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

COMPLEX SALTS OF QUINOLINE, METALLIC CHLORIDES, WATER AND HYDROGEN CHLORIDE

BY WILLIAM M. DEHN

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As described in the literature, and in this and a later paper, metallic halides can form with quinoline, water and hydrogen halides, the following types of salts:

1.	Q.MXn	Bi, Cd, Co, Hg, Th, Zn.
2.	Q.MXn.HX	Hg, Ag, Au, Bi, Fe, Mn, Pb, Sb, Sn.
3.	Q.MXn.HX.H_2O	Cd, Mn.
4.	Q.MXn.HX.2H_2O	As, Bi, Sb, Hg.
5.	2Q.MXn	Ag, Cd, Co, Cu, Hg, Mn, Pb, Pd, Pt, Zn, Zr.
6.	2Q.MXn.HX	Hg.
7.	2Q.MXn.2HX	Au, Bi, Cd, Ce, Hg, Pb, Pd, Sn, Te, Ti, Tl, Ur.
8.	2Q.MXn.2HX.2H_2O	Ca, Co, Cu, Hg, Ni, Sr, Pt, Zn.
9.	2Q.3MXn.2HX	Hg.
10.	3Q.MXn	Tl.
11.	3Q.MXn.3HX	Bi.
12.	4Q.MXn	Co, Cu.
13.	5Q.2MXn.H_2O	Co.
14.	7Q.3MXn.HX	Hg.
15.	11Q.5MXn.HX	Hg.

It is probable that some of these salts are hydrolytic or dissociated products, or are mixtures of two or more other types, or represent erroneous interpretation of data.

Quinoline is the ideal base for the study of double salts with metallic chlorides, etc., on account of its high molecular weight, characteristic odor, stability toward oxidation and nitration, and especially on account of its tertiary nature because, unlike primary and secondary bases, it does not possess labile hydrogen atoms to split off with chlorine through the influence of heat or solvents.

In the following experiments, the same method was employed throughout in order, if possible, to obtain salts of Type 8 of the common metals. One molecular equivalent or more of quinoline dissolved in concd. hydrochloric acid was treated with one molecular equivalent of the metallic chloride. The mixture was heated until a clear solution was obtained, more concd. hydrochloric acid being added if necessary. The hot concentrated solution was then permitted to stand and crystallize. When the salt was very soluble, the solution was evaporated until crystallization resulted on standing. The salt thus formed was filtered off as dry as possible, or was washed with a little concd. hydrochloric acid. It was then dried on filter paper. Some of the salts were recrystallized from alcohol or acetone or acetonitrile.

Whereas the method yielded salts of Type 8 for only copper, cobalt, nickel, zinc, calcium and strontium, the same method and conditions yielded salts of Type 2 for lead and ferric iron; Type 7 for cadmium; Type 4 for arsenic, antimony and bismuth; Type 3 for manganese. The salts of aluminum and magnesium were too hygroscopic to be separated and analyzed. Barium chloride showed no affinity for quinoline hydrochloride. Both stannous chloride and stannic chloride yielded Borsbach's salt $(C_9H_7NHCl)_2SnCl_4$.

Diquinoline Hydrochloride Copper Chloride.—Dichromate-colored, thin rhombohedral plates were obtained, softening at 90°, melting at 110°, dissolving easily in water. Cuprous chloride gave the same salt.

Anal. Calcd. for $(C_9H_7NHCl)_2.CuCl_2.2H_2O$: Cl, 28.51. Found: 28.65.

Diquinoline Hydrochloride Cobaltous Chloride.—Large, beautiful, dark blue, rhombohedral plates were obtained melting at 118°, dissolving easily in hot alcohol and acetonitrile. The dried salt softens at 125° and melts at 155°.

Anal. Calcd. for $(C_9H_7NHCl)_2.CoCl_2.2H_2O$: Cl, 28.66; Co, 11.90; H_2O, 7.25. Found: Cl, 28.77; Co, 11.76; H_2O, 7.15.

Anal. Calcd. for $(C_9H_7NHCl)_2CoCl_2$: Cl, 13.07. Found: 13.01.

Diquinoline Hydrochloride Nickel Chloride.—Yellowish needles were obtained, coloring green at 125°, not melting at 250°, dissolving very easily in water.

Anal. Calcd. for $(C_9H_7NHCl)_2NiCl_2.2H_2O$: Cl, 28.55. Found: 28.65.

Diquinoline Hydrochloride Zinc Chloride.—Large rhombohedrons were obtained, melting at 119°, and dissolving with moderate difficulty in alcohol.

Anal. Calcd. for $(C_9H_7NHCl)_2ZnCl_2.2H_2O$: Cl, 28.17; Zn, 12.98; H_2O, 7.16. Found: Cl, 28.15; Zn, 13.12; H_2O, 7.02.

Diquinoline Hydrochloride Calcium Chloride.—This substance formed very soluble white needles.

Anal. Calcd. for $(C_9H_7NHCl)_2.CaCl_2.2H_2O$: Cl, 29.54. Found: 29.48.

Diquinoline Hydrochloride Strontium Chloride.—This was obtained as hygroscopic white needles that do not melt at 250°.

Anal. Calcd. for $(C_9H_7HCl)_2SrCl_2.2H_2O$: Cl, 26.98. Found: 26.73.

Quinoline Hydrochloride Lead Chloride.—Long silvery needles were obtained, not melting at 250°, and dissolving with difficulty in concd. hydrochloric acid.

Anal. Calcd. for $C_9H_7NHCl.PbCl_2$: Cl, 24.26; Pb, 49.07. Found: Cl, 24.13; Pb, 49.18.

Quinoline Hydrochloride Ferric Chloride.—This salt was prepared by Borsbach and was obtained when either one molecule or two of quinoline was used.

Diquinoline Hydrochloride Cadmium Chloride.—A matted mass of snow-white needles was obtained, not melting at 250°, and dissolving easily in water.

Anal. Calcd. for $(C_9H_7NHCl)_2.CdCl_2$: Cl, 27.57. Found: 27.49.

Quinoline Hydrochloride Arsenic Trichloride.—Transparent hexagonal prisms with rectangular and beveled ends were obtained, softening at 120° and melting at 145°.

Anal. Calcd. for $C_9H_7NHCl.AsCl_3.2H_2O$: Cl, 36.79. Found: 36.61.

Quinoline Hydrochloride Antimony Trichloride.—Thin rhomboid needles 2.5 cm. long were obtained melting at 198°, dissolving with difficulty in concd. hydrochloric acid.

Anal. Calcd. for $C_9H_7N.HCl.SbCl_3.2H_2O$: Cl, 33.13. Found: 33.10.

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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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

[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.