The following salts, for the most part beautifully crystallized, have been prepared:

1. Diammonated silver ammonoacetate, $CH_3CONHAg.2NH_3$.

2. Thallous ammonoacetate, $CH_3CONHTl$ and the diammonate, $CH_3CONHTl.2NH_3$.

3. Lead ammonoacetate.

4. Silver ammonobenzenesulfonate, $C_6H_5SO_2NHAg$, the monammonate, $C_6H_5SO_2NHAg.NH_3$ and the diammonate, $C_6H_5SO_2NHAg.2NH_3$.

5. Thallous ammonobenzenesulfonate, $C_6H_5SO_2NHTl$, the monammonate, $C_6H_5SO_2NHTl.NH_3$ and the diammonate, $C_6H_5SO_2NHTl.2NH_3$.

6. Thallous ammono-*p*-toluenesulfonate, $CH_3C_6H_4SO_2NHTl$ and the monammonate, $CH_3C_6H_4SO_2NHTl.NH_3$.

7. Diammonated cuprous ammono-*p*-toluenesulfonate, $CH_3C_6H_4SO_2NHCu.2NH_3$.

8. Cupric ammono-*p*-toluenesulfonate, $(CH_3C_6H_4SO_2NH)_2Cu$.

9. Cuprous ammonobenzenesulfonate, $C_6H_5SO_2NHCu$ and the diammonate, $C_6H_5SO_2NHCu.2NH_3$.

10. Cupric ammonobenzenesulfonate tetrammonate, $(C_6H_5SO_2NH)_2Cu.4NH_3$ and the heptammonate, $(C_6H_5SO_2NH)_2Cu.7NH_3$.

11. Silver phenylammonoacetate, $CH_3CONAgC_6H_5$ and the monammonate, $CH_3CONAgC_6H_5.NH_3$.

12. Thallous phenylammonoacetate, $CH_3CONTlC_6H_5$.

13. Potassium benzyl ammonoacetate monammonate, $CH_3CONKCH_2C_6H_5.NH_3$.

14. Potassium *p*-phenetol ammonoacetate, $CH_3CONKC_6H_4OC_2H_5$.

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POTASSIUM AMMONOBARATE, AMMONOSTRONTIATE AND AMMONOCALCIATE.

BY EDWARD C. FRANKLIN.

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Introduction.

Investigations[1] conducted in this laboratory have shown that a reaction similar to that which accompanies the solution of the hydroxide of zinc in aqueous potassium hydroxide takes place when the amide of zinc is treated with a liquid ammonia solution of potassium amide. These strikingly similar reactions proceed in accordance with the equations,

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O^2$$

$$Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2 + 2NH_3,$$

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[1] Fitzgerald, THIS JOURNAL, 29, 660 (1907), and Franklin, *Ibid.*, 29, 1275 (1907).

[2] As a matter of fact this equation, which is frequently written to represent the action of potassium hydroxide on zinc hydroxide, seems never to have been experimentally demonstrated (cf. Comey and Jackson, *Am. Chem. J.*, 11, 145 (1894)).

which represent, respectively, the formation of an aquozincate and an ammonozincate of potassium, the one a salt of the water system of acids, bases and salts, the other, a salt of the ammonia system.

Following the successful preparation of the ammonozincate and the ammonoplumbite[1] of potassium, which are the analogs of known aquo-compounds, other metallic amides (imides and nitrides) were studied with respect to their behavior toward liquid ammonia solutions of potassium amide, with the result—perhaps contrary to what was to have been expected in view of the fact that only a limited number of metallic hydroxides are known to react with potassium hydroxide—that the capacity of forming salts similar to potassium ammonozincate came to be recognized as a property possessed by many, perhaps a majority, of the commoner metals. In the course of these investigations it has been found that potassium amide reacts with cadmium amide to form an ammonocadmiate of potassium,[2] with nickel amide to form an ammononickelate,[1] with silver amide to form an ammonoargentate,[3] with cuprous imide to form an ammonocuprite,[4] with thallous nitride to form an ammonothallite[5] and even with the amide of the strongly electropositive magnesium to form an ammonomagnesate of potassium.[6] The isolation of compounds such as these, and especially the preparation of an ammonomagnesate of potassium as a compound of sharply definite composition, suggested the possibility that the amides of the more positive metals, barium, strontium and calcium, might be capable of reacting with potassium amide to form similar ammono salts.

Before passing to a description of the experimental part of this research it is interesting to note that—in contrast with the difficulties encountered by other investigators in their efforts to prepare satisfactory specimens[7] of the aquozincates and aquoplumbites and even of the aquo-aluminates—the ammono salts mentioned above are easily prepared, and for the most part have been obtained beautifully crystallized and of sharply definite composition. The formation of amorphous products

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[1] *J. Phys. Chem.*, 15, 511 (1911).

