6.  $\text{Hg}_3\text{NHO}_2$ . Hofmann and Marburg<sup>8</sup> obtained a compound of approximately this composition by drying Millon's base *in vacuo* over sulphuric acid. They give no analytical data and remark that the product is probably a mixture.

7.  $\text{Hg}_4\text{N}_2\text{O}$  and 8.  $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_3$ . These two dehydration products of Millon's base, prepared respectively by Weyl<sup>9</sup> and by Millon<sup>10</sup> should, in

<sup>1</sup> G-K: 816; Hofmann and Marburg: Ann. 305, 207. The records given in Gmelin-Kraut's Handbuch der anorganischen Chemie have been taken as representing the state of knowledge of the mercury nitrogen compounds at the date of the publication of the sixth edition in 1875. In the interest of brevity the frequent references which will be made to the third volume of this work will be shortened to a statement of the page preceded by the initials G-K.

<sup>2</sup> Monatsl. 23, 1154.

<sup>3</sup> J. pr. Chem. 146, 562.

<sup>4</sup> Ann. 305, 206.

<sup>5</sup> G-K: 816.

<sup>6</sup> G-K: 817; Hofmann and Marburg: Ann. 305, 206.

<sup>7</sup> Monatsl. 23, 1156.

<sup>8</sup> Ann. 305, 207.

<sup>9</sup> G-K: 815.

<sup>10</sup> Ibid. 816.

all probability, be stricken from the list of known compounds inasmuch as Hofmann and Marburg<sup>1</sup> were unable to confirm the existence of either.

9.  $\text{Hg}_4\text{N}_2\text{H}_8\text{O}_5$  and 10.  $\text{Hg}_6\text{N}_3\text{H}_{13}\text{O}_8$ . Gerresheim's<sup>1</sup> efforts to prepare Millon's base led him to a product having the composition of the former of the preceding formulas, while Rammelsberg<sup>2</sup> found his preparation to have the composition represented by the latter. The fact that Millon's base readily loses water to form the compound (4) page 46 may account for the results obtained by these investigators.

AMMONIATED MERCURIC SALTS. MERCURIAMINES. MERCURIC SALTS WITH AMMONIA OF CRYSTALLIZATION, OR WITH BOTH AMMONIA AND WATER OF CRYSTALLIZATION.

All the complex formulas which have been proposed for the various compounds described below are avoided, and at the same time the behavior of these salts is much better explained, when it is assumed that the members of the group are compounds in which the ammonia plays a part analogous to that of water in salts with water of crystallization. Any new knowledge of the function of water and ammonia in such compounds is distinctly disclaimed, and indeed such knowledge is beside the purpose of this paper. It is sufficient here to insist on the removal of these compounds from the class of the so-called mercuriammonium compounds and to recognize them as belonging to the large class of salts with ammonia of crystallization.

The following salts, which have been found described in the literature, are here formulated as simple addition products.

TABLE II.

11. $\text{HgCl}_2 \cdot \text{NH}_3$	22. $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$
12. $2\text{HgCl}_2 \cdot 3\text{NH}_3$	23. $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$
13. $\text{HgCl}_2 \cdot 2\text{NH}_3$	24. $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$
14. $\text{HgCl}_2 \cdot 12\text{NH}_3$	25. $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$
15. $\text{HgCl}_2 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	26. $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3$
16. $\text{HgBr}_2 \cdot \text{NH}_3$	27. $\text{HgSO}_4 \cdot 2\text{NH}_3$
17. $\text{HgBr}_2 \cdot 2\text{NH}_3$	28. $\text{HgSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$
18. $\text{HgI}_2 \cdot \text{NH}_3$	29. $2\text{Hg}(\text{SCN})_2 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$
19. $3\text{HgI}_2 \cdot 4\text{NH}_3$	30. $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$
20. $\text{HgI}_2 \cdot 2\text{NH}_3$	31. $\text{HgCr}_2\text{O}_7 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$
21. $\text{HgI}_2 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$	

11.  $\text{HgCl}_2 \cdot \text{NH}_3$ .<sup>3</sup> This compound has been prepared by passing ammonia gas over warm mercuric chloride,<sup>4</sup> by distilling mercuric oxide

<sup>1</sup> l. c.

<sup>2</sup> Ann. 195, 373.

<sup>3</sup> J. pr. Chem. 146, 561.

<sup>4</sup> It is interesting to note the unlikely formulas,  $(\text{ClHg})\text{NH}_3\text{Cl}$ ;  $\text{HgN}_2\text{H}_6\text{Cl}_2$ .  $\text{HgCl}_2 \cdot \text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl} \cdot 2\text{HgCl}_2$ ; and  $(\text{NHg}_2\text{Cl} \cdot \text{NH}_4\text{Cl}) \cdot 2(\text{HgCl}_2 \cdot \text{NH}_4\text{Cl})$ ; which have been variously assigned to this compound.

with ammonium chloride,<sup>1</sup> by heating the infusible white precipitate,<sup>2</sup> and by the action of ammonia gas on a solution of mercuric chloride in benzonitrile.<sup>3</sup> Dammer,<sup>4</sup> and Hofmann and Marburg<sup>5</sup> have expressed doubts of the existence of such a compound.

12.  $2\text{HgCl}_2 \cdot 3\text{NH}_3$ . Varet<sup>6</sup> obtained a product of this composition by the action of alcoholic ammonia on the double salt,  $\text{HgCl}_2 \cdot \text{Hg}(\text{CN})_2$ .

13.  $\text{HgCl}_2 \cdot 2\text{NH}_3$ . This is the well known fusible white precipitate. It was first definitely distinguished from the long known white precipitate of the pharmacists by Kane,<sup>7</sup> who proposed for it the name, Wöhler's precipitate. Its preparation and properties have already been discussed.<sup>8</sup>

14.  $\text{HgCl}_2 \cdot 12\text{NH}_3$ . Franklin and Kraus<sup>9</sup> prepared this compound by the action of liquid ammonia on mercuric chloride.

15.  $\text{HgCl}_2 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ . By passing a current of ammonia gas through a warm solution of mercuric oxide in aqueous ammonium chloride or by the addition of this solution to warm aqua ammonia, André<sup>10</sup> obtained a product of this composition. It is safe to assume that the existence of such a compound needs confirmation.

16.  $\text{HgBr}_2 \cdot \text{NH}_3$ . A compound of this composition has been obtained by the action of ammonia gas on melted mercuric bromide,<sup>11</sup> and as a sublimate by heating the compound  $\text{HgBrNH}_2$ .<sup>12</sup>

17.  $\text{HgBr}_2 \cdot 2\text{NH}_3$ . Pesci<sup>12</sup> has prepared this compound by the action of ammonium bromide solution on the ammonobasic bromides,  $4\text{Hg}_2\text{NBr} \cdot 5\text{NH}_4\text{Br}$  (40) and  $\text{NHg}_2\text{Br}$  (41), as well as by the action of aqua ammonia on a solution of mercuric bromide containing ammonium bromide. He also obtained it by the action of ammonia on an alcoholic solution of mercuric bromide.

18.  $\text{HgI}_2 \cdot \text{NH}_3$ , 21.  $\text{HgI}_2 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$ . According to Gmelin-Kraut<sup>13</sup>

<sup>1</sup> G-K : 840.

<sup>2</sup> G-K : 834.

<sup>3</sup> Naumann : Ber. 32, 1000.

<sup>4</sup> Handb. anorg. Chem (1894) 2.2, 903.

<sup>5</sup> Ann. 305, 202.

<sup>6</sup> Bull. soc. chim. (3) 6, 223.

<sup>7</sup> Ann. chim. phys. 72, 380.

<sup>8</sup> Weyl considers the compound formed by the action of liquid ammonia on mercuric chloride to be different from Wöhler's precipitate and gives it the formula,  $2\text{HgCl}_2 \cdot 4\text{NH}_3$ . (G-K : 840) Franklin and Kraus (Am. Ch. J. 23, 300) were unable to distinguish Weyl's preparation from the white precipitate obtained by other methods.

<sup>9</sup> Am. Ch. J. 23, 300. Weyl's statement (G-K : 840.) to the effect that mercuric chloride is readily soluble in liquid ammonia is an error. Liquid ammonia, in a closed tube, at laboratory temperature unites with mercuric chloride to form a dense liquid which is but slightly soluble in excess of the ammonia.

<sup>10</sup> Compt. rend. 112, 860.

<sup>11</sup> G-K : 832.

<sup>12</sup> Jsb. Chem. 1890, 629.

<sup>13</sup> G-K : 830.

the compound represented by the first of these formulas has been obtained by a number of investigators. Nessler's preparation contained from 3.2 to 3.5 per cent. water for which reason the second formula is found in the literature. Pesci's attempts<sup>1</sup> to prepare the compound  $\text{HgI}_2 \cdot \text{NH}_3$  led him to a product to which he gave the formula,  $3\text{NHg}_2\text{I} \cdot 4\text{HgI}_2 \cdot 8\text{NH}_4\text{I}$ . Instead of a compound of this unlikely formula Pesci probably had in his hands a slightly ammonolyzed mixture,  $9\text{HgI}_2 \cdot x\text{NH}_3 \cdot \text{NH}_2\text{HgI}$ .

In view of the fact that François,<sup>2</sup> by vapor pressure measurements, has proved the existence of the two following ammoniated mercuric iodides only, it follows that the earlier data pointing to the existence of the compound,  $\text{HgI}_2 \cdot \text{NH}_3$ , must be in error.

19.  $3\text{HgI}_2 \cdot 4\text{NH}_3$ . A colorless compound of this composition has been shown by François<sup>3</sup> to have a definite decomposition tension from which it follows that the formula must represent a chemical individual.

20.  $\text{HgI}_2 \cdot 2\text{NH}_3$ . This compound has often been prepared by the action of ammonia gas, of aqua ammonia and of liquid ammonia on mercuric iodide.<sup>4</sup> It is soluble in ether and in alcohol, in each case, however, leaving behind a yellow or brown residue, the result in all probability, of slight ammonolysis of the salt. Its decomposition tension is considerable so that the compound rapidly loses its ammonia on exposure.

