version into titanium nitride or imide or titanium nitride bromide. Titanium seems to be too weak a base forming element to permit the formation of titanium bromide in the presence of an excess of ammoniacal hydrobromide acid.[1] The salt is vigorously hydrolyzed in the presence of water; with a limited supply of water the temperature of the reacting mass may rise to incandescence. It is not explosive, as are many of the heavy metal derivatives of ammonia.

Summary.

In this investigation it has been shown that potassium amide in liquid ammonia solution reacts with titanium nitride bromide to form potassium ammonotitanate in accordance with the equation,

$$N\equiv Ti\text{-}Br + 2KNH_2 = N\equiv Ti\text{-}NHK + KBr + NH_3,$$

thus adding another representative to the rather small group of ammono salts of inorganic ammono acids.

HYGIENIC LABORATORY,
UNITED STATES PUBLIC HEALTH AND MARINE HOSPITAL SERVICE.
WASHINGTON, July, 1912.

THE ACTION OF POTASSIUM AMIDE ON CUPRIC NITRATE IN LIQUID AMMONIA SOLUTION.

(CUPROUS IMIDE, CUPROUS NITRIDE AND POTASSIUM AMMONOCUPRITE.)

BY EDWARD C. FRANKLIN.

Received August 30, 1912.

Introduction.

In a paper published some years ago, Fitzgerald[2] made note of the fact that the precipitate formed by the action of potassium amide on cupric nitrate in liquid ammonia solution readily goes into solution again upon the addition of an excess of potassium amide. This behavior suggests the formation of a copper compound related to ammonia as the familiar alkali zincates are related to water. The experimental proof of the existence of such a compound would be a matter of considerable interest; and such interest is considerably enhanced when the fact is recalled that cuprous hydroxide (oxide), the water analogue of cuprous amide, is apparently devoid of amphoteric properties, that is to say, it is incapable of forming a salt with potassium hydroxide. It was for the purpose of isolating and determining the composition and some of the more obvious properties of the compound formed by the solution of cuprous amide[3] in potassium amide solution that the investigation described in this paper was undertaken. Incidentally some observations

---

[1] Ammonium bromide in solution in liquid ammonia.

[2] THIS JOURNAL, 29, 657 (1907).

[3] The precipitate is assumed to be cuprous amide. When dried under conditions described elsewhere in this paper, cuprous imide and cuprous nitride, respectively, are obtained.

made by Fitzgerald and, before him, by Mr. A. R. Miller (working in the chemical laboratory of Stanford University) upon the precipitate mentioned above, have been recovered from their note books and are recorded here.

Ammonated Cupric Nitrate.—For use in the experiments described below, any salt of copper—either cuprous or cupric—may be chosen, which is soluble in liquid ammonia and which at the same time can be prepared free from water. Cupric nitrate, although impossible of desiccation by any of the common methods, is readily obtained in the form of beautiful, deep blue crystals of the composition represented by the formula $Cu(NO_3)_2.4NH_3$ by recrystallizing the ordinary hydrated salt, first from concentrated aqua ammonia, and then from liquid ammonia. This ammonated cupric nitrate, first prepared by Kane,[1] is stable in contact with atmospheric air, is readily soluble in liquid ammonia, and is therefore an ideal salt for the purpose of this investigation.

Cuprous Imide, Cu_2NH and Cuprous Nitride, Cu_3N.

Fitzgerald[2] has shown that the action of potassium amide upon cupric nitrate in liquid ammonia solution results in the formation of an insoluble, dark green precipitate, which, when heated *in vacuo* to 160°, is converted into a black mass of the composition represented by the formula Cu_3N. Fitzgerald also records the fact that it is necessary to heat the precipitate for a considerable time in order to eliminate the last portions of ammonia and thus to bring the composition of the product into agreement with the above formula. This behavior points to the existence of cuprous imide or amide and as a matter of fact a study of analytical data obtained by Fitzgerald, and by Miller, shows that both these investigators had specimens of cuprous imide in their hands.

Preparation and Properties.—On allowing the liquid ammonia to evaporate from the precipitate obtained in the manner described by Fitzgerald[3] and then exhausting the containing tube at laboratory temperature to a few millimeters pressure, Miller found three specimens to show the composition recorded in the table below under the superscriptions I, II and III. Following the same procedure, Fitzgerald obtained, in addition to the results already published,[3] three specimens which analysis showed to have the composition given under IV, V and VI:

	Calculated for Cu_2NH.	Found.					
		I.	II.	III.	IV.	V.	VI.
Cu	89.4	83.3	89.2	87.4	85.5	90.7	89.6
N	9.9	10.9	10.0	11.9	11.2	9.2	12.0 ?
H	0.7	..	..	..	..	..	..

