[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE ACTION OF LIQUID AMMONIA SOLUTIONS OF AMMONIUM SALTS ON METALLIC BERYLLIUM. AMMONATED BERYLLIUM HALIDES AND AMMONOBASIC BERYLLIUM SALTS

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Franklin and Kraus[1] have pointed out that many substances, among which are the hydrogen halides, are acids in liquid ammonia solution as well as in water. It has indeed been shown that solutions of these acids in liquid ammonia, in the form of course of their ammonium salts, react with most elements more electropositive than nickel.[2] One should then expect the electropositive element beryllium to react readily with solutions of ammonium salts in liquid ammonia. Since aqueous solutions of the normal salts of beryllium dissolve this metal to form very soluble aquo basic salts, it should be possible to prepare a series of ammonobasic beryllium salts by the action of solutions of the normal salts in liquid ammonia upon an excess of beryllium. Bearing in mind the difficulties encountered in crystallizing basic beryllium salts from water,[3] it became of added interest to attempt their preparation in liquid ammonia in the hope of obtaining crystallizable compounds. As a secondary purpose of this investigation it was hoped to prepare beryllium amide by the action of potassium amide upon a soluble beryllium salt, in the sense of the equation $BeI_2 + 2KNH_2 = Be(NH_2)_2 + 2KI$.

Newton C. Jones,[4] working under Dr. Franklin at Western Reserve University in the summer of 1926, found that beryllium dissolves readily in liquid ammonia solutions of an excess of ammonium chloride, ammonium ammono nitrate (ammonium azide), ammonium thiocyanate, ammonium iodide and ammonium cyanide with the evolution of hydrogen. From the solutions so prepared Jones was in most cases able to crystallize the corresponding normal salts of beryllium with ammonia of crystallization, but he was unable definitely to determine their composition in the limited time at his disposal.

Beryllium Chloride Diammonate and Tetrammonate, $BeCl_2 \cdot 2NH_3$ and $BeCl_2 \cdot 4NH_3$.—Normal beryllium chloride may readily be prepared by dissolving beryllium in a solution of more than two equivalents of ammonium chloride in liquid ammonia. From this solution, cooled to −40°,

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[1] Franklin and Kraus, *Am. Chem. J.*, **23**, 305 (1900); THIS JOURNAL, **27**, 822 (1905).

[2] Bergstrom, *J. Phys. Chem.*, **29**, 160 (1925).

[3] Parsons, "The Chemistry and Literature of Beryllium," The Chemical Publishing Co., Easton, Pa., **1909**, pp. 61–71, where references are given to the literature prior to 1909.

[4] Unpublished work.

there separates an abundant crop of well formed, colorless crystals which, after drying in a vacuum at −40° or at room temperature, correspond in composition to the formula $BeCl_2{\cdot}4NH_3$. When heated in a vacuum at 210–255°, two molecules of ammonia of crystallization are lost and $BeCl_2{\cdot}2NH_3$ is formed.

Unlike most metallic chlorides, beryllium chloride is readily soluble in liquid ammonia at room temperature. Solutions of beryllium chloride of proper concentrations separate into two liquid phases which have a lower consolute temperature between 0 and −40°. Other compounds have been found which exhibit a similar behavior in liquid ammonia.[5]

A description of a typical preparation of beryllium chloride will serve to illustrate the general method by which all of the normal and ammonobasic halides of beryllium were made.

In one leg of a two-legged liquid ammonia reaction tube[6] was placed 0.10 g. of metallic beryllium[7] together with 0.63 g. or 2.5 equivalents of ammonium chloride. Ammonia was distilled into the tube to dissolve the ammonium chloride, after which the apparatus was set aside for a few hours until all of the beryllium had gone into solution. To effect separation from a small quantity of insoluble material, the clear solution of beryllium chloride was decanted into the other leg of the reaction tube. By cooling this solution in a bath of liquid ammonia there was obtained a good crop of colorless crystals. After one recrystallization, the salt was dried in a vacuum at 20 and 210°, hydrolyzed by water and dissolved in dilute sulfuric acid. Beryllium in an aliquot portion of this solution was determined as oxide after a previous precipitation as hydroxide according to the method of Bleyer and Boshart.[8] On other aliquot portions, chlorine was determined as silver chloride and nitrogen was estimated volumetrically as ammonia.

