Quinoline Hydrochloride Bismuth Chloride.—Aggregates of transparent prisms were obtained, melting at 212°.

Anal. Calcd. for $C_9H_7N.HCl.BiCl_3.2H_2O$: Cl, 27.38. Found: 27.22.

Quinoline Hydrochloride Manganous Chloride.—Faintly pink, very soluble needles, not melting at 250°.

Anal. Calcd. for $C_9H_7NHCl.Mn.Cl_2.H_2O$; Cl, 34.37; H_2O, 5.82. Found: Cl, 34.27; H_2O, 5.42.

Summary and Conclusions

1. Definite conditions must be employed to yield double salts of quinoline or other bases with metallic chlorides and hydrogen chloride. The same conditions with different metallic chlorides can yield different types of salts.

2. Probably some salts given in the literature are derived products or mixtures of two or more simple types.

3. Some new salts of known types and salts of two new types have been prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

COMPLEX SALTS OF QUINOLINE, MERCURIC HALIDES, WATER AND HYDROHALOGEN ACIDS

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This investigation was undertaken to ascertain what types of salts, as indicated in the previous paper,[1] are possible with mercuric halides and quinoline. The only quinoline salts of mercuric chloride given in the literature are $7Q.3HgCl_2.HCl$ of Gerhardt,[2] $Q.HgCl_2$ of Hofmann,[3] $2Q.HgCl_2.2HCl.2H_2O$ of Borsbach,[4] and $2Q.HgCl_2$, and $11Q.5HgCl_2.HCl$ of Pesci.[5] The only other mercuric halide salts of quinoline are $Q.HgBr_2$ and $Q.HgI_2$ of Borsbach. In this paper new salts of mercury are described of Types II, IV, VI, VII and IX of which Types VI and IX are new for all quinoline salts. All experiments directed to the formation of

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[1] THIS JOURNAL, **48,** 275 (1926).

[2] Gerhardt, *Ann.*, **42,** 312 (1842); **44,** 279 (1842). Gerhardt obtained fine needles using quinoline from alkaloids.

[3] Hofmann, *Ann. chim. phys.*, [3] **9,** 173 (1843). Hofmann treated "leucol" (quinoline obtained from coal distillate) with $HgCl_2$ in alcoholic solution and obtained $C_9H_7N.HgCl_2$ (recalculated data). Pesci's $2C_9H_7N.2HgCl_2$ is identical with Hofmann's salt, since it can be shown that $C_9H_7N.HgCl_2 + C_9H_7N = (C_9H_7N)_2HgCl_2$ and, conversely $(C_9H_7N)_2.HgCl_2 + HgCl_2 = 2(C_9H_7N.HgCl_2)$.

[4] Borsbach, *Ber.*, **23,** 438 (1890).

[5] Pesci, (a) *Gazz. chim. ital.*, [1] **25,** 399 (1895). (b) Pesci contributed Type V and rediscovered Hofmann's salt I. His two anomalous forms, like Gerhardt's one form, are probably mixtures. This conclusion is evidenced by the methods of formation.

$Q.HgCl_2.HCl$, $Q.HgCl_2HCl.H_2O$, $Q.HgCl_2.2HCl$, $Q.2HgCl_2$ and $HgCl_2.HCl$[6] have failed; however, $Q.HgBr_2.HBr$, $Q.HgBr_2.HBr.2H_2O$ and $Q.HgI_2.HI$ were formed.

The only mercuric chloride salts whose existence is definitely established are of Types I, V, VI, VII, VIII and IX. The inter-relations of these six salts are indicated by the following experiments. All forms are converted into Type I by boiling water and quinoline is easily detected in the steam thereof. Continued boiling further hydrolyzes I, for free mercuric chloride increases in the solution, as can be proved by adding quinoline, whereby I is reprecipitated. With concd. hydrochloric acid, Type VIII is formed from the other types. With quinoline, I yields V and conversely, with mercuric chloride, V yields I. With quinoline hydrochloride, I yields VI and with quinoline, IX yields VI.

All of these salts, except VIII, are best prepared in anhydrous solutions, such as of alcohol, acetone, acetonitrile or acetic anhydride. It is suspected that the presence of water accounts for the formation of some of the anomalous salts of organic bases and metallic salts, as found in the literature, and this is more probable with primary and secondary bases.

From these experiments it is concluded that the conditions and relative quantities of materials, as well as the nature of the solvent used, are very important in the method of preparation of double salts of organic bases. This is further emphasized by the following observations.