[2] *Ibid.*, October, 1915.

[3] THIS JOURNAL, 37, 854 (1915).

[4] *Ibid.*, 34, 1501 (1912).

[5] *J. Phys. Chem.*, 16, 682 (1912).

[6] THIS JOURNAL, 35, 1455 (1913). An ammonostannate (*Ibid.*, 29, 1693 (1907)), and an ammonotitanate of potassium (*Ibid.*, 34, 1497 (1912)), analogous to the familiar aquostannate and aquotitanate, have also been prepared in this laboratory, but since stannic and titanic hydroxides are distinct acids and scarcely show amphoteric properties, their ammono salts are not of very particular interest in the present connection.

[7] Prescott, THIS JOURNAL, 2, 27 (1880), Comey and Jackson, *Am. Chem. J.*, 11, 145 (1894), Allen and Rogers, *Ibid.*, 24, 304 (1901), Hantzsch, *Z. anorg. Chem.*, 30, 289 (1902).

interferes with the isolation of pure aquo salts. Nothing of the kind appears to stand in the way of the preparation of the ammono salts.

Experimental.

Since the special methods which have been developed in this laboratory for the manipulation of liquid ammonia solutions have been described elsewhere,[1] it is unnecessary to go into detail concerning them here.

Potassium Ammonobarate, $BaNK.2NH_3$, $Ba(NH_2)_2.KNH_2$ or $[Ba(NH_2)_3]K$.—When a barium salt and an excess of potassium amide are brought together in liquid ammonia solution a white, insoluble precipitate is formed which has been shown to have the composition represented by the above formulas. Preparatory to analysis, the pure, dry[2] salt was hydrolyzed by the action of water vapor, then treated with liquid water and finally dissolved in dilute hydrochloric acid. From an aliquot portion of the acid solution the barium was removed and weighed as sulfate. The filtrate from barium sulfate was evaporated to dryness and the residue ignited and weighed as potassium sulfate. From another portion of the solution ammonia was removed by distillation with excess of potassium hydroxide and determined by titration after the usual manner with standard acid.

Preparation I.—Into a large excess of potassium amide was run a solution of 1 g. of barium nitrate which had been previously dried by gentle ignition. The resulting precipitate was washed many times, by the process of decantation described elsewhere, in order to be sure of removing all the potassium nitrate formed in the reaction, together with the excess of potassium amide used.

Dried in vacuum at 20° the preparation weighed 1.1525 g. One-half gave 0.6040 g. $BaSO_4$. One-fifth gave 0.0515 g. NH_3. One-fifth of the filtrate from $BaSO_4$ gave 0.0916 g. K_2SO_4.

Preparation II.—After pouring barium nitrate solution into a solution containing a large excess of potassium amide, the reaction tube with its contents—subjected to occasional shaking—was allowed to stand several days with the object in view of ascertaining whether a compound richer in potassium than Preparation I might be obtained. After thorough washing the precipitate was dried in vacuum, first at —40° and then at 20°. By this treatment the preparation lost only 0.0012 g., thus showing that at the lower temperature the compound retains but two molecules of ammonia.

Dried at 20° the specimen weighed 1.2873 g. One-fourth gave 0.3371 g. $BaSO_4$. Another fourth gave 0.0608 g. N. The filtrate from $BaSO_4$ gave 0.1244 g. K_2SO_4.

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[1] THIS JOURNAL, **27**, 820 (1905); **29**, 656 and 1693 (1907); **35**, 1455 (1913); *J. Phys. Chem.*, **15**, 509 (1911); **16**, 682 (1912).

[2] Free from uncombined ammonia.

Preparation III.—This experiment was a duplicate of the preceding, excepting that instead of pouring the barium nitrate into an excess of potassium amide the order of mixing the solutions was reversed.

Dried at 20° in vacuum the specimen weighed 1.2900 g. One-fourth gave 0.3366 g. $BaSO_4$ and 0.1260 g. K_2SO_4. One-fourth gave 0.0602 g. N.

Preparation IV.—This and the succeeding preparation were made by the action of potassium amide on the very soluble barium sulfocyanate. A solution of 0.55 g. of the salt, which had been dried for several weeks in vacuum over sulfuric acid, was added to an excess of potassium amide in liquid ammonia solution. The precipitate formed was thoroughly washed preparatory to analysis.

The specimen dried at 20° in vacuum weighed 0.5480 g. and gave 0.5506 g. $BaSO_4$. One-half of the filtrate from $BaSO_4$ gave 0.1149 g. K_2SO_4; one-fifth gave 0.0204 g. N.