The compounds 22, 23, 24 and 25 have been prepared by Varet<sup>5</sup> by the action of ammonia on mercuric cyanide under various conditions.<sup>6</sup>

26.  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3$ . Pesci<sup>7</sup> prepared this crystalline ammonia addition product of mercuric nitrate by the action of a fifty per cent. solution of ammonium nitrate upon the mixed basic nitrate (73) and upon the hydrobasic nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot \text{HgO}$ . This is an example of the conversion of a basic salt into a normal one by the action of a solution of an ammonium salt.

27.  $\text{HgSO}_4 \cdot 2\text{NH}_3$ . Millon<sup>8</sup> obtained a compound of this composition by saturating aqua ammonia with mercuric sulphate and evaporating

<sup>1</sup> J. Chem. Soc. 60, 270.

<sup>2</sup> Compt. rend. 129, 296.

<sup>3</sup> loc. cit.

<sup>4</sup> G-K : 831; Pesci : Jsb. Chem. 1890, 632; François : loc. cit.

<sup>5</sup> Bull. soc. chim. (3) 6, 220.

<sup>6</sup> Franklin and Kraus also prepared the addition product,  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ , Since their results were never published it seems worth while to give their data here. Mercuric cyanide was dissolved in liquid ammonia, after which the excess of liquid was allowed to evaporate. In two experiments 1.198 gm. and 1.655 gm. mercuric cyanide retained respectively 0.1465 gm. and 0.2240 gm. ammonia. Calculated for  $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$ , 11.90 per cent. ammonia. Found respectively, 10.90 and 11.93 per cent. The compound readily loses its ammonia.

<sup>7</sup> Jsb. Chem. 1890, 630.

<sup>8</sup> G-K : 825.

the solution to dryness. Pesci,<sup>1</sup> following Millon's directions, obtained a product of the same composition which, however, he assumed to be a mixture.

28.  $\text{HgSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ . Schmieder<sup>2</sup> prepared this compound in the form of beautiful crystals by dissolving mercuric oxide in a solution of ammonium sulphate and evaporating the solution until a crop of crystals was obtained. Heated to  $115^\circ$  this compound loses its water.<sup>3</sup> Following Schmieder's directions, Pesci<sup>4</sup> obtained a compound of the same composition to which he gave the formula,  $(\text{NHg}_2)_2\text{SO}_4 \cdot 3(\text{NH}_4)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ .<sup>5</sup>

29.  $2\text{Hg}(\text{SCN})_2 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$ . Fleischer<sup>6</sup> dissolved mercuric oxide in a hot solution of ammonium sulphocyanide when on allowing the solution to cool an ammoniated mercuric sulphocyanide separated out in well developed crystals. Analyses of different specimens showed a rather wide variation in the amount of ammonia and water present. The same, or a similar compound, was obtained by Ehrenberg<sup>7</sup> by adding aqua ammonia to a solution of the double sulphocyanide of mercury and ammonium.

30.  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ .  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Hirzel<sup>8</sup> obtained a compound of the former formula by dissolving mercuric oxide in ammonium acetate and allowing the solution to crystallize. By the same method Balestra<sup>9</sup> obtained a product to which he gave the formula,  $\text{NHg}_2\text{C}_2\text{H}_3\text{O}_2 \cdot 3\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$ , thus representing the compound as containing half a molecule of water less than found by Hirzel. It is soluble in little water but, according to Balestra, is converted by an excess into the product,  $\text{Hg}_2\text{NC}_2\text{H}_3\text{O}_2$  (48).

31.  $\text{HgCr}_2\text{O}_7 \cdot 2\text{NH}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ . Hensgen<sup>10</sup> obtained this compound in the form of golden yellow needles by dissolving mercuric oxide in a solution of ammonium dichromate and allowing the solution to crystallize.

#### AMMONOBASIC MERCURIC SALTS.

Just as the normal chloride of mercury with ammonia of crystallization is ammonolyzed by the action of water or of aqua ammonia, giving rise to the formation of ammonobasic products, so it will be clear from the descriptions of the methods by which the many mercuric nitrogen compounds enumerated in the following pages have been prepared, that the

<sup>1</sup> J. Chem. Soc. 60, 269.

<sup>2</sup> G-K : 825.

<sup>3</sup> G-K : loc. cit.

<sup>4</sup> Jsb. Chem. 1890, 631.

<sup>5</sup> Ley, in Abegg's Handb. anorg. Chem. 2.2, 676, wrongly gives this formula with two molecules of water instead of four.

<sup>6</sup> Ann. 179, 225.

<sup>7</sup> J. pr. Chem. 138, 62.

<sup>8</sup> Jsb. Chem. 1851, 437; 1852, 421.

<sup>9</sup> Ibid. 1892, 815.

<sup>10</sup> Ibid. 1886, 478.



principles elucidated above likewise apply to them. The presence of solutions of ammonium salts in contact with the various ammonobasic precipitates tends to convert them into less basic products, even into the normal salts in case the concentration of the ammonium salts is great enough, while the action of water, aqua ammonia or potassium hydroxide always has the effect of rendering the precipitate more basic.

In the following table, which includes all the ammonobasic mercuric salts which have been found described in the literature, is given in the first column the empirical formulas, in the second column formulas representing the compounds as basic mixtures after the manner ordinarily employed in formulating the more familiar hydrobasic salts, while in the third column the attempt is made to give the constitutional formulas.

TABLE III.

I.	II.	III.
32. $\text{Hg}_2\text{N}_3\text{H}_8\text{Cl}_3$	$3\text{HgCl}_2 \cdot \text{Hg}(\text{NH}_2)_2 \cdot 4\text{NH}_3$	$\text{HgCl}_2 \cdot 2\text{NH}_3 \cdot \text{NH}_2\text{Hg}-\text{Cl}$
33. $\text{HgNH}_2\text{Cl}$	$\text{HgCl}_2 \cdot \text{Hg}(\text{NH}_2)_2$	$\text{NH}_2-\text{Hg}-\text{Cl}$
34. $\text{Hg}_2\text{NCl}$	$\text{HgCl}_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{Cl}$
35. $\text{Hg}_2\text{NHCl}_2$	$\text{HgCl}_2 \cdot \text{HgNH}$	$(\text{Cl}-\text{Hg})_2\text{NH}$
36. $\text{Hg}_2\text{NH}_2\text{Cl}_3$	$3\text{HgCl}_2 \cdot \text{Hg}(\text{NH}_2)_2$	$\text{HgCl}_2 \cdot \text{NH}_2-\text{Hg}-\text{Cl}$
37. $\text{Hg}_5\text{N}_2\text{Cl}_4$	$2\text{HgCl}_2 \cdot \text{Hg}_3\text{N}_2$	$(\text{Cl}-\text{Hg})_2 : \text{N}-\text{Hg}-\text{N} : (\text{Hg}-\text{Cl})_2$
38. $\text{Hg}_2\text{NH}_4\text{Cl}_5$	$2\text{HgCl}_2 \cdot \text{NH}_4\text{Cl}$	
39. $\text{HgNH}_2\text{Br}$	$\text{HgBr}_2 \cdot \text{Hg}(\text{NH}_2)_2$	$\text{NH}_2-\text{Hg}-\text{Br}$
40. $\text{Hg}_8\text{N}_6\text{H}_{20}\text{Br}_9$		$\text{HgBr}_2 \cdot 2\text{NH}_3 \cdot 7\text{NH}_2-\text{Hg}-\text{Br}$
41. $\text{Hg}_2\text{NBr}$	$\text{HgBr}_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{Br}$
42. $\text{Hg}_5\text{N}_2\text{Br}_4$	$2\text{HgBr}_2 \cdot \text{Hg}_3\text{N}_2$	$(\text{BrHg})_2 : \text{N}-\text{Hg}-\text{N} : (\text{HgBr})_2$
43. $\text{HgNH}_2\text{I}$	$\text{HgI}_2 \cdot \text{Hg}(\text{NH}_2)_2$	$\text{NH}_2-\text{Hg}-\text{I}$
44. $\text{Hg}_2\text{NI}$	$\text{HgI}_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{I}$
45. $\text{HgNH}_2\text{F}$	$\text{HgF}_2 \cdot \text{Hg}(\text{NH}_2)_2$	$\text{NH}_2-\text{Hg}-\text{F}$
46. $\text{Hg}_2\text{N} \cdot \text{NO}_3$	$\text{Hg}(\text{NO}_3)_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{NO}_2$
47. $\text{Hg}_2\text{N} \cdot \text{NO}_2$	$\text{Hg}(\text{NO}_2)_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{NO}_2$
48. $\text{Hg}_2\text{N} \cdot \text{C}_2\text{H}_3\text{O}_2$	$\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Hg}_3\text{N}_2$	$\text{Hg}:\text{N}-\text{Hg}-\text{C}_2\text{H}_3\text{O}_2$

32.  $\text{Hg}_2\text{N}_3\text{H}_8\text{Cl}_3$ . According to Hirzel<sup>1</sup> a compound of this composition is formed by the action of a solution of Alembroth salt on an excess of aqua ammonia. The product was obviously an equimolecular mixture of the fusible and infusible white precipitates.

33.  $\text{HgNH}_2\text{Cl}$ . This is the long known and thoroughly identified infusible white precipitate. Its preparation and properties have already been discussed.

34.  $\text{Hg}_2\text{NCl}$ . This ammonobasic salt, known as dimercuriammonium chloride, was first prepared by Weyl<sup>2</sup> by the action of alcoholic hydrochloric acid on the base,  $\text{Hg}_2\text{NOH}$ , (3), and by treating the basic chloride,  $3\text{HgO} \cdot \text{HgCl}_2$ , with liquid ammonia. Rammelsberg<sup>3</sup> states that the same compound is formed by the dehydration of the chloride of Millon's

<sup>1</sup> Jsb. Chem. 1853, 381.

<sup>2</sup> G-K : 834.