All efforts to prepare salts of Type II, using molecular quantities of mercuric chloride and quinoline hydrochloride, resulted in the formation of salts of Types VII or IX. Here, owing to the great insolubility of $2QHCl.3HgCl_2$, partition in solution resulted in accordance with the equation, $4QHCl + 4HgCl_2 = 2QHCl.3HgCl_2 + 2QHCl.HgCl_2$.

Another type of partition in solution resulted when quinoline mercuric chloride was treated, molecule for molecule, with pyridine in alcohol solution. $2QHgCl_2 + 2C_5H_5N = 2C_5H_5N.HgCl_2 + 2Q.HgCl_2$, white needles, melting at 108°, proving to be $2C_5H_5N.HgCl_2$, prepared by Pesci[7] was obtained as the first crop of crystals.

When bromine or iodine was involved in these salts, in general, analogous salts were formed. However, with bromine Type IV resulted when II was sought, and with iodine Types II and VII resulted when Types IV and VIII were sought. These experiments demonstrate, therefore, that the specific affinities of the respective halogens can exercise an influence on the nature of the salt formed, when all other conditions are held constant.

The presence of traces of water in the solvents always gave rhombo-

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[6] That mercuric chloride tends to unite with HCl is evidenced in the literature. Ditte, *Ann. chim. phys.*, [5] **22**, 551 (1881). Berthelot, *ibid.*, [5] **29**, 231 (1883). Le Blanc and Noyes, *Z. physik. Chem.*, **6**, 389 (1890).

[7] Ref. 5 a, p. 428.

hedrons of compounds of Type VIII when other types of salts such as V, VI and IX were sought. In general the appearance of two crystalline forms indicated faulty technique employed to prepare a desired salt.

Experimental Part

Type I

Quinoline Mercuric Chloride was first prepared by Hofmann in 1843. It can be prepared either in water or alcohol by treatment of quinoline with an excess of mercuric chloride or by treatment of the corresponding compound of Type V with mercuric chloride. It crystallizes from hot water as prismatic needles and from alcohol, acetone, benzene, etc., as large, transparent, rhombohedral prisms and plates with asymmetrical beveled and truncated angles. It is less soluble in alcohol than are the corresponding compounds of Type V. It melts sharply at 223.5°. With quinoline it yields the Type V compound, with hydrochloric acid it yields the Type VIII and with quinoline hydrochloride it yields the Type VI compound.

The analogous bromide and iodide were prepared by Borsbach.

Type II

The chloride could not be prepared.

Quinoline Hydrobromide Mercuric Bromide.—This was prepared from $C_9H_7NHBr.HgBr_2.2H_2O$ by dehydration and recrystallization from acetonitrile. Large transparent rhombohedrons melting at 121°.

Anal. Calcd. for $C_9H_7NHBr.HgBr_2$: Br, 42.03. Found: 42.12.

Quinoline Hydro-iodide Mercuric Iodide.—This was prepared in hot acetone or in acetonitrile solutions in which it is very soluble. Long, yellow needles melting sharply at 147°, were obtained.

Anal. Calcd. for $C_9H_7NHI.HgI_2$: I, 53.52; Hg, 28.19. Found: I, 53.79; Hg, 28.40.

When heated with water, yellow needles of the compound precipitated with mercuric iodide and fern-like aggregates of diquinoline hydro-iodide mercuric iodide, $2C_9H_7N.HI.HgI_2$; therefore partial partition in solution resulted: $2(C_9H_7NHI.HgI_2) = 2C_9H_7NHI.HgI_2 + HgI_2$.

Type III

Whereas cadmium chloride and manganese chloride form salts of Type III, mercury halides could not be made to yield salts of this type.

Type IV

Quinoline Hydrobromide Mercuric Bromide.—This compound was prepared from equimolecular quantities of the materials in hot acetone solution. Long, transparent, prismatic needles with beveled ends, also coarse prisms, were obtained. The crystals become opaque on exposure to air, soften at 100° and melt at 118°.

Anal. Calcd. for $C_9H_7NHBr.HgBr_2.2H_2O$: Br, 39.53; Hg, 33.08; H_2O, 5.94. Found: Br, 39.60; Hg, 32.97; H_2O, 6.09.

Type V

Diquinoline Mercuric Chloride was first prepared in 1895 by Pesci. It is best prepared by adding slowly an absolute alcoholic solution of mercuric chloride to an absolute alcoholic solution of an excess of two molecular equivalents of quinoline, then heating on the water-bath for such time as is necessary to convert the precipitated compound of Type I into V. It can also be prepared by warming the compound of Type I with quinoline. I have found that it can also be prepared from calomel by heating it with an excess of quinoline, mercury being separated in accordance with the reaction, $2C_9H_7N + Hg_2Cl_2 = (C_9H_7N)_2HgCl_2 + Hg$. It softens at 145° and melts completely only above 200°, indicating thus the decomposition $(C_9H_7N)_2HgCl_2 = C_9H_7N.HgCl_2 + C_9H_7N$. It crystallizes in short, transparent prisms with beveled angles.