---

[1] *Ann. chim. phys.*, [2] **72**, 273 (1839).

[2] THIS JOURNAL, **29**, 657 (1907).

[3] *Loc. cit.*

While in sharpness these results are by no means all that could be desired, they may nevertheless be taken as affording fair evidence of the existence of cuprous imide.

When a very low vacuum is maintained over cuprous imide, slow evolution of ammonia continues for a long time but apparently ceases short of the formation of pure cuprous nitride. At a temperature of 160°, as Fitzgerald has shown, cuprous imide is rapidly converted into cuprous nitride.

The fresh precipitate—probably cuprous amide—formed by the action of potassium amide on cupric nitrate is dark olive green in color, changing in the course of time to brick red. Cuprous imide is dark brown, cuprous nitride is black. The green and red precipitates, cuprous imide and cuprous nitride, dissolve readily in liquid ammonia solutions of ammonium nitrate forming cuprous nitrate,[1] and in solutions of potassium amide to form potassium ammonocuprite, a compound, the preparation and properties of which are described below. They are readily hydrolyzed in the presence of water. Hydrochloric acid dissolves the hydrolytic products forming cuprous chloride and ammonium chloride. Sulfuric acid acting on the hydrolytic products forms cupric sulfate, metallic copper and ammonium sulfate. Cuprous nitride is explosive, although by no means so sensitive to shock as some of the other nitrides which have been prepared by the writer.

It is interesting to note that, after washing until practically free from electrolyte, the red precipitate mentioned above begins to go into solution in the colloidal state. The experimental observations upon which this statement is based are as follows: During the washing of the red precipitate for use in Experiment IV[2]—and a similar behavior has been several times noticed—the precipitate settled well, leaving the supernatant liquid perfectly clear. After the tenth washing, the liquid remained cloudy and refused to settle clear even after standing for several hours. After the eleventh washing, the red cloudiness was much more conspicuous and quite as persistent.

Preparation Potassium Ammonocuprite, $CuNK_2.3NH_3$, $CuNK_2.2NH_3$ and $CuNK_2.NH_3$.

As stated above, the red or green ammonated cuprous nitride dissolves in a liquid ammonia solution of potassium amide to a clear, colorless solution. From this solution, when sufficiently concentrated and at a low temperature, a crop of very soluble, colorless, deliquescent—deliquescent in the sense that they melt in an atmosphere of ammonia in equilibrium with liquid ammonia at ordinary laboratory temperatures—crystals may be obtained. The experimental procedure followed in the iso-

---

[1] Cf. Sloan, THIS JOURNAL, 32, 72 (1910).

[2] p. 1505.

lation of this compound and in preparing it for analysis was practically identical with that already described for the preparation of potassium ammonoplumbite.[1] Its description may therefore be omitted here. The great solubility of potassium ammonocuprite, together with its habit of crystallizing in the form of a bulky, fibrous mass, from which the mother liquor drains but poorly, have made the purification of the compound by recrystallization an operation of considerably more difficulty than the corresponding operations in connection with the lead compound.

Ammonia of Crystallization.—The determinations of ammonia of crystallization which were carried out in the manner described in the paper above cited are satisfactory in so far as the ammonia retained at laboratory temperature is concerned. Serious difficulties, however, were encountered in the efforts to determin the amount of ammonia retained at low temperatures. In accordance with the requirements of the phase rule, the saturated solution of the salt ought to show a constant vapor pressure so long as any portion of the solution remains mixed with the solid phase. With continued abstraction of ammonia, and immediately upon the disappearance of the last portions of the solution the vapor pressure should fall to a new constant value, which marks the decomposition tension of the ammonated salt. Practically, however, no such behavior could be recognized, so that it became a difficult matter to distinguish between the point at which the last portions of the solvent disappeared and the beginnings of efflorescence on the part of the ammonated salt.