<sup>3</sup> J. pr. Chem. 146, 562.

base (59) at 200° and André<sup>1</sup> considered that he had proved its presence in certain mixtures formed by the interaction of mercuric chloride, potassium hydroxide and ammonium chloride in aqueous solution. Hofmann and Marburg<sup>2</sup>, on the other hand were unable to obtain this compound by the action of ethereal hydrochloric acid on  $\text{Hg}_2\text{NOH}$ ; and they furthermore insist that the chloride of Millon's base can not be dehydrated without decomposition.<sup>3</sup>

35.  $\text{Hg}_2\text{NHCl}_2$ . Balestra<sup>4</sup> obtained a product of this composition by the action of aqua ammonia on an excess of boiling mercuric chloride solution and assigned the formula,  $\text{Hg}_2\text{NCl.HCl}$ . In disagreement with the results of Balestra, Millon earlier obtained a product of the composition,  $\text{Hg}_5\text{N}_3\text{H}_6\text{O}_2\text{Cl}_3$ , (56) by the action of ammonia on an excess of hot mercuric chloride solution. In case a definite compound of this composition exists it may be given the formula,  $\text{ClHgNHHgCl}$ , which represents it as a deammoniated product of the infusible white precipitate.

36.  $\text{Hg}_2\text{NH}_2\text{Cl}_3$ .<sup>5</sup> Millon<sup>6</sup> and Balestra<sup>7</sup> report the preparation of a compound of this composition by the gradual addition of ammonia to a large excess of a cold solution of mercuric chloride. Balestra gives this compound the formula  $\text{Hg}_2\text{NCl.2HCl}$ , and assumes erroneously that he has proved its constitution when he finds that in accordance with Pesci's reaction<sup>8</sup> two molecules of ammonia are set free when it is treated with an excess of ammonium bromide, and that hydrogen sulphide acts upon it to liberate two molecules of hydrochloric acid. Hofmann and Marburg<sup>9</sup> have shown that Pesci's reaction is of no significance whatever in proving the presence of the dimercuriammonium radical in a compound. It also appears that the liberation of hydrochloric acid by the action of hydrogen sulphide no more proves the constitution of this compound to be  $\text{Hg}_2\text{NCl.2HCl}$  than does the liberation of hydriodic acid by the action of

<sup>1</sup> Compt. rend. 108, 1108 and 1164.

<sup>2</sup> Ann. 305, 209; Z. anorg. Chem. 23, 128.

<sup>3</sup> The writer has attempted to determine whether this compound may be prepared from  $\text{NH}_2\text{HgCl}$  and from  $\text{HOHgNHHgCl}$  by prolonged washing with liquid ammonia on the hypothesis that the former compound may undergo ammonolysis and that the latter may lose water as the result of the mass action of the ammonia. The infusible white precipitate was found to give off ammonium chloride and both compounds yielded products somewhat richer in mercury than the original compounds, but in neither case did the washed salt give analytical results corresponding to the compound  $\text{Hg}_2\text{NCl}$ . Further work along this line was arrested for the time being by the demoralization of our laboratory resulting from the recent earthquake.

<sup>4</sup> Jsb. Chem. 1891, 586.

<sup>5</sup> Watts' Dictionary, 3, 208-209, (1892), is in error in stating that Millon prepared this compound by heating the infusible white precipitate slowly to 340°.

<sup>6</sup> G-K : 837.

<sup>7</sup> Jsb. Chem. 1891, 584.

<sup>8</sup> J. Chem. Soc. 58, 1213.

<sup>9</sup> Ann. 305, 205; Z. anorg. Chem. 23, 133. Cf. however Pesci: Ibid. 21, 373.

hydrogen sulphide on the basic iodide of lead,  $\text{PbOPbI}_2 \cdot \text{H}_2\text{O}$ , for example, prove the constitution of this compound to be  $2\text{PbO} \cdot 2\text{HI}$ .

37.  $\text{Hg}_5\text{N}_2\text{Cl}_4$ . Mitscherlich<sup>1</sup> obtained this compound in the form of small, red, crystalline aggregates by heating the infusible white precipitate. Rây<sup>2</sup> gives the formula,  $2\text{Hg}_2\text{NCl} \cdot \text{HgCl}_2$ , to a product approximating Millon's compound in composition which he obtained by the action of potassium hydroxide upon a dilute solution of the following double salt.

38.  $\text{Hg}_2\text{NH}_4\text{Cl}_5$ . This compound was prepared by Rây<sup>3</sup> by dissolving his basic nitrite (86), in hydrochloric acid and evaporating nearly to dryness.

Pesci's theory that all the mercury nitrogen compounds are to be formulated as dimercuriammonium derivatives, while obviously leading Balestra far afield when he formulates his two compounds  $\text{Hg}_2\text{NHCl}_2$ , (35), and  $\text{Hg}_2\text{NH}_2\text{Cl}_3$ , (36), as  $\text{Hg}_2\text{NCl} \cdot \text{HCl}$  and  $\text{Hg}_2\text{NCl} \cdot 2\text{HCl}$ , respectively, reaches a climax of uselessness when Rây<sup>4</sup> is thereby induced to formulate a new double salt,  $2\text{HgCl}_2 \cdot \text{NH}_4\text{Cl}$ , as a compound of dimercuriammonium chloride with four molecules of hydrochloric acid,  $\text{Hg}_2\text{NCl} \cdot 4\text{HCl}$ .

39.  $\text{HgNH}_2\text{Br}$ . 40.  $\text{Hg}_8\text{N}_8\text{H}_{20}\text{Br}_9$ . A compound of the former formula, the bromine analogue of the infusible white precipitate, was first prepared by Mitscherlich<sup>5</sup> by the action of aqua ammonia on a solution of mercuric bromide. More recently, however, Pesci,<sup>6</sup> in his attempts to prepare the same compound, obtained instead a product to which he gave the formula,  $4\text{Hg}_2\text{NBr} \cdot 5\text{NH}_4\text{Br}$ . It seems not improbable that Pesci's preparation was a mixture as indicated in the table above.

41.  $\text{Hg}_2\text{NBr}$ . Pesci<sup>7</sup> prepared this compound by the action of boiling water or of a dilute potassium hydroxide solution on the compound above (39) as well as by the action of dilute hydrobromic acid on Millon's base. Hofmann and Marburg<sup>8</sup> were unable to obtain such a compound, either by the action of aqua ammonia on a solution of mercuric bromide, by the dehydration of the bromide of Millon's base, or by the action of dilute hydrobromic acid on Millon's base. However, there can be no doubt of its existence, for, in addition to the evidence given by the writer in a former paper,<sup>9</sup> Mr. F. F. Fitzgerald, working in this labora-

<sup>1</sup> G-K : 834

<sup>2</sup> J. Chem. Soc. 81, 649.

<sup>3</sup> Ibid. 81, 648.

<sup>4</sup> Proc. Chem. Soc. 17, 96; 18, 86; Dammer : Handb. anorg. Chem. 1903, 4, 631. Abegg : Handb. anorg. Chem. 2.2, 677.

<sup>5</sup> G-K : 832.

<sup>6</sup> Jsb. Chem. 1890, 628.

<sup>7</sup> Ibid, 1890, 628; Z. anorg. Chem. 21, 372.

<sup>8</sup> Ann. 305, 213; Z. anorg. Chem. 23, 128.

<sup>9</sup> This Journal, 27, 840.

tory, has recently obtained a product giving excellent analytical results.

42.  $\text{Hg}_3\text{N}_2\text{Br}_4$ . Mitscherlich<sup>1</sup> obtained this compound by heating  $\text{NH}_2\text{HgBr}$  (39) to  $340^\circ$ . Remarking that "the compound is not easy to get," Rây<sup>2</sup> finds that a product of this composition is formed by the action of potassium hydroxide on an excess of a solution of his double bromide,  $2\text{HgBr}_2 \cdot \text{NH}_4\text{Br}$ .

43.  $\text{HgNH}_2\text{I}$ . François<sup>3</sup> obtained this, the iodine analogue of the infusible white precipitate, by the action of concentrated aqueous ammonia, added slowly and at long intervals, upon the ammoniated mercuric iodide,  $\text{HgI}_2 \cdot 2\text{NH}_3$ . It was thus obtained as a white, microcrystalline powder. According to François large quantities of aqua ammonia added at once give the brown compound,  $\text{Hg}_2\text{NI}$ . François showed the reaction  $\text{HgI}_2 \cdot 2\text{NH}_3 \rightleftharpoons \text{NH}_2\text{HgI} + \text{NH}_4\text{I}$  to be a reversible one and that in aqueous ammonia of 0.923 specific gravity at  $21^\circ$  the concentration of ammonium iodide at equilibrium was 0.020 to 0.023 normal.

44.  $\text{Hg}_2\text{NI}$ . This compound was first prepared by the action of liquid ammonia on the basic iodide,  $3\text{HgO} \cdot \text{HgI}_2$ .<sup>4</sup> More recently François<sup>5</sup> has prepared the same compound by the action of aqua ammonia on mercuric iodide, and by the action of potassium hydroxide on  $\text{HgI}_2 \cdot 2\text{NH}_3$ . The writer has shown<sup>6</sup> that this ammonobasic salt is formed by the ammonolytic action of liquid ammonia on mercuric iodide as well as by the action of potassium amide on an excess of mercuric iodide in solution in liquid ammonia.

45.  $\text{HgNH}_2\text{F}$ . The fluorine analogue of the infusible white precipitate has recently been prepared as a light yellow, amorphous powder by adding concentrated aqueous ammonia and then alcohol to a solution of mercuric fluoride.<sup>7</sup>

46.  $\text{Hg}_2\text{N} \cdot \text{NO}_3$ . This ammonobasic nitrate has been prepared by Pesci<sup>8</sup> and by Hofmann and Marburg<sup>9</sup> by the action of a slight excess of ammonia on an aqueous solution of mercuric nitrate. Pesci<sup>10</sup> obtained it also by washing the compound,  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3$  (26), with hot water. Rây<sup>11</sup> was unable to obtain the anhydrous compound.

<sup>1</sup> G-K : 832. Watts' Dictionary, 3, 209, (1890), erroneously gives  $\text{Hg}_3\text{NBr}_3$  as the compound formed.

<sup>2</sup> J. Chem. Soc. 81, 649.

<sup>3</sup> Compt. rend. 130, 1022.

<sup>4</sup> G-K : 829.

<sup>5</sup> Compt. rend. 130, 571.

<sup>6</sup> This Journal, 27, 838.

<sup>7</sup> Böhm : Z. anorg. Chem. 43, 332.