Diquinoline Mercuric Bromide.—This was prepared in hot acetonitrile solution. Thin, white, hexagonal plates, softening at 145° and melting at 185°, were obtained.

Anal. Calcd. for $2C_9H_7N.HgBr_2$: Br, 25.84; Hg, 32.43. Found: Br, 25.80; Hg, 32.52.

Diquinoline Mercuric Iodide.—This was prepared in hot acetonitrile solution. Light yellow, hexagonal plates, softening at 145° and melting at 154°, were obtained.

Anal. Calcd. for $2C_9H_7N.HgI_2$: I, 35.62. Found: 35.49.

Type VI

Diquinoline Mercuric Chloride Hydrochloride.—This compound can be prepared in three ways.

a. A hot saturated absolute alcoholic or acetonitrile solution of compound of Type I is treated with a like solution of quinoline hydrochloride. As the solution cools, crystals melting at 141° are obtained.

Anal. Calcd. for $2C_9H_7N.HgCl_2.HCl$: Cl, 18.79; Hg, 35.43. Found: Cl, 18.67; Hg, 35.57.

b. Powdered compound of Type VIII is warmed with quinoline, or with quinoline in absolute alcoholic solution. The powder becomes caked at once owing to chemical reaction. When the cake is dissolved by the application of moderate heat, crystals melting at 139° are obtained.

Anal. Found: Cl, 18.74.

c. Powdered compound of Type IX with or without alcohol is warmed with an excess of quinoline. When the material cools, crystals melting at 143° are obtained.

Anal. Found: Cl, 18.44.

Method *a* is the most direct and yields the purest product; when acetonitrile was used as the solvent, compound of Type VIII came down in the last crop of crystals. The crystals obtained by the three methods were recrystallized from acetone and then all melted at 142°. They are irregular hexagonal plates with asymmetrical truncations. With hot water the substance yields compound of Type I; with concd. hydrochloric acid, it yields compound of Type VIII.

Diquinoline Mercuric Bromide Hydrobromide.—This was prepared in acetonitrile solution from equimolecular quantities of $C_9H_7N.HBr$, $HgBr_2$ and C_9H_7N. Aggregates of short prisms with asymmetrical and acutely beveled ends, m. p. 147°, were obtained.

Anal. Calcd. for $2C_9H_7N.HgBr.HBr$: Br, 34.27. Found: 34.14.

Diquinoline Mercuric Iodide Hydro-iodide.—This was prepared in acetonitrile solution. Compact aggregates of yellow prisms, m. p. 106°, were obtained.

Anal. Calcd. for $2C_9H_7N.HgI_2.HI$: I, 45.30. Found: 45.10.

This compound melts in hot water, gives off quinoline therefrom and yields needles of the compound $C_9H_7NHI.HgI_2$ by loss of quinoline.

Type VII

Diquinoline Hydrochloride Mercuric Chloride.—This compound is prepared from two molecules of quinoline hydrochloride and one of mercuric chloride in anhydrous solvents. It is conveniently prepared from compound of Type VIII by dehydration and recrystallization from acetonitrile, from which it yields long, white needles. From acetone it yields white prisms with rhomboid cross section and beveled ends. It softens at 95° and melts completely only at 130°. It is very insoluble in chloroform or benzene; about 2 g. will dissolve in 1 liter of boiling acetone. It is very soluble in hot acetonitrile or nitrobenzene. It is more soluble in alcohol than compound of Type IX. With hot water it hydrolyzes to compound of Type I. With concd. hydrochloric acid it gives compound of Type VIII.

Anal. Calcd. for $2C_9H_7NHCl.HgCl_2$: Cl, 23.62; Hg, 33.29. Found: Cl, 23.50; Hg, 33.36.

Diquinoline Hydrobromide Mercuric Bromide.—This compound was prepared from the compound $2C_9H_7NHBr.HgBr_2.2H_2O$ by dehydration and recrystallization from hot acetonitrile in which it is very soluble. Large hexagonal plates, softening at 70° and melting at 118°, were obtained.

Anal. Calcd. for $2C_9H_7NHBr.HgBr_2$: Br, 40.96. Found: 40.85.

Diquinoline Hydro-iodide Mercuric Iodide.—This compound can be prepared directly by dissolving two molecular proportions of quinoline hydro-iodide and one of mercuric iodide in hot hydriodic acid. Yellow fern-like aggregates of rhomboid and hexagonal plates, softening at 110° and melting at 160°, were obtained. It melts in hot water, yields therefrom no mercuric iodide but a mixture of the compound $C_9H_7NHI.HgI_2$ and unchanged material.