Anal. Calcd. for $BeCl_2{\cdot}4NH_3$: Be, 6.1; N, 37.8; Cl, 47.9. Found, dried in a vacuum at 20°: Be, 6.2, 6.5; N, 37.9, 37.8; Cl, 47.8, 47.7. When these specimens were heated in a vacuum at 210 and 255°, they lost, respectively, 22.0 and 23.0% of ammonia; calculated for the loss of two molecules of ammonia from the tetrammonate, 23.0%. Beryllium chloride retains only four molecules of ammonia in a vacuum at −40°.

Beryllium Bromide Tetrammonate, $BeBr_2{\cdot}4NH_3$.—Beryllium bromide is readily obtained by dissolving beryllium in an excess of a liquid ammonia solution of ammonium bromide. Following the preliminary work

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[5] Bergstrom, *J. Phys. Chem.*, **29**, 162 (1925); THIS JOURNAL, **46**, 1559 (1924).

[6] For more complete descriptions of the manipulations necessary for the preparation of compounds in liquid ammonia and their subsequent analysis, see Franklin and co-workers, (a) THIS JOURNAL, **27**, 831 (1905); (b) **29**, 1694 (1907); (c) **35**, 1460 (1913); (d) *J. Phys. Chem.*, **15**, 510 (1911); (e) **16**, 694 (1912).

[7] The beryllium, which was in the form of small chips, was found to be practically free from other metals.

[8] Bleyer and Boshart, *Z. anal. Chem.*, **51**, 754 (1912).

of Jones,[4] it was expected that an ammonated beryllium bromide would crystallize from solutions at low temperature, but for some reason protracted cooling of a concentrated solution of this specimen at −40° failed to cause the formation of crystals. The reaction tube was then set aside for a week to allow a gradual concentration of the solution by leakage of ammonia past a defective stopcock. The well formed crystals of beryllium bromide thus obtained were washed with a small quantity of solvent, dried in a vacuum at 20° and analyzed.

Anal. Calcd. for $BeBr_2 \cdot 4NH_3$: Be, 3.8; N, 23.6; Br, 67.4. Found: Be, 3.7; N, 24.2; Br, 67.4.

Biltz and Messerknecht[9] have prepared beryllium chloride with 2, 4, 6 and 12 molecules, and beryllium bromide with 4, 6 and 10 molecules, of ammonia of crystallization.

Ammonobasic Beryllium Chloride.—A solution of ammonium chloride in liquid ammonia dissolves metallic beryllium to form normal beryllium chloride, and this in turn reacts with an excess of the metal to form a colorless, very slightly soluble ammonobasic beryllium chloride. One preparation was found on analysis to be a little more basic than indicated by the formula, $BeCl_2 \cdot Be(NH_2)_2 \cdot xNH_3$. However, one of Dr. E. C. Franklin's students at Western Reserve University reports a number of preliminary analyses agreeing more closely with this formula. Perhaps this is not a definite compound, for the basic halides of the composition $Be(NH_2)_2 \cdot BeBr_2$ and $Be(NH_2)_2 \cdot BeI_2$ have not been obtained.

Ammonobasic Beryllium Bromides: $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$, $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$ and $3Be(NH_2)_2 \cdot BeBr_2 \cdot 8NH_3$. **Experiment 1.**—A liquid ammonia solution of 0.69 g. of ammonium bromide was poured upon 0.06 g., or one atomic proportion, of beryllium in one leg of a reaction tube. There resulted a rather brisk evolution of hydrogen. Upon examining the reaction tube the next morning, it was found that the beryllium had disappeared, being in part replaced by a number of small white crystals of an ammonobasic beryllium bromide. The solution in equilibrium with this precipitate consisted of two liquid phases which had a lower consolute temperature between 10 and 15°. The crystals were washed to free them from material soluble in liquid ammonia. After evaporation of solvent from the reaction tube, the two legs were separated before the blast lamp and their respective contents submitted to analysis.[10]

Excepting that larger quantities of ammonium bromide and beryllium were used, the subsequent experiments were essentially duplicates of the first. In Experiment 3 the sparingly soluble crystals alone were analyzed.

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[9] Biltz and Messerknecht, *Z. anorg. Chem.*, **148**, 157 (1925).