<sup>8</sup> J. Chem. Soc. 60, 268; 2. Z. anorg. Chem. 21, 372.

<sup>9</sup> Z. anorg. Chem. 23, 131.

<sup>10</sup> Jsb. Chem. 1890, 630.

<sup>11</sup> Z. anorg. Chem. 33, 209.

47.  $\text{Hg}_2\text{N}\cdot\text{NO}_2$ . Rây<sup>1</sup> reports the preparation of a compound of this composition by the action of ammonia on a solution of mercuric nitrite. His analyses, however, show the presence of some water in his preparation. (Cf 86).

48.  $\text{Hg}_2\text{N}\cdot\text{C}_2\text{H}_3\text{O}_2$ . By digesting the yellow oxide of mercury with a solution of ammonium acetate, and by the action of water on the compound  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)\cdot 2\text{NH}_3\cdot\text{H}_2\text{O}$ , (30), Balestra<sup>2</sup> obtained this ammonobasic acetate in the form of an amorphous white powder.

#### MIXED HYDROBASIC-AMMONOBASIC MERCURIC SALTS.

Both the oxygen and halogen salts of mercury give with ammonia in the presence of large quantities of water or of dilute alkaline hydroxides representatives of this class of compounds, the result of simultaneous ammonolysis and hydrolysis. Certain of them have also been prepared by the action of dilute acids on the mixed hydro ammono bases, on the carbonates of Millon's base, by double decomposition, and by the action of ammonium salt solutions, not too concentrated, on mercuric oxide. They are variously known in the literature as salts of Millon's base, as oxymercuriammonium salts, as hydrated dimercuriammonium salts, and as hydrated mixed salts of dimercuriammonium with ammonium salts, or with mercuric salts, or with both ammonium salts and mercuric salts. With certain exceptions the members of the group have been obtained as amorphous powders varying in color from pure white, through light shades of yellow, to pure yellow. The iodide is brown. They are insoluble in water and in liquid ammonia and in mixtures of these two solvents, but dissolve readily in dilute hydrochloric acid and in solutions of ammonium salts. They are decomposed by the action of potassium iodide or by potassium sulphide and are rendered more basic by the action of dilute potassium hydroxide. Concentrated hot caustic alkalies effect their decomposition with evolution of ammonia.

#### THE HALOGEN SALTS.

In the table are included all the preparations which have been found described in the literature, arranged in the order of their basicity. In the first column is given the purely empirical formula, in the second the members are formulated as basic mixtures containing, as the case may be, two or more of the known compounds,  $\text{HgCl}_2$ ,  $\text{NH}_2\text{HgCl}$ ,  $\text{HOHgNHHgCl}$ ,  $\text{HgNHgCl}$  and  $\text{HgO}$ . It seems safe to assume that investigation will prove many of these products to be mixtures.

<sup>1</sup> J. Chem. Soc. 81, 647.

<sup>2</sup> Ibid. 64, 304.

TABLE IV.

I.	II.
49. $\text{Hg}_4\text{N}_2\text{H}_4\text{OCl}_4$	$(\text{HgCl}_2, \text{HgO}) \cdot 2\text{NH}_2\text{HgCl}$
50. $\text{Hg}_6\text{N}_3\text{H}_{10}\text{OCl}_3$	$4\text{NH}_2\text{HgCl} \cdot \text{HOHgNHHgCl}$
51. $\text{Hg}_5\text{N}_2\text{H}_2\text{OCl}_4$	$(\text{HgCl}_2, \text{HgO}) \cdot \text{NH}_2\text{HgCl} \cdot \text{Hg}_2\text{NCl}$ or $\text{Hg}_5\text{N}_2\text{Cl}_4 \cdot \text{H}_2\text{O}$
52. $\text{Hg}_{10}\text{N}_4\text{H}_2\text{OCl}_3$	$2\text{HgCl}_2 \cdot \text{HOHgNHHgCl} \cdot 3\text{Hg}_2\text{NCl}$ or $\text{Hg}_5\text{N}_2\text{Cl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
53. $\text{Hg}_4\text{N}_3\text{H}_4\text{OCl}_3$	$2\text{NH}_2\text{HgCl} \cdot \text{HOHgNHHgCl}$
54. $\text{Hg}_3\text{N}_2\text{H}_4\text{OCl}_2$	$\text{NH}_2\text{HgCl} \cdot \text{HOHgNHHgCl}$
55. $\text{Hg}_6\text{N}_4\text{H}_6\text{OCl}_4$	$2\text{NH}_2\text{HgCl} \cdot \text{HOHgNHHgCl} \cdot \text{Hg}_2\text{NCl}$
56. $\text{Hg}_5\text{N}_3\text{H}_6\text{OCl}_3$	$\text{NH}_2\text{HgCl} \cdot 2\text{HOHgNHHgCl}$
57. $\text{Hg}_5\text{NH}_2\text{O}_3\text{Cl}_3$	$(3\text{HgO} \cdot \text{HgCl}_2) \cdot \text{NH}_2\text{HgCl}$
58. $\text{Hg}_7\text{N}_4\text{H}_4\text{OCl}_4$	$\text{NH}_2\text{HgCl} \cdot \text{HOHgNHHgCl} \cdot 2\text{Hg}_2\text{NCl}$
59. $\text{Hg}_2\text{NH}_2\text{OCl}$	$\text{HOHgNHHgCl}$ or $\text{NH}_2\text{HgCl} \cdot \text{HgO}$
60. $\text{Hg}_4\text{N}_2\text{H}_2\text{OCl}_2$	$\text{HOHgNHHgCl} \cdot \text{Hg}_2\text{NCl}$
61. $\text{Hg}_6\text{N}_3\text{H}_4\text{OCl}_3$	$2\text{HOHgNHHgCl} \cdot \text{Hg}_2\text{NCl}$
62. $\text{Hg}_5\text{N}_3\text{H}_4\text{OCl}_2$	$2\text{HOHgNHHgCl} \cdot \text{HgO}$
63. $\text{Hg}_3\text{NH}_2\text{O}_2\text{Cl}$	$\text{HOHgNHHgCl} \cdot \text{HgO}$
64. $\text{Hg}_2\text{NH}_2\text{OBr}$	$\text{HOHgNHHgBr}$
65. $\text{Hg}_2\text{NH}_2\text{O}_2\text{Br}$	$\text{HOHgNHHgBr} \cdot \text{H}_2\text{O}$
66. $\text{Hg}_4\text{N}_2\text{H}_2\text{OBr}_2$	$\text{HOHgNHHgBr} \cdot \text{Hg}_2\text{NBr}$
67. $\text{Hg}_2\text{NH}_2\text{OI}$	$\text{HOHgNHHgI}$
68. $\text{Hg}_2\text{NH}_2\text{OCN}$	$\text{HOHgNHHgCN}$
69. $\text{Hg}_2\text{NH}_2\text{OFI}_2$	$(\text{FIHg})_2\text{NH} \cdot \text{H}_2\text{O}$

49.  $\text{Hg}_4\text{N}_2\text{H}_4\text{OCl}_4$ , and 57.  $\text{Hg}_5\text{NH}_2\text{O}_3\text{Cl}_3$ . These basic mixtures were prepared by Thümmel,<sup>1</sup> by the action of ammoniacal solutions of ammonium carbonate and hydrogen sodium carbonate, respectively, on solutions of mercuric chloride. Both products are undoubtedly mixtures, the one formed by means of the sodium carbonate being the more basic. It will be noted that the former compound approximates the ammonobasic chloride (35), in composition; it is therefore possible that, in this preparation, Thümmel had an imperfectly dried specimen of  $\text{Hg}_2\text{NHCl}_2$  in his hands.

50.  $\text{Hg}_6\text{N}_3\text{H}_{10}\text{OCl}_3$ . Millon<sup>2</sup> obtained a product of this composition by adding a boiling solution of mercuric chloride to a large excess of aqua ammonia, followed by thorough washing of the precipitate with cold water. By following Millon's directions, Balestra<sup>3</sup> found that the infusible white precipitate is formed, which gradually becomes yellow as it is repeatedly washed, to give finally the chloride of Millon's base (59). As indicated in the table, Millon's product was probably a specimen of the infusible white precipitate, partially changed into the chloride of Millon's base.

51.  $\text{Hg}_5\text{N}_2\text{H}_2\text{OCl}_4$ . Balestra<sup>4</sup> obtained a product of this composition, to which he gave the formula,  $2\text{Hg}_2\text{NCl} \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$ , by washing the compound,  $\text{Hg}_2\text{NH}_2\text{Cl}_3$  (36), with cold water. This product may be formulated as an imperfectly dried specimen of the compound,  $\text{Hg}_5\text{N}_2\text{Cl}_4$  (37).

<sup>1</sup> Jsb. Chem. 1887, 579.

<sup>2</sup> G-K : 837.

<sup>3</sup> Jsb. Chem. 1891, 584.

<sup>4</sup> Ibid. 1891, 585.

52.  $\text{Hg}_{10}\text{N}_4\text{H}_2\text{OCl}_8$ . Balestra found the preceding preparation to lose one-half a molecule of water at  $110-115^\circ$ , which leads to a product still more closely approximating in composition the compound,  $\text{Hg}_5\text{N}_2\text{Cl}_4$ .

56.  $\text{Hg}_3\text{N}_3\text{H}_8\text{O}_2\text{Cl}_3$ . Millon<sup>1</sup> prepared this product by thoroughly washing the compound,  $\text{Hg}_2\text{NH}_2\text{Cl}_3$  (36), with cold water, and also by adding aqua ammonia slowly to a large excess of boiling mercuric chloride solution. Following Millon's first method, just mentioned, Balestra<sup>2</sup> was unable to prepare the same compound, but obtained instead,  $\text{Hg}_3\text{N}_2\text{H}_2\text{OCl}_4$  (51). Following Millon's second method, he obtained the compound,  $\text{Hg}_2\text{NHCl}_2$  (35).