Anal. Calcd. for $2C_9H_7NHI.HgI_2$: I, 52.42; Hg, 20.71. Found: I, 52.16; Hg, 20.91.

Type VIII

Hydrated Diquinoline Mercuric Chloride Dihydrochloride.—This compound was prepared by Borsbach. When any one of the other types of salts is dissolved in hot concd. hydrochloric acid and the solution is cooled, rhombohedra are obtained. Slow crystallization yields large transparent calcite-like rhombohedra. The crystals melt sharply at 91°.

Anal. Calcd. for $2C_9H_7N.HgCl_2.2HCl.2H_2O$: Cl, 22.21. Found: 22.51.

Boiling this compound with water or treatment with sodium bicarbonate yields compound of Type I. With quinoline in alcoholic solution this substance yields compound of Type VI.

Hydrated Diquinoline Hydrobromide Mercuric Bromide.—This compound was prepared from two molecular proportions of quinoline hydrobromide and one of mercuric bromide in hot hydrobromic acid solution, also in hot ordinary alcohol. The former solution gave rhombohedral plates; the latter, white needles. Both soften below 100° and melt at 120°.

Anal. Calcd. for $2C_9H_7NHBr.HgBr_2.2H_2O$: Br, 39.15; Hg, 24.05; H_2O, 4.42. Calcd. for $2C_9H_7NHBr.HgBr_2$: Br, 40.96; Hg, 25.70. Found: H_2O, 4.52. Found after drying: Br, 40.67; Hg, 25.34.

The analogous iodine salt could not be prepared, since the compound of Type VII always results.

Type IX

Diquinoline Hydrochloride Tri-Mercuric Chloride.—This new compound was formed when equimolecular quantities of quinoline hydrochloride and mercuric chloride were brought together in hot anhydrous solvents, such as alcohol or acetonitrile, glistening short white needles of it being precipitated first; then crystals of the compound

$2C_9H_7NHCl.HgCl_2$ appear. The first crop was filtered off and washed with acetonitrile; m. p., 160°. The salt is best prepared by dissolving two molecular proportions of quinoline hydrochloride and three of mercuric chloride in hot acetonitrile.

Anal. Calcd. for $2C_9H_7NHCl.3HgCl_2$: Cl, 24.76; Hg, 52.53. Found: Cl, 24.57; Hg, 52.50.

With boiling water, compound of Type I is obtained. With concd. hydrochloric acid, it is changed to compound of Type VIII. With quinoline hydrochloride, compound of Type VII is formed. With quinoline, compound of Type VI is obtained. With hydrogen chloride in toluene solution, there is no apparent change; with hydrogen chloride in acetone solutions, compound of Type VII is formed, through the withdrawal of mercuric chloride to yield a condensation product with acetone.[8]

Diquinoline Hydrobromide Tri-Mercuric Bromide.—When two molecular proportions of quinoline hydrobromide and 3 of mercuric bromide are dissolved in hot acetonitrile, and the solution is cooled, long transparent prisms, m. p. 145°, are obtained.

Anal. Calcd. for $2C_9H_7NHBr.3HgBr_2$: Br, 42.52; Hg, 40.08. Found: Br, 42.34; Hg, 40.28.

The corresponding iodine compound could not be formed, for when the same molecular quantities were taken mercuric iodide crystallized with elongated *parallelepipedon prisms*. Since the proportions necessary to yield the compound $C_9H_7NHI.HgI_2$ gave *needles* it was suspected that the compound $4C_9H_7NHI.5HgI_2$ constituted the prisms formed. This will be further investigated.

Table I indicates all the salts thus far established.

TABLE I

SALTS FORMED

	Cl		Br		I	
Type	Form	M. p., °C.	Form	M. p., °C.	Form	M. p., °C.
I	prisms	223	prisms	204	rhomboids	168
II			rhombohedrons	121	needles	147
IV			prisms	118		
V	prisms	210	hexagons	185	hexagons	154
VI	prisms	142	prisms	147	prisms	106
VII	needles	130	hexagons	118	hexagons	160
VIII	rhombohedrons	91	rhombohedrons	120		
IX	needles	160	prisms	145		

Summary and Conclusions

1. Complex double salts involving halogen, quinoline and mercury conform to six types for chlorine, eight types for bromine and five types for iodine.

2. Their preparations involve definite conditions and are largely influenced by the specific affinities of the respective halides.

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[8] For example, see Auld and Hantzsch, *Ber.*, **38**, 2678 (1905).