Preparation V.—In this experiment an excess of potassium amide was added to a solution of 0.61 g. barium sulfocyanate. The precipitate was thoroughly washed.

Dried in vacuum at 100° the specimen weighed 0.4404 g. and gave 0.4432 g. $BaSO_4$. One-half of the filtrate from $BaSO_4$ gave 0.0923 g. K_2SO_4; the other half gave 0.0415 g. N.

	Calc. for $BaNK.2NH_3$.	Found.				
		I.	II.	III.	IV.[1]	V.[1]
Ba	61.2	61.6	61.6	61.3	59.2	59.2
N	18.7	18.4	18.9	18.7	18.6	18.8
K	17.4	17.8	17.4	17.5	18.8	18.6

Potassium ammonobarate, which is formed in accordance with the equation

$$Ba(NO_3)_2 + 3KNH_2 = BaNK + 2KNO_3 + 2NH_3,$$

when barium nitrate in solution in liquid ammonia is poured into an excess of a solution of potassium amide, is obtained as an amorphous or microcrystalline precipitate of the composition represented by the formula $BaNK.2NH_3$. Temperatures up to 100° have no effect on the compound. It is insoluble in liquid ammonia, but is decomposed and dissolved in liquid ammonia solutions of ammonium nitrate. It is hydrolyzed vigorously in contact with water into potassium hydroxide, barium hydroxide and ammonia.

Barium Amide, $Ba(NH_2)_2$.—Although barium amide has been previously prepared[2] it was thought desirable in this connection to show that it may be obtained by the action of potassium amide on barium salts in liquid ammonia solution. Accordingly, in one experiment potassium

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[1] The barium thiocyanate used in making these preparations was supposed, at the time it was used, to be dry. It was subsequently found to contain water. The high content of potassium and the low results for barium are, therefore, due to the presence of potassium hydroxide formed by the action of the water on potassium amide.

[2] Mentrel, *Bull. soc. chim.* (France), [3] **29**, 497 (1903); Guntz et Mentrel, *Ibid.*, [3] **29**, 578 (1903).

amide was run into a large excess of a solution of barium nitrate, in another, barium nitrate was added to two equivalents of potassium amide, in a third, equivalent quantities of barium sulfocyanate and potassium amide were mixed, and in a fourth, a dilute solution of potassium amide was run very slowly—with constant shaking—into a large excess of barium sulfocyanate solution in the hope that the inclusion of any potassium ammonobarate in the precipitate might thus be avoided. The realization of a pure compound, however, was defeated by the presence of water in the barium thiocyanate used, which, of course, resulted in the contamination of the precipitate with a small quantity of potassium hydroxide. Since barium amide is a compound already known, the inclusion of the analytical data here is unnecessary. Following are the results obtained:

	Calc. for $Ba(NH_2)_2$.	Found.			
		I.	II.	III.	IV.
Ba	81.0	79.7	79.4	80.6	80.5
N	16.6	15.7	16.0	15.3	15.6
K	0.0	....	....	....	1.5

These results show that barium amide is formed by the action of potassium amide on a salt of barium in solution in liquid ammonia, but obviously the preparation of a pure compound in this manner is a matter of considerable difficulty. The action is represented by the equation

$$Ba(NO_3)_2 + 2KNH_2 = Ba(NH_2)_2 + 2KNO_3.$$

Barium amide was obtained as a white precipitate insoluble in liquid ammonia, but readily soluble in a solution of ammonium nitrate.

Potassium Ammonostrontiate, $SrNK.2NH_3$, $Sr(NH_2)_2.KNH_2$ or $[Sr(NH_2)_3]K$.—Excepting that a soluble strontium salt was substituted for the barium salt, the procedure followed for the preparation of potassium ammonostrontiate was the same as that described above for obtaining potassium ammonobarate. The strontium was determined as carbonate and the potassium as chloride.

Preparation I.—One gram of strontium nitrate, dried by gentle ignition, was dissolved in liquid ammonia and added to a solution of four equivalents of potassium amide. A bulky, amorphous precipitate resulted. Due to a leaky stopcock the solvent evaporated away while the preparation tube stood over night, leaving the precipitate in the form of lumpy masses which were not broken up by the washing to which they were subjected. There was, therefore, some doubt as to the efficiency of the washing.

The specimen dried in vacuum at 20° weighed 0.9725 g. One-fourth gave 0.1976 g. $SrCO_3$ and 0.1114 g. KCl. One-fifth gave 0.0439 g. N.

Preparation II.—This specimen was made by running a solution of 1 g. of strontium nitrate into a solution containing approximately three equivalents of potassium amide. The precipitate was thoroughly washed preparatory to analysis.