59.  $\text{Hg}_2\text{NH}_2\text{OCl}$ . This well characterized compound, the chloride of Millon's base,<sup>3</sup> has been prepared by a number of investigators, especially by the action of water or dilute potassium hydroxide solution on the white precipitates. It is also formed by the action of dilute hydrochloric acid, or of ammonium chloride, on Millon's base, and in general by the action of water or dilute potassium hydroxide solution on any of the less basic chlorides listed in this or the preceding section, or by the action of ammonium chloride on any of the more basic compounds. An interesting method of formation is that of the action of ammonium chloride on an aqueous solution of mercuric acetamide.<sup>4</sup>

60.  $\text{Hg}_4\text{N}_2\text{H}_2\text{OCl}_2$ . Although, according to Hofmann and Marburg,<sup>5</sup> the chloride of Millon's base does not lose water without complete decomposition, a product of the above composition has nevertheless been prepared.<sup>6</sup>

62.  $\text{Hg}_5\text{N}_4\text{H}_4\text{O}_3\text{Cl}_2$ . 63.  $\text{Hg}_3\text{NH}_2\text{O}_2\text{Cl}$ . Schmieler<sup>7</sup> obtained the former of these products by dissolving the compound,  $\text{HgSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$  (28), in dilute hydrochloric acid, and pouring the solution into a slight excess of potassium hydroxide solution. He obtained the latter compound by boiling the former with a concentrated solution of potassium hydroxide. Since, according to Schmieler, continued boiling of the latter compound with potassium hydroxide gives finally mercuric oxide, it seems fair to conclude that both of the above preparations were nothing more than mixtures of the chloride of Millon's base with mercuric oxide.

In addition to the preparation (60), which had previously been described by others, André<sup>8</sup> obtained also the basic mixtures (53), (54), (55), (58) and (61), by the interaction of ammonia and mercuric chloride,

<sup>1</sup> G-K : 837.

<sup>2</sup> Jsb. Chem. 1891, 585.

<sup>3</sup> G-K : 837.

<sup>4</sup> Fürth : Monatsh. 23, 1155.

<sup>5</sup> Ann. 305, 213.

<sup>6</sup> André : Compt. rend. 108, 1110 and 1165; Ray : J. Chem. Soc. 81, 648; Sen: Z. anorg. Chem. 33, 206.

<sup>7</sup> G-K : 838.

<sup>8</sup> Compt. rend. 108, 233, 290, 1108 and 1164.

in some cases with, in others without the introduction of potassium hydroxide into the reaction mixture. In view of the fact that at least some of André's preparations have been assumed to be chemical individuals,<sup>1</sup> it may be pointed out that the conditions under which he worked were ideal for the formation of basic mixtures, and that, in all probability, his preparations were not compounds at all, but were mixtures which happened to approximate molecular proportions.

Millon was well aware of the danger of reporting mixtures of the mercury nitrogen compounds as chemical individuals. He tells us in one place<sup>2</sup> that by pouring ammonia into solutions of mercuric chloride he obtained precipitates containing an amount of mercury varying from 75.5 to 84.7 per cent., depending upon the temperature of the mercuric chloride solution and the extent to which the washing was carried.

64.  $\text{Hg}_2\text{NH}_2\text{OBr}$ . 65.  $\text{Hg}_2\text{NH}_4\text{O}_2\text{Br}$ . 66.  $\text{Hg}_4\text{N}_2\text{H}_2\text{OBr}_2$ . Hofmann and Marburg<sup>3</sup> prepared the bromide of Millon's base corresponding to the first of the preceding formulas by the action of dilute hydrobromic acid on Millon's base, while by the action of ammonia on a solution of mercuric bromide, which presumably should give the same compound, they obtained a product of the second formula.<sup>4</sup> Rây<sup>5</sup> has obtained a bromide corresponding to the third formula.

67.  $\text{Hg}_2\text{NH}_2\text{OI}$ . This compound, Nessler's precipitate, has frequently been the subject of investigation.<sup>6</sup> It is formed by the action of aqua ammonia on mercuric iodide and in general when mercuric iodide and ammonia are brought together in alkaline solution. According to François<sup>7</sup> the anhydrous compound,  $\text{Hg}_2\text{NI}$ , alone, exists.

68.  $\text{Hg}_2\text{NH}_2\text{OCN}$ . The cyanide of Millon's base has been obtained by Hofmann and Marburg,<sup>8</sup> in the form of brilliant yellow crystals, by the action of alcoholic ammonia on mercuric cyanide.

69.  $\text{Hg}_2\text{NH}_3\text{OF}_2$ .<sup>9</sup> Finkener<sup>10</sup> has obtained an amorphous powder of this composition by the action of ammonia on a solution of mercuric fluoride. The compound may be formulated as a hydrated ammonobasic fluoride,  $\text{Hg}_2\text{NHF}_2 \cdot \text{H}_2\text{O}$ , or as a mixture of Böhm's compound,  $\text{NH}_2\text{HgF}$ , with the hydrobasic salts,  $\text{HOHgF}$ , as indicated in the table above.

<sup>1</sup> Watts' Dict. Chem. 3, 208. (1892)

<sup>2</sup> Ann. chim. phys. (3) 18, 421.

<sup>3</sup> Ann. 305, 212.

<sup>4</sup> Z. anorg. Chem. 23, 129.

<sup>5</sup> J. Chem. Soc. 81, 649.

<sup>6</sup> G-K : 829.

<sup>7</sup> Compt. rend. 130, 571.

<sup>8</sup> Z. anorg. Chem. 23, 130.

<sup>9</sup> Ley, in Abegg's Handbuch der anorganischen Chemie, 2.2, 676, erroneously gives the formula,  $\text{OHg}_2\text{NH}_2\text{F}$ .

<sup>10</sup> G-K : 843.



## NITRATES.

The following basic nitrates have been found described in the literature. The empirical formulas are given in the first column. In the second column they are given as basic mixtures after the manner used in formulating the chlorides above, notwithstanding the fact that the nitrate,  $\text{NH}_2\text{HgNO}_3$ , corresponding to the infusible white precipitate has never been prepared.

TABLE V.

I.	II.
70. $\text{Hg}_2\text{N}_3\text{H}_{10}\text{O}_2 \cdot 3\text{NO}_3$	$\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O} \cdot \text{NH}_2\text{HgNO}_3$
71. $\text{Hg}_2\text{N}_3\text{H}_{12}\text{O}_2 \cdot 3\text{NO}_3$	$\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O} \cdot \text{NH}_2\text{HgNO}_3$
72. $\text{Hg}_2\text{N}_2\text{H}_6\text{O}_2 \cdot 2\text{NO}_3$	$\text{NH}_2\text{HgNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ or $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_3\text{HgO}$
73. $\text{Hg}_3\text{N}_2\text{H}_4\text{O}_2 \cdot 2\text{NO}_3$	$\text{NH}_2\text{HgNO}_3 \cdot \text{HOHgNHHgNO}_3$
74. $\text{Hg}_3\text{N}_2\text{H}_4 \cdot 4\text{NO}_3$	$\text{Hg}(\text{NO}_3)_2 \cdot 4\text{HgO} \cdot 2\text{Hg}_2\text{NNO}_3$
75. $\text{Hg}_2\text{NH}_2\text{O} \cdot \text{NO}_3$	$\text{HOHgNHHgNO}_3$
76. $\text{Hg}_4\text{N}_2\text{H}_2\text{O} \cdot 2\text{NO}_3$	$\text{HOHgNHHgNO}_3 \cdot \text{Hg}_2\text{NNO}_3$
77. $\text{Hg}_3\text{NH}_2\text{O}_2 \cdot \text{NO}_3$	$\text{HOHgNHHgNO}_3 \cdot \text{HgO}$

71.  $\text{Hg}_2\text{N}_3\text{H}_{12}\text{O}_2 \cdot 3\text{NO}_3$ .<sup>1</sup> This compound, known as Kane's salt, was first prepared<sup>2</sup> by dissolving Soubeiran's salt, (75), or mercuric oxide in a boiling solution of ammonium nitrate and allowing the solution to cool, when the salt crystallizes out in the form of small brilliant needles. Pesci<sup>3</sup> has confirmed the existence of this salt and finds that when heated to  $110^\circ$ — $115^\circ$ , it loses one molecule of water to give a product of the composition of (70) in the table above.

72.  $\text{Hg}_2\text{N}_2\text{H}_6\text{O}_2 \cdot 2\text{NO}_3$ . This compound has been prepared by dissolving Mitscherlich's salt,<sup>4</sup> (73) or Soubeiran's salt,<sup>5</sup> (75), in a solution of ammonium nitrate and evaporating the solution when a compound of the above composition crystallizes out; and also by evaporating to crystallization the solution formed by adding ammonia or ammonium carbonate to a solution of mercuric nitrate until the precipitate at first formed is redissolved.<sup>4</sup> Pesci<sup>6</sup> obtained the same compound by supersaturating a dilute solution of mercuric nitrate with ammonia, a process similar to that which previously had given Pagenstecher the more basic product,  $\text{Hg}_3\text{NH}_2\text{O}_2 \cdot \text{NO}_3$ , (77), and gave it the formula,  $\text{Hg}_2\text{NNO}_3 \cdot \text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{O}$ . This compound is especially interesting for the reason that it approximates in composition the nitric acid analogue of the infusible white precipitate as indicated in the table above.

<sup>1</sup> Fehling, Handwörterb. Chem. (1890), 5, 1099, describes a compound,  $\text{NHg}_2\text{NO}_3 \cdot 2\text{NH}_4\text{NO}_3$ , which can be none other than Kane's salt in the formulation of which the water has been omitted.

<sup>2</sup> Kane: Ann. chim. phys. 72, 248; G-K: 848.

<sup>3</sup> Jsb. Chem. 1890, 630.

<sup>4</sup> G-K: 847.

<sup>5</sup> Kane: Ann. chim. phys. 72, 248.

<sup>6</sup> J. Chem. Soc. 60, 268.

73.  $\text{Hg}_3\text{N}_2\text{H}_4 \cdot 2\text{ONO}_3$ ,  $\text{Hg}_3\text{N}_2\text{H}_6\text{O}_2 \cdot 2\text{NO}_3$ , or  $\text{Hg}_3\text{N}_2\text{H}_2 \cdot 2\text{N}_3\text{O}$  This so-called Mitscherlich's salt is obtained as a white, delicate precipitate by treating dilute, barely acid mercuric nitrate solution, with dilute aqueous ammonia not in excess, and by boiling the basic nitrate,  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO}$ , with a solution of ammonium nitrate.<sup>1</sup> Pesci found that this compound is also formed by the action of cold water on the salt  $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{NH}_4$  (26). Fehling<sup>2</sup> describes a compound  $3\text{Hg}_2\text{NNO}_3 \cdot \text{NH}_4\text{NO}_3$ , which can be none other than Mitscherlich's salt in the formulation of which the water has been omitted.