Analytical Data and Conclusions.—For analysis the compound was hydrolyzed by the action of water vapor and the hydrolytic products dissolved in dilute hydrochloric acid. The copper, potassium and ammonia contained in this solution were determined by ordinary quantitative methods, which need not be described here. The experimental data obtained in connection with the preparation of five specimens of potassium ammonocuprite are as follows:

Preparation I. The salt recrystallized once—that is, crystallized from the original solution, drained of mother liquor, washed with a small quantity of solvent, dissolved in fresh solvent, again crystallized, drained of mother liquor, and washed with small quantity of solvent—and dried *in vacuo* at 70° weighed 0.3428 gram. The specimen thus obtained gave 0.1562 gram Cu_2S, 0.5020 gram mixed NH_4Cl and KCl and 0.2835 gram KCl. The specimen dried at —40° lost 0.0478 gram NH_3 on warming to 70°. Preparation II. The specimen dried *in vacuo* at 0° weighed 0.5440 gram and gave 0.2354 gram Cu_2S, 0.1183 gram N and 0.4273 gram KCl. The specimen dried at —40° lost 0.0507 gram NH_3 at 0°. Preparation III. The specimen recrystallized twice and dried *in vacuo* at 165° gave 0.3344 gram Cu, 0.1792 gram N and 0.4084 gram K. Dried at —40° the salt lost 0.0896 gram NH_3 at 20° and 0.0681 gram NH_3 additional at 165°. The weight of the specimen is unknown. Assuming it to be the sum of the weights

---

[1] *J. Physic. Chem.*, 15, 509 (1911).

of the copper, potassium and nitrogen found, plus three equivalents of hydrogen or 0.9370 gram, then the results given under III are calculated. Preparation IV. Recrystallized twice and dried *in vacuo* at 20°, the specimen weighed 0.8083 gram and was found to contain 0.2610 gram Cu, 0.1627 gram N and 0.3328 gram K. The amount of ammonia retained at —40° was not determined. Preparation V. This salt was crystallized from the combined mother liquors from preparations III and IV and recrystallized twice. The salt dried *in vacuo* at 20° weighed 0.7053 gram and was found to contain 0.2365 gram Cu, 0.1516 gram N and 0.2868 gram K Ammonia lost between —40° and 20° was 0.0511 gram.

When crystallizing the last specimen, it was observed that a small quantity of substance separated in the form of small, granular crystals, different in habit from the salt of the formula $CuNK_2.3NH_3$ and apparently much less soluble. It is impossible to say what this substance is, but in view of the fact that the atomic ratios of Cu to K in all the products prepared, with the exception of preparation IV, are less than 1 to 2, it is surmised that it may be a monopotassium ammonocuprite of the formula $CuNHK.nNH_3$. The attempt will be made, when opportunity offers, to determin whether such a compound can be isolated.

The percentage composition of two specimens of the salt dried *in vacuo* at 160° to 200°, together with the amount of ammonia lost by drying the compound $CuNK_2.3NH_3$ at 20° and 160°, respectively, expressed in percentage of the compound $CuNK_2.NH_3$, is given herewith:

	Found.	
Calculated for $CuNK_2.NH_3$.	I.	III.
Cu 36.8	36.4	35.7
N 16.2	16.5	19.1
K 45.2	43.3	43.7
H_3 ..	..	..
Calculated for 1 mol. NH_3 9.8.		
20° to 160°	..	7.3[1]
—40 to +20	..	9.6
—40 to 160	14.0	16.9

A table follows showing the percentage composition of three specimens of the salt dried *in vacuo* at 20°, together with the amount of ammonia lost by drying the compound $CuNK_2.3NH_3$ at 20° expressed in percentage of the salt dried at 20°:

		Found.	
Calculated for $CuNK_2.2NH_3$.	II.	IV.	V.
Cu 33.5	34.5	32.3	33.5
N 22.1	21.8	20.1	21.5
K 41.2	41.1	41.2	40.7
H 3.2	..	..	..
Calculated for 1 mol. NH_3 8.9.			
—40 to +20	9.3	..	7.3

---

[1] It will be noted that the low percentage of ammonia here is coincident with a high percentage of nitrogen retained in the compound dried at 160°.

From the above described investigation it follows, first, that the action of potassium amide on liquid ammonia solutions of cupric nitrate results in the formation of an ammonated cuprous nitride in accordance with the equation,

$3Cu(NO_3)_2.4NH_3 + 6KNH_2 = Cu_3N.nNH_3$[1] $+ 6KNO_3 + (16-n)NH_3 + N$; second, that the nitride, imide or amide of copper dissolves in an excess of potassium amide to form potassium ammonocuprite as represented by the equation,

$$Cu_3N.nNH_3 + 6KNH_2 + (5-n)NH_3 = 3CuNK_2.3NH_3;$$

and, third, that the salt of the composition represented by the formula $CuNK_2.3NH_3$ readily loses one molecule of ammonia to form a compound of the formula $CuNK_2.2NH_3$, which in turn, at higher temperature, loses a further molecule of ammonia to form the monoammonated potassium ammonocuprite of the formula $CuNK_2.NH_3$. The monoammonated salt does not lose ammonia at a temperature of 220°.