Dried at 100° in vacuum the specimen weighed 0.7816 g. One-half gave 0.3329 g. $SrCO_3$ and 0.1680 g. KCl. One-eighth gave 0.0233 g. N.

	Calc. for $SrNK.2NH_3$	Found.	
		I.	II.
Sr	50.1	48.3	50.4
N	24.0	22.6	23.8
K	22.4	24.0	22.6

Although obtained in the form of a bulky, amorphous precipitate there can be no doubt of the formation of an ammonostrontiate of potassium as the result of the action of potassium amide in excess on solutions of strontium salts. The reaction is represented by the equation

$$Sr(NO_3)_2 + 3KNH_2 = SrNK + 2KNO_3 + 2NH_3.$$

The salt is insoluble in liquid ammonia but dissolves in solutions of ammonium nitrate to form the nitrates of strontium and potassium. It is hydrolyzed vigorously by water into strontium hydroxide, potassium hydroxide and ammonia.

Potassium Ammonocalciate, $CaNK.2NH_3$, $Ca(NH_2)_2.KNH_2$ or $[Ca(NH_2)_3]K$.—This salt has been prepared by the action of potassium amide on metallic calcium and by adding calcium thiocyanate to an excess of a solution of potassium amide. Preparatory to analysis the salt was hydrolyzed by water vapor and dissolved in dilute hydrochloric acid. The calcium was precipitated as oxalate and weighed as oxide. Potassium was weighed as chloride and ammonia was determined by the usual volumetric method.

Preparation I.—Into the two legs of the familiar reaction tube were introduced, respectively, 0.2 g. metallic calcium and 0.4 g. metallic potassium, the latter together with a small quantity of platinum black. As soon as the potassium had been converted into potassium amide, the solution of this ammono base was poured into the leg containing the metallic calcium. The blue color of the calcium solution disappeared in the course of an hour, leaving a white, amorphous precipitate, which, after thorough washing, was submitted to analysis.

The specimen dried in vacuum at 80° weighed 0.5707 g. One-half gave 0.1221 g. CaO and 0.1817 g. KCl. One-fourth gave 0.0457 g. N.

Preparation II.—This experiment was practically a duplicate of the preceding.

Dried in vacuum at 100° the precipitate weighed 0.6285 g. One-fourth gave 0.0694 g. CaO and 0.0944 g. KCl. Another fourth gave 0.0510 g. N.

Preparation III.—Six-tenths of a gram of calcium sulfocyanate, which had been dried by heating to 100° in vacuum for several hours, was dissolved in liquid ammonia and added to an excess of potassium amide solution. The pulverulent precipitate formed was washed many times by the decantation method and dried at 110° for analysis.

The specimen weighed 0.4754 g. Six-tenths gave 0.1258 g. CaO and 0.1735 g. KCl. Two-tenths gave 0.0300 g. N.

	Calc. for $CaNK.2NH_3$.	Found. I.	II.	III.
Ca	31.5	30.6	31.5	31.5
N	33.1	32.0	32.5	31.6
K	30.8	33.4	31.4	31.8

Although the analytical results are distinctly unsatisfactory there can scarcely be a doubt of the formation of a potassium ammonocalciate of the formula $CaNK.2NH_3$, first, by the action of potassium amide on metallic calcium as represented by the equation

$$Ca + KNH_2 = CaNK + 2H,$$

and second, by the action of excess of potassium amide on a solution of a salt of calcium as represented by the equation

$$Ca(SCN)_2 + 3KNH_2 = CaNK + 2KSCN + 2NH_3.$$

The salt is apparently amorphous, but settles well to a fairly dense, granular precipitate which is easily washed. It dissolves readily in liquid ammonia solution of ammonium nitrate. In contact with water it is energetically hydrolyzed to calcium hydroxide, potassium hydroxide and ammonia.

Summary.

It has been shown in this paper that just as the amides of zinc and magnesium are acted upon by potassium amide in liquid ammonia solution to form an ammonozincate and an ammonomagnesate of potassium, so the amides of barium, strontium and calcium, when submitted to the action of solutions of the ammono base, are similarly converted into an ammonobarate, an ammonostrontiate and an ammono calciate of potassium, respectively.

General formulas for the compounds obtained are the following: $MeNK.2NH_3$, $NH_2MeNHK.NH_3$, $Me(NH_2)_2.KNH_2$ or following Werner, $[Me(NH_2)_3]K$.

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LIQUID JUNCTION POTENTIALS.

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A concentration cell with transference, consisting of two similar reversible electrodes in contact with two differently concentrated solutions