74.  $\text{Hg}_6\text{N}_2\text{O}_4 \cdot 4\text{NO}_3$ . This complex, to which the formula,  $2[\text{NHg}(\text{HgOHg})\text{OHgNO}_3] \cdot \text{Hg}(\text{NO}_3)_2$ , has been given was prepared by Hirzel<sup>3</sup> by thoroughly triturating freshly precipitated mercuric oxide with a moderately concentrated solution of ammonium nitrate, followed by washing of the residue with hot water. The powder thus obtained was obviously a mixture. In any event Pesci<sup>1</sup> was unable to prepare such a compound but obtained instead the compound (46).

75.  $\text{Hg}_2\text{NH}_2\text{O} \cdot \text{NO}_3$ . The nitrate of Millon's base, known also as Soubeiran's salt, has been prepared by the action of slight excess of ammonia on a dilute solution of mercuric nitrate,<sup>4</sup> by the action of boiling water on Mitscherlich's salt,<sup>5</sup> (73), and by the action of water on Kane's salt,<sup>7</sup> (71). More recently Fürth<sup>6</sup> has prepared this compound by the action of ammonium nitrate on a solution of mercury acetamide.

By the action of water on certain of the basic nitrates here given, Pesci has obtained a product which he calls dimercuriammonium nitrate. He is so thoroughly convinced that the compound,  $\text{Hg}_2\text{NNO}_3$ , is a never-failing constituent of these nitrates that he apparently refers to  $\text{Hg}_2\text{NNO}_3$ , and  $\text{HOHgNHgNO}_3$  indifferently as dimercuriammonium nitrate. It is not possible from a study of the abstracts of his papers to know always to which compound he refers.

76.  $\text{Hg}_4\text{N}_2\text{H}_2\text{O} \cdot 2\text{NO}_2$ . Rây<sup>8</sup> obtained a compound of this composition by treating his dimercuriammonium nitrite (47) with nitric acid.

77.  $\text{Hg}_3\text{NH}_2\text{O}_2 \cdot \text{NO}_3$ . Pagenstecher obtained this compound, known as dioxytrimercuriammonium nitrate, by treating a concentrated solution of mercuric nitrate with a large excess of ammonia. Pagenstecher probably had a mixture in his hands.

<sup>1</sup> G-K : 846; Pesci : J. Chem. Soc. 60, 268.

<sup>2</sup> Handwörterb. Chem. (1890) 5, 1099.

<sup>3</sup> G-K : 847.

<sup>4</sup> Jsb. Chem. 1890, 630; Z. anorg. Chem. 21, 372.

<sup>5</sup> G-K : 846.

<sup>6</sup> Ann. chim. phys. 72, 549.

<sup>7</sup> Monatsh. 23, 1156.

<sup>8</sup> Z. anorg. Chem. 33, 209.

<sup>9</sup> G-K : 846.

## SULPHATES.

TABLE VI.

I.	II.
78. $\text{Hg}_{20}\text{N}_{38}\text{H}_{144}\text{O}_{16}\cdot 19\text{SO}_4$	$19(\text{HgSO}_4\cdot 2\text{NH}_3)\cdot 15\text{H}_2\text{O}\cdot \text{HgO}$
79. $\text{Hg}_2\text{N}_2\text{H}_6\text{O}\cdot \text{SO}_4$	$\text{HgSO}_4\cdot 2\text{NH}_3\cdot \text{HgO}$ or $(\text{NH}_2\text{Hg})_2\text{SO}_4\cdot \text{H}_2\text{O}$
80. $\text{Hg}_3\text{N}_2\text{H}_6\text{O}_2\cdot \text{SO}_4$	$\text{HgSO}_4\cdot 2\text{NH}_3\cdot 2\text{HgO}$ or $\text{NH}_3\text{Hg}-\text{SO}_4-\text{HgNHHgOH}\cdot \text{H}_2\text{O}$
81. $\text{Hg}_7\text{N}_4\text{H}_2\cdot 2\text{SO}_4$	$(\text{NH}_2\text{Hg})_2\text{SO}_4\cdot 3(\text{Hg}_2\text{N})_2\text{SO}_4$
82. $\text{Hg}_7\text{N}_4\text{H}_8\text{O}_3\cdot 2\text{SO}_4$	$(\text{NH}_2\text{Hg})_2\text{SO}_4\cdot 3(\text{HOHgNHHg})_2\text{SO}_4$
83. $\text{Hg}_4\text{N}_2\text{H}_2\text{O}\cdot \text{SO}_4$	$(\text{HOHgNHHg})_2\text{SO}_4\cdot (\text{Hg}_2\text{N})_2\text{SO}_4$
84. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2\cdot \text{SO}_4$	$(\text{HOHgNHHg})_2\text{SO}_4$
85. $\text{Hg}_5\text{N}_2\text{H}_4\text{O}_3\cdot \text{SO}_4$	$(\text{HOHgNHHg})_2\text{SO}_4\cdot \text{HgO}$ .

78.  $\text{Hg}_{20}\text{N}_{38}\text{H}_{144}\text{O}_{16}\cdot 19\text{SO}_4$ . By saturating concentrated aqua ammonia with mercuric sulphate, adding an equal volume of aqua ammonia saturated at  $0^\circ$ , and allowing the solution to stand for twenty-four hours, Pesci<sup>1</sup> obtained a crop of well formed, prismatic crystals which gave analytical data leading to the above complex formula. Pesci gave his product the very unlikely formula,  $5(\text{Hg}_2\text{N})_2\text{SO}_4\cdot 14(\text{NH}_4)_2\text{SO}_4\cdot 16\text{H}_2\text{O}$ . The crystals lose water readily on exposure to the air, and are converted into the sulphate of Millon's base, (84) by the action of cold water. As indicated in the table above, Pesci's product was, in all probability a partially dehydrated, slightly basic specimen of the compound  $\text{HgSO}_4\cdot 2\text{NH}_3\cdot \text{H}_2\text{O}$ , (28).

79.  $\text{Hg}_2\text{N}_2\text{H}_6\text{O}\text{SO}_4$ , 80.  $\text{Hg}_3\text{N}_2\text{H}_6\text{O}_2\cdot \text{SO}_4$ , Millon<sup>2</sup> prepared these two complexes, together with the compound,  $\text{HgSO}_4\cdot 2\text{NH}_3$  (27), all in the form of large prismatic crystals, by dissolving mercuric sulphate in concentrated aqua ammonia to saturation, and evaporating the solution in an atmosphere of ammonia. Following Millon's directions, Pesci<sup>3</sup> was unable to obtain either of these basic sulphates, but obtained instead, the sulphate of Millon's base or ammonia turpith (84).

82.  $\text{Hg}_7\text{N}_4\text{H}_8\text{O}_3\cdot 2\text{SO}_4$ . Schmieder<sup>4</sup> obtained a product of this composition by the action of cold water on  $\text{HgSO}_4\cdot 2\text{NH}_3\cdot \text{H}_2\text{O}$ , (28), and by pouring a solution of ammonium sulphate saturated with mercuric oxide into much cold water. He found that boiling water removes ammonium sulphate, and that boiling potassium hydroxide solution gradually converts the compound into mercuric oxide. Schmieder found also that his compound is reconverted into  $\text{HgSO}_4\cdot 2\text{NH}_3\cdot \text{H}_2\text{O}$  by the action of concentrated ammonium sulphate solution. Following Schmieder's directions, Pesci<sup>5</sup> obtained a compound of the same composition, which he found to be converted into ammonia turpith, (84), by the action of boiling water, and which contrary to Jørgensen,<sup>6</sup> loses three molecules of

<sup>1</sup> Jsb. Chem. 1890, 631.

<sup>2</sup> G-K : 825.

<sup>3</sup> J. Chem. Soc. 60, 269.

<sup>4</sup> G-K : 826.

<sup>5</sup> J. Chem. Soc. 60, 269.

<sup>6</sup> G-K : 824.

water when heated to  $115^{\circ}$ , to give a compound of the composition,  $\text{Hg}_4\text{N}_4\text{H}_2 \cdot 2\text{SO}_4$ , (81) in the table above.

84.  $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2 \cdot \text{SO}_4$ . 83.  $\text{Hg}_4\text{N}_2\text{H}_2\text{O} \cdot \text{SO}_4$ . Ammonia turpith, or the sulphate of Millon's base is the most thoroughly established of the mixed hydrobasic-ammonobasic sulphates of mercury. Jørgensen<sup>1</sup> gives the result of analyses by Kane, Millon, Hirzel and Schmieder which agree closely with the first of the above formulas. The compound is formed by the action of aqua ammonia on a solution of mercuric sulphate; by dissolving mercuric sulphate in concentrated aqua ammonia and diluting with water; by the action of a solution of ammonium sulphate on mercuric oxide or on the basic sulphate of mercury,  $\text{HgSO}_4 \cdot 2\text{HgO}$ ; by the action of boiling water on  $\text{HgSO}_4 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ ; and by the action of dilute sulphuric acid on Millon's base, or on the hydro-ammonio base,  $\text{Hg} : \text{N} - \text{Hg} - \text{OH}$ ; all of which methods are in strict accordance with the theory outlined elsewhere in this paper for the formation of mixed hydrobasic-ammonobasic salts. It has most frequently been obtained as a white or yellowish dense powder, occasionally as a crystalline crust. Pesci<sup>2</sup> obtained it in the form of octahedral crystals. According to Schmieder<sup>3</sup> ammonia turpith does not lose water at  $115^{\circ}$ .

Abegg,<sup>4</sup> and Danmer,<sup>5</sup> in their respective dictionaries, erroneously describe ammonia turpith under the second of the above formulas. Rây<sup>6</sup> also uses this formula but gives no analytical data supporting it.