[10] The crystals were sealed off in the leg of the reaction tube to which the stopcock was attached. The leg containing the washings of the crystals was drawn down in the blast flame and a small stopcock tied on with rubber tubing.

TABLE I

ANALYSES OF THE SPARINGLY SOLUBLE AMMONOBASIC BROMIDE

	Calcd. for $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$	Found, dried in a vacuum at 20° 1	2	3	4
Be	10.0	10.5	10.4	10.4	10.3
N	38.9	38.8	38.8	38.7	38.6
Br	44.4	45.2	44.4	44.5	44.3

When dried in a vacuum at −40°, specimen No. 3 corresponded in composition to $3Be(NH_2)_2 \cdot BeBr_2 \cdot 8NH_3$. Calcd.: Be, 8.4; N, 45.8; Br, 37.4. Found: Be, 8.8; N, 45.3; Br, 37.7.

TABLE II

ANALYSES OF THE SOLUBLE AMMONOBASIC BROMIDE

	Calcd. for $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$	Found, dried in a vacuum at 20° 1	2	4
Be	5.2	5.3	5.4	5.2
N	27.2	27.8	27.4	27.6
Br	62.0	61.2	61.8	61.5

The low bromine and high nitrogen analyses are due in part to the presence in solution of a small quantity of the salt, $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$. There is perhaps some doubt as to the chemical individuality of a substance which could not even be crystallized from solution at −78°, and therefore was analyzed without purification. In support of the view that this salt is a definite compound, it was found that the composition of the soluble material in equilibrium with the crystals of $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$ did not change over a period of two weeks. Thus, in the three experiments 1, 2 and 4 the solution was in contact with the crystals of the sparingly soluble basic bromide for 3, 8 and 12 days, respectively.

Ammonobasic Beryllium Iodides (1), $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$.—A solution of ammonium iodide in liquid ammonia reacts rapidly with an excess of beryllium to form the normal iodide and then very soluble ammonobasic iodides. One of these, $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, can easily be separated in definite crystalline form by cooling a solution of one to two atomic proportions of beryllium in one molecular proportion of ammonium iodide to −40° in a bath of liquid ammonia.

The two preparations, analyses of which are given below, were crystallized in good yield from solutions prepared by the action of ammonium iodide upon one atomic proportion of beryllium.[11] The salt which separated from solution on cooling was again crystallized, dried in a vacuum at 20°, dissolved in dilute sulfuric acid and analyzed. Found: Be, 8.2, 8.1; N, 30.7, 30.6; I, 55.4, 55.8. Calcd. for $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$; Be, 7.9; N, 30.8; I, 55.9. This salt lost very little ammonia when heated in a vacuum at 130°, but lost approximately one molecule when heated to 205°.

(2), $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$.—If a liquid ammonia solution of $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ is brought in contact with metallic beryllium, the

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[11] In view of this it seems very doubtful whether a salt of the formula $Be(NH_2)_2 \cdot BeI_2 \cdot xNH_3$ exists.

latter slowly dissolves and within the course of a few weeks a point is reached at which an amorphous, white precipitate begins to form. The liquid ammonia solution, separated at this stage by decantation from the unused beryllium and the white precipitate, can be concentrated to an almost unpourable sirup at 20° without crystallization. An analysis of the crude, white solid remaining after evaporation of the solvent ammonia from the reaction tube gave 9.8% Be, 35.4% N and 48.9% I, corresponding roughly to a compound of the formula $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, which requires 10.1% Be, 36.6% N and 47.3% I.

In an attempt to prepare this compound in a purer condition, the foregoing experiment was repeated. When a moderately concentrated solution of the salt was cooled for some time in an ether-carbon dioxide snow mixture, an abundant crop of small, colorless crystals was obtained. These were freed from mother liquor, dried in a vacuum at 20°, hydrolyzed with water,[12] dissolved in dilute sulfuric acid and analyzed. There was found 10.3% Be, 37.2% N and 47.1% I, in better concordance with the calculated composition of $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ given in the preceding paragraph.

Potassium amide throws down from a solution of the basic salt, $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, a flocculent, white precipitate, which was shown by analysis to be an ammonobasic mixture containing approximately ten atoms of beryllium per atom of iodine. In one experiment the solution in equilibrium with this precipitate was found to contain three atoms of beryllium for each atom of iodine,[13] indicating the dissolved substance to be $5Be(NH_2)_2 \cdot BeI_2 \cdot xNH_3$.