Properties.—Potassium ammonocuprite is obtained in the manner described above as a colorless solid which is extremely soluble in liquid ammonia. When a concentrated solution is cooled to the temperature of a bath of liquid ammonia the salt separates as a mass of needle like crystals. It is extremely sensitive to the action of air or moisture; the least trace of atmospheric air gaining entrance to the preparation tube produces instantly a brown red discoloration, due in all probability to the oxidation of cuprous copper. Liquid ammonia solutions of ammonium nitrate added to a solution of potassium ammonocuprite gives a white precipitate[2] which, on further addition to the ammonium salt, goes into solution as cuprous nitrate. The crystals of the salt dried at a low temperature undergo efflorescence as the temperature rises, grow dark and finally black as the composition of the product approaches that represented by the formula $CuNK_2.NH_3$. The black mass dissolves in liquid ammonia to a colorless solution from which the triammonate, $CuNK_2.3NH_3$, may again be crystallized. Potassium ammonocuprite is explosive, though it is by no means so sensitive nor are its detonations so violent as those of the analogous lead and thallium compounds.

The writer is under obligations to Mr. E. Elvove for most of the analyses recorded in this paper.

Summary.

The investigation of which this paper gives an account has yielded the following results:

---

[1] $Cu_3N.nNH_3 = Cu_3N$, Cu_2NH or $CuNH_2$.

[2] Why this precipitate is white, while the precipitate obtained by the action of potassium amide on cupric nitrate is green, is not known. Assuming the white precipitate to be cuprous amide the above described reactions may be represented by the equations $CuNK_2 + 2NH_4NO_3 = CuNH_2 + 2KNO_3 + NH_3$ and $CuNH_2 + NH_4NO_3 = CuNO_3 + 2NH_3$, respectively.

1. A precipitate of ammonated cuprous nitride, of the formula $Cu_3N\text{-}nNH_3$, is formed by the action of potassium amide on a liquid ammonia solution of cupric nitrate in accordance with the equation,

$$3Cu(NO_3)_2 + 6KNH_2 = Cu_3N.nNH_3 + 6KNO_3 + (4-n)NH_3 + N.$$

When heated *in vacuo* at laboratory temperature, the precipitate is converted into cuprous imide, Cu_2NH; when heated to 160° cuprous nitride, Cu_3N, is formed.

2. The products of the general formula, $Cu_3N.nNH_3$, dissolve readily in liquid ammonia solutions of potassium amide to form solutions from which well crystallized specimens of a colorless salt of the composition represented by the formula, $CuNK_2.3NH_3$, have been obtained.

3. This salt, potassium ammonocuprite, with three molecules of ammonia of crystallization or triammonated potassium ammonocuprite, loses one molecule of ammonia, when heated *in vacuo* to laboratory temperature, to form a salt of the composition represented by the formula $CuNK_2.2NH_3$. When diammonated potassium ammonocuprite is heated to higher temperatures it, in turn, loses one molecule of ammonia to form a monoammonated salt of the formula $CuNK_2.NH_3$.

Hygienic Laboratory,
U. S. Public Health and Marine Hospital Service,
Washington.

AN UNUSUAL CASE OF SPECIFIC GRAVITY.[1]

By A. L. Hyde.

Received August 30, 1912.

Attention is here called to the unusual behavior of paranitrotoluene when dissolved in carbon bisulfide. The usual rule is that when a solid heavier than a liquid is dissolved in this liquid, the resulting solution has a higher specific gravity than the pure liquid; but when paranitrotoluene, a solid of higher specific gravity than carbon bisulfide, is dissolved in this liquid, the specific gravity of the solution is less than that of pure carbon bisulfide. In other words, the two substances occupy a larger volume when together in solution than their total volume when separate. The following results of a few determinations will show this: The determinations were made with a Westphal balance and a specific gravity bottle. All specific gravities are based on water at 15° and the determinations were made at 20°.

The carbon bisulfide used had a specific gravity at 20° of 1.2660. The

---

[1] Published by permission of the Director of the Bureau of Mines. Dr. Washburn has called attention to the fact that solutions of lithium nitrate, ammonium chloride, or ammonium bromide in water are in each case lighter than the mean of the specific gravity of the salts and of water. These cases are parallel to the case of carbon bisulfide and sulfur, in which, although the specific gravity is increased by addition of the solid, there is an increase in the volume caused by solution.