85.  $\text{Hg}_5\text{N}_2\text{H}_4\text{O}_3 \cdot \text{SO}_4$ . Schmieder<sup>7</sup> prepared this compound by dissolving  $\text{HgSO}_4 \cdot 2\text{NH}_2 \cdot \text{H}_2\text{O}$  (28) in dilute sulphuric acid, pouring the solution into an excess of a dilute solution of potassium hydroxide and washing the precipitate with warm water. Following Schmieder's directions Pesci<sup>8</sup> failed to get this compound but obtained ammonia turpith, (84), instead.

#### MISCELLANEOUS SALTS

In addition to the halogen salts, the nitrates and sulphates given in the tables above, a considerable number of other salts found described in the literature are listed together in

TABLE VII.

I.	II.
86. $\text{Hg}_4\text{N}_2\text{H}_2\text{O} \cdot 2\text{NO}_2$	$\text{HOHgNHHgNO}_2 \cdot \text{Hg}_2\text{NNO}_2$
87. $\text{Hg}_2\text{NH}_2\text{O} \cdot \text{NO}_2$	$\text{HOHgNHHgNO}_2$
88. $\text{Hg}_2\text{NH}_2\text{O} \cdot \text{BrO}_3$	$\text{HOHgNHHgBrO}_3$

<sup>1</sup> G-K : 824.

<sup>2</sup> J. Chem. Soc. 60, 269.

<sup>3</sup> G-K : 824.

<sup>4</sup> Handb. anorg. Chem. 2.2, 677.

<sup>5</sup> Ibid. 2.2, 906.

<sup>6</sup> Proc. Chem. Soc. 20, 250.

<sup>7</sup> G-K : 827.

<sup>8</sup> J. Chem. Soc. 60, 269.

TABLE VII. *Continued.*

I.	II.
89. $\text{Hg}_2\text{N}_3\text{H}_{10}\text{O}_3\cdot 3\text{IO}_3$	$\text{Hg}(\text{IO}_3)_2\cdot 2\text{NH}_3\cdot \text{H}_2\text{O}\cdot \text{NH}_2\text{HgIO}_3$
90. $\text{Hg}_6\text{N}_3\text{H}_{12}\text{O}_5\cdot 2\text{IO}_4$	$\text{NH}_2\text{HgIO}_4\cdot 2\text{HgO}\cdot \text{NH}_3\cdot \frac{1}{2}\text{H}_2\text{O}$
91. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2\cdot \text{CrO}_4$	$(\text{HOHgNHHg})_2\text{CrO}_4$
92. $\text{Hg}_8\text{N}_2\text{H}_4\text{O}_3\cdot 4\text{CrO}_4$	$3\text{HgCrO}_4\cdot \text{HgO}\cdot (\text{HOHgNHHg})_2\text{CrO}_4$
93. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2\cdot \text{SeO}_4$	$(\text{HOHgNHHg})_2\text{SeO}_4$
94. $\text{Hg}_5\text{N}_2\text{H}_4\text{O}_2\cdot 2\text{SO}_3$	$(\text{HgSO}_3\cdot 2\text{HgO})\cdot (\text{NH}_2\text{Hg})_2\text{SO}_3$ or $\text{HgSO}_3\cdot (\text{HOHgNHHg})_2\text{SO}_3$
95. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2\cdot \text{CO}_3$	$(\text{HOHgNHHg})_2\text{CO}_3$
96. $\text{Hg}_6\text{N}_4\text{H}_{10}\text{O}_5\cdot 2\text{CO}_3$	$(\text{HOHgNHHg})_2\text{CO}_3\cdot \frac{1}{2}\text{H}_2\text{O}$
97. $\text{Hg}_4\text{N}_2\text{H}_6\text{O}_3\cdot \text{CO}_3$	$(\text{HOHgNHHg})_2\text{CO}_3\cdot \text{H}_2\text{O}$
98. $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2\cdot \text{C}_2\text{O}_4$	$(\text{HOHgNHHg})_2\text{C}_2\text{O}_4$
99. $\text{Hg}_2\text{NH}_2\cdot \text{PO}_4$	$\text{Hg} : \text{PO}_4\text{-Hg-NH}_2$
100. $\text{Hg}_3\text{NH}_2\text{O}\cdot \text{PO}_4$	$\text{Hg} : \text{PO}_4\text{-Hg-NH-Hg-OH}$
101. $\text{Hg}_{10}\text{N}_5\text{H}_{22}\text{O}_{12}\cdot \text{PO}_4$	$\text{Hg}_2\text{NH}_2\text{PO}_4\cdot 4(2\text{HgO}\cdot \text{NH}_3\cdot \text{H}_2\text{O})$
102. $\text{Hg}_2\text{NH}_2\cdot \text{AsO}_4$	$\text{Hg} : \text{AsO}_4\text{-Hg-NH}_2$
103. $\text{Hg}_8\text{N}_6\text{H}_{10}\text{O}_3\cdot 3\text{C}_4\text{H}_4\text{O}_6$	$2(\text{NH}_2\text{Hg})_2\text{C}_4\text{H}_4\text{O}_6\cdot (\text{Hg}_2\text{N})_2\text{C}_4\text{H}_4\text{O}_6\cdot \text{H}_2\text{O}$
104. $\text{Hg}_6\text{N}_2\text{H}_{10}\text{O}_5\cdot 2\text{C}_4\text{H}_4\text{O}_6$	$(\text{HOHgNHHg})_2\text{C}_4\text{H}_4\text{O}_6\cdot \frac{1}{2}\text{H}_2\text{O}$
105. $\text{Hg}_3\text{N}_2\text{H}_8\text{O}_3\cdot \text{C}_4\text{H}_4\text{O}_6$	$\text{NH}_2\text{Hg-C}_4\text{H}_4\text{O}_6\text{-HgNHHgOH}\cdot 2\text{H}_2\text{O}$
106. $\text{Hg}_4\text{N}_2\text{H}_{20}\cdot 7\text{C}_7\text{H}_5\text{O}_3$	$3[\text{Hg}(\text{C}_7\text{H}_5\text{O}_3)_2\cdot 2\text{NH}_3]\cdot \text{NH}_2\text{HgC}_7\text{H}_5\text{O}_3$
107. $\text{Hg}_2\text{NH}_4\text{O}_2\cdot \text{C}_2\text{H}_3\text{O}_2$	$\text{HOHgNHHgC}_2\text{H}_3\text{O}_2\cdot \text{H}_2\text{O}$
108. $\text{Hg}_2\text{NH}_2\text{O}\cdot \text{SCN}$	$\text{HOHgNHHgSCN}$

86.  $\text{Hg}_4\text{N}_2\text{H}_2\text{O}\cdot 2\text{NO}_2$ . 87.  $\text{Hg}_2\text{NH}_2\text{O}\cdot \text{NO}_2$ . Besides the formula,  $\text{Hg}_2\text{N}\cdot \text{NO}_2(47)$ , which Rây assigns to his dimercuriammonium nitrite, he, in other places,<sup>1</sup> gives his compound the formula,  $2\text{Hg}_2\text{NNO}_2\cdot \text{H}_2\text{O}$ . Hofmann and Marburg<sup>2</sup> state that the formula is  $\text{Hg}_2\text{NH}_2\text{O}\cdot \text{NO}_2$ , and that the compound does not lose water either over sulphuric acid or when heated to  $125^\circ$  in a current of ammonia.

88.  $\text{Hg}_2\text{NH}_2\text{O}\cdot \text{BrO}_3$  or  $\text{Hg}_4\text{N}_2\text{H}_6\text{O}_3\cdot 2\text{BrO}_3$ . Rammelsberg<sup>3</sup> obtained a compound of the former formula as a yellow, bulky powder by the action of ammonia on a solution of mercuric bromate. In a later paper Rammelsberg<sup>4</sup> gives the formula  $2\text{NHg}_2\text{BrO}_3\cdot 3\text{H}_2\text{O}$ .

89.  $\text{Hg}_2\text{N}_3\text{H}_{10}\text{O}_3\cdot 3\text{IO}_3$ ,  $\text{Hg}_2\text{N}_3\text{H}_{12}\text{O}_2\cdot 3\text{IO}_3$ .  $\text{Hg}_2\text{N}_3\text{H}_8\cdot 3\text{IO}_3$ . Millon<sup>5</sup> prepared a compound of the composition of the first or second formula above by the action of an excess of aqua ammonia on mercuric iodate. By heating mercuric iodate with ammonia Rammelsberg<sup>6</sup> obtained a product to which he gave the formula,  $\text{Hg}_2\text{NIO}_3\cdot 2\text{NH}_4\text{IO}_3$ , corresponding to the third of the above formulas. Very probably the compounds of Millon and Rammelsberg were mixtures of mercuric iodate with ammonia of crystallization and the ammonobasic salt,  $\text{NH}_2\text{HgIO}_3$ , as indicated by the formula,  $\text{Hg}(\text{IO}_3)_2\cdot 2\text{NH}_3\cdot \text{NH}_2\text{HgIO}_3\cdot x\text{H}_2\text{O}$ .

<sup>1</sup> Pr. Chem. Soc. 17, 96; and 18, 85; Z. anorg. Chem. 33, 194.

<sup>2</sup> Ann. 305, 214.

<sup>3</sup> G-K : 833.

<sup>4</sup> J. pr. Chem. 146, 568.

<sup>5</sup> G-K : 832; Ann. chim. phys. (3) 18, 411.

<sup>6</sup> J. pr. Chem. 146, 568.

90.  $\text{Hg}_5\text{N}_4\text{H}_{12}\text{O}_5 \cdot 2\text{IO}_4$ . Rammelsberg's<sup>1</sup> product of this composition, which he prepared by digesting the basic periodate,  $\text{Hg}(\text{IO}_4)_2 \cdot 4\text{HgO}$ , with ammonia, was very probably, a mixture of  $\text{NH}_2\text{HgIO}_4$  and Millon's base,  $\text{NH}_2\text{HgIO}_4 \cdot (2\text{HgO} \cdot \text{NH}_3 \cdot x\text{H}_2\text{O})$ .