Ammonobasic Beryllium Cyanide.—A solution of mercuric cyanide in liquid ammonia reacts with beryllium, as it does with aluminum,[14] to form a double beryllium-mercuric cyanide, and then a very soluble normal beryllium cyanide, which was not isolated in a state of purity because of the ready formation of soluble ammonobasic cyanides by further reaction with beryllium.

Discussion

It is well known that solutions of the normal beryllium salts in water can dissolve large quantities of beryllium hydroxide, extending in the case of the acetate to six equivalents, while the chloride can hold four and the sulfate three.[3,15] On diluting these solutions with water, precipitates of

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[12] This salt is hydrolyzed by water with evolution of heat to form ammonia, ammonium iodide, beryllium hydroxide and possibly aquo basic salts of beryllium.

[13] That is, per atom of iodine not present in the solution as potassium iodide. The latter salt is also a product of the reaction, as the following equation shows: $3[3Be(NH_2)_2 \cdot BeI_2] + 2KNH_2 = 2[5Be(NH_2)_2 \cdot BeI_2] + 2KI$.

[14] Bergstrom, THIS JOURNAL, **46**, 1559 (1924).

[15] Sidgwick and Lewis, *J. Chem. Soc.*, **129**, 1287–1302 (1926).

a highly basic nature are thrown down, while on evaporation gummy, non-crystalline masses are obtained. Perhaps the only basic beryllium compounds which have been prepared in a state of purity are the salts of the type of basic beryllium acetate, $3Be(CH_3COO)_2 \cdot BeO$ or $Be_4O(CH_3COO)_6$.[16] In contrast with the difficulty of obtaining aquo basic salts of beryllium in a state of purity from water is the relative ease with which many crystalline ammonobasic halides of beryllium can be prepared in liquid ammonia. It is noteworthy though unexpected fact that the very basic compound, $5Be(NH_2)_2 \cdot BeI_2$, is much more soluble in liquid ammonia at $-40°$ than the less basic $3Be(NH_2)_2 \cdot BeI_2$.

In conclusion, the author wishes to thank Dr. E. C. Franklin for his interest in this work and for looking over the manuscript prior to publication.

Summary

1. Beryllium dissolves in liquid ammonia solutions of an excess of ammonium chloride and bromide to form normal beryllium halides with ammonia of crystallization. The salts, $BeCl_2 \cdot 4NH_3$, $BeCl_2 \cdot 2NH_3$ and $BeBr_2 \cdot 4NH_3$ have been prepared.

2. Solutions of the normal halides of beryllium in liquid ammonia readily react with metallic beryllium to form ammonobasic halides; $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$, $3Be(NH_2)_2 \cdot BeBr_2 \cdot 8NH_3$, $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ and $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ have been prepared in crystalline form. There is good evidence for the existence of $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$, although it has not been obtained in crystalline form.

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[Contribution from the Chemical Laboratory of the University of Rochester]

THE SOLUBILITY OF SILVER IN MERCURY[1]

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In connection with work on solutions in this Laboratory, attention was directed to the lack of conclusive data on the solubility of silver in mercury. Many determinations have been made at isolated temperatures[2] but, to our knowledge, Joyner[3] has made the only systematic attempt to investigate this system over a range of temperatures. Yet his work,

[16] Parsons, ref. 3, pp. 62–64; Bragg and Morgan, *Proc. Roy. Soc.* (*London*), **104A**, 437 (1923); Morgan and Astbury, *ibid.*, **112A**, 441 (1926).

[1] This paper was presented by one of the authors (C. B. H.) at the 1927 Spring Meeting of the American Chemical Society, held in Richmond, Virginia.

[2] (a) Gouy, *J. phys.*, [3] **4**, 320 (1895); (b) Humphreys, *J. Chem. Soc.*, **69**, 243 (1896); (c) Reinders, *Z. physik. Chem.*, **27**, 285 (1898); (d) Ogg, *ibid.*, **50**, 209 (1905); (e) Eastman and Hildebrand, This Journal, **36**, 2020 (1914).

[3] Joyner, *J. Chem. Soc.*, **99**, 195 (1911).