91.  $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2 \cdot \text{CrO}_4$ . Hirzel<sup>2</sup> prepared this compound, the chromate of Millon's base, as a light yellow amorphous powder, by the action of aqua ammonia on the following compound, (92). It has also been prepared by Heusgen<sup>3</sup> by the action of boiling ammonia or potassium hydroxide solution on the ammoniated mercuric dichromate, (31), or by diluting a solution of mercuric chromate in ammonium chromate with much water.

92.  $\text{Hg}_2\text{N}_2\text{H}_4\text{O}_3 \cdot 4\text{CrO}_4$ . Hirzel<sup>4</sup> obtained a dense, orange-red, basic mixture of this composition by heating mercuric oxide with a solution of ammonium dichromate.

93.  $\text{Hg}_1\text{N}_2\text{H}_4\text{O}_2 \cdot \text{SeO}_4$ . According to Watts' Dictionary<sup>5</sup> the selenate of Millon's base has been prepared by dissolving the basic selenate,  $\text{HgSeO}_4 \cdot 2\text{HgO}$ , in concentrated aqueous ammonia and precipitating by the addition of much water.

94.  $\text{Hg}_5\text{N}_2\text{H}_4\text{O}_2 \cdot 2\text{SO}_3$ .<sup>6</sup>  $\text{Hg}_3\text{N}_2\text{H}_2\text{O} \cdot 2\text{SO}_3$ .<sup>7</sup> This basic mixture was prepared by Hirzel by the action of potassium hydroxide on a solution of the double salt,  $\text{HgSO}_3 \cdot (\text{NH}_4)_2\text{SO}_3$ .

95.  $\text{Hg}_4\text{N}_2\text{H}_4\text{O}_2 \cdot \text{CO}_3$ . 96.  $\text{Hg}_2\text{N}_4\text{H}_{10}\text{O}_5 \cdot 2\text{CO}_3$ . 97.  $\text{Hg}_1\text{N}_2\text{H}_6\text{O}_3 \cdot \text{CO}_3$ . Rammelsberg<sup>8</sup> prepared a carbonate of Millon's base, corresponding to the first of these formulas, by boiling the base with a solution of sodium carbonate. A compound corresponding to the second formula was prepared by Millon,<sup>9</sup> by the action of carbon dioxide on a suspension of Millon's base, and by treating the base with ammonium carbonate or acid potassium carbonate solutions. Hirzel<sup>3</sup> obtained the same product by boiling an ammonium carbonate solution in contact with mercuric oxide. A product of the composition represented by the third formula was obtained by Hirzel<sup>10</sup> by digesting mercuric oxide with ammonium carbonate solution in the cold. Certainly these compounds cannot be essentially different.

98.  $\text{Hg}_1\text{N}_2\text{H}_4\text{O}_2 \cdot \text{C}_2\text{O}_4$ . Millon<sup>11</sup> obtained this oxalate as a white pow-

<sup>1</sup> J. pr. Chem. 146, 569.

<sup>2</sup> Jsb. Chem. 1852, 421.

<sup>3</sup> Ibid. 1886, 478.

<sup>4</sup> Ibid. 1852, 421.

<sup>5</sup> (1892) 3, 209.

<sup>6</sup> G-K : 823.

<sup>7</sup> Danimer : Handb. anorg. Chem. 2.2, 906 (1894).

<sup>8</sup> J. pr. Chem. 146, 567.

<sup>9</sup> G-K : 819; Ann. chim. phys. 18, 333.

<sup>10</sup> G-K : 819; Jsb. Chem. 1852, 421.

<sup>11</sup> Ann. chim. phys. (3) 18, 409.

der by digesting mercuric oxalate with aqua ammonia in excess. The same compound was also prepared by Hirzel<sup>1</sup> by the action of a solution of ammonium oxalate on mercuric oxide.

99.  $\text{Hg}_2\text{NH}_2\cdot\text{PO}_4$ . This compound was prepared by Rây<sup>2</sup> and by him formulated as dimercuriammonium acid phosphate,  $\text{Hg}_2\text{NPO}_4\text{H}_2$ . The formula given in the table represents it as an ammonobasic salt.

100.  $\text{Hg}_3\text{NH}_2\text{O}\cdot\text{PO}_4$ . Hirzel<sup>3</sup> obtained a white powder of this composition by the action of a solution of ammonium phosphate on mercuric oxide.

101.  $\text{Hg}_{10}\text{N}_5\text{H}_{22}\text{O}_{12}\cdot\text{PO}_4$ . Rammelsberg<sup>4</sup> obtained a product to which he gave the formula,  $(\text{NHg}_2)_3\text{PO}_4\cdot 2\text{NHg}_2\text{OH}\cdot 10\text{H}_2\text{O}$ , by heating Millon's base with an excess of phosphoric acid. His preparation may be formulated as a mixture of the compound,  $\text{Hg}_2\text{NH}_2\text{PO}_4$ , (98), with unchanged Millon's base as indicated in the preceding table.

102.  $\text{Hg}_2\text{NH}_2\text{AsO}_4$ . A compound of this composition was prepared by Hirzel<sup>5</sup> by the action of a solution of ammonium arsenate upon mercuric oxide.

103.  $\text{Hg}_8\text{N}_6\text{H}_{10}\text{O}\cdot 3\text{C}_4\text{H}_4\text{O}_6$ . A product of this composition was obtained by Balestra<sup>6</sup> by diluting an ammonium tartrate solution of mercuric oxide with water. The preparation to which Balestra gave the formula,  $2(\text{Hg}_2\text{N})_2\text{C}_4\text{H}_4\text{O}_6\cdot (\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6\cdot \text{H}_2\text{O}$ , was in all probability a mixture.

104.  $\text{Hg}_8\text{N}_4\text{H}_{10}\text{O}_3\cdot 2\text{C}_4\text{H}_4\text{O}_6$ . Balestra<sup>7</sup> prepared this compound, to which he gave the formula,  $2[(\text{NHg}_2)_2\text{C}_4\text{H}_4\text{O}_6]\cdot 5\text{H}_2\text{O}$  by dissolving mercuric tartrate in aqua ammonia and evaporating the solution over sulphuric acid. The preparation was probably an imperfectly dried specimen of tartrate of Millon's base.

105.  $\text{Hg}_3\text{N}_2\text{H}_8\text{O}_3\cdot \text{C}_4\text{H}_4\text{O}_6$ . Hirzel<sup>8</sup> found that mercuric oxide dissolves for ammonium tartrate giving a thick viscous solution. On evaporation well formed crystals were deposited which, however, he did not succeed in sufficiently freeing from mother liquor for analysis. As is uniformly the case when mercuric salts separate from a solution containing a sufficient concentration of the corresponding ammonium salt, there is formed the normal salt with ammonia of crystallization, so here in all probability, Hirzel had an ammoniated tartrate in his hands. When the viscous solution was diluted Hirzel obtained a precipitate of the above composition which may be formulated as a hydrated mixture of  $(\text{NH}_2\text{Hg})_2\text{C}_4\text{H}_4\text{O}_6$  and  $(\text{HOHgNHHg})_2\text{C}_4\text{H}_4\text{O}_6$ .

<sup>1</sup> Jsb. Chem. 1852, 421.

<sup>2</sup> Pr. Chem. Soc. 20, 250.

<sup>3</sup> G-K : 820.

<sup>4</sup> J. pr. Chem. 146, 567.

<sup>5</sup> Jsb. Chem. 1852, 420.

<sup>6</sup> Ibid. 1892, 816.

<sup>7</sup> l. c.

<sup>8</sup> Jsb. Chem. 1852, 422.

106.  $\text{Hg}_4\text{N}_2\text{H}_{20}\cdot 7\text{C}_7\text{H}_5\text{O}_3$ . Balestra<sup>1</sup> prepared this compound by dissolving mercuric oxide in ammonium salicylate and evaporating the solution to crystallization. Balestra gave his product the formula,  $2\text{Hg}_2\text{N}\cdot\text{C}_7\text{H}_5\text{O}_3\cdot\text{NH}_4\cdot\text{C}_7\text{H}_5\text{O}_3$ . More probably, however, it was a somewhat ammonolyzed specimen of the normal salt as indicated by the formula in Table VII. It is decomposed by the action of water.

107.  $\text{Hg}_2\text{NH}_4\text{O}_2\cdot\text{C}_2\text{H}_3\text{O}_2$ . Hirzel<sup>2</sup> obtained a compound of this composition by heating the ammoniated mercuric acetate, (30). According to Gerresheim<sup>3</sup> the acetate of Millon's base is formed by the action of acetic acid on the base.

108.  $\text{Hg}_2\text{NH}_2\text{O}\cdot\text{SCN}$  This sulphocyanide of Millon's base<sup>4</sup> has been prepared by the action of ammonia on a solution of mercuric sulphocyanide, on a solution of the double potassium mercuric sulphocyanide, and by the action of water on the ammoniated mercuric sulphocyanide, (29). It forms a yellow amorphous powder.

The material contained in this paper was collected during the earlier part of the past year, for the purpose of determining whether or not the writer's theory concerning the constitution of the mercury nitrogen compounds is worthy of further consideration, and to serve as a basis for a thorough experimental review of the whole field. It was not the original intention to publish, until after a reasonable amount of experimental work had been done, which, it is expected, will eliminate as definite chemical compounds many of the products which have been described in the past. However, as a result of the demoralization of our laboratory by the great earthquake and the consequent impossibility of carrying on much research work in the immediate future, it seems advisable to print this summary at the present time. Experimental work will be continued as soon as possible.

STANFORD UNIVERSITY, CALIFORNIA, AUTUMN, 1906.

## DETERMINATION OF ANTIMONY AND TIN IN BABBITT, TYPE METAL OR OTHER ALLOYS,

[APPLICABLE ALSO WHEREVER THE ANTIMONY AND TIN ARE OBTAINED AS SULPHIDES.]

BY WILSON H. LOW.

Received Oct. 11, 1906.

The accurate determination of antimony and tin in alloys has always been a more or less troublesome operation, and almost all of the published

<sup>1</sup> Jsb. Chem. 1892, 816.

<sup>2</sup> Ibid. 1852, 421.

<sup>3</sup> Ann. 195, 378.

<sup>4</sup> Philipp: Ibid. 180, 341. Ehrenberg: J. pr. Chem. 138, 62.