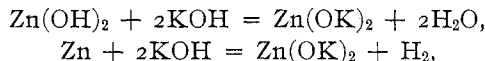


POTASSIUM AMMONOSODIATE, POTASSIUM AMMONOLITHIATE, RUBIDIUM AMMONOSODIATE  
AND RUBIDIUM AMMONOLITHIATE

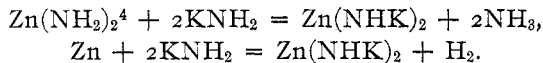
BY EDWARD C. FRANKLIN

Introduction

It will be recalled that F. F. Fitzgerald was able to prepare an ammonozincate of potassium<sup>1</sup> by means of reactions taking place in liquid ammonia which are analogous to those which, in aqueous solution, result in the formation of aquozincate of potassium.<sup>2</sup> Fitzgerald found that just as an aqueous solution of potassium hydroxide dissolves zinc hydroxide or metallic zinc to form the aquozincate in accordance with the equations<sup>3</sup>



so potassium amide, the potash of the ammonia system, acts upon the amphoteric zinc amide and upon metallic zinc to form an ammonozincate of potassium as represented by the equations



<sup>1</sup> Jour. Am. Chem. Soc., 29, 56, 1274 (1907).

<sup>2</sup> Potassium zincate belongs to a water system of acids, bases and salts and is here referred to as the aquozincate in order to distinguish it from the ammonozincate, a similar salt of the ammonia system. For a detailed exposition of the ammonia system of acids, bases and salts, cf. Am. Chem. Jour., 47, 285 (1912).

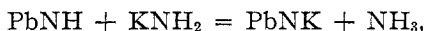
<sup>3</sup> Among the phenomena with which the student of chemistry early becomes familiar is the solubility of zinc hydroxide in solutions of potassium hydroxide and he soon learns to write confidently the first of the equations as representing the reaction which takes place, notwithstanding the fact that, apparently, a zincate of potassium has never been isolated. [Cf. Comey and Jackson: Am. Chem. Jour., 11, 145 (1889); Förster and Günther: Zeit. Elektrochemie 6, 301 (1900); Hantzsch: Zeit. anorg. Chem., 30, 289 (1903); Wood: Jour. Chem. Soc., 97, 878 (1910).]

<sup>4</sup> Zinc amide is to be looked upon as a tetrabasic acid which might be expected to react with potassium amide to form a mono-, di-, tri-, or tetra-potassium salt, though the likelihood that all the hydrogen in a weak polybasic acid,

The former reactions taking place in water solution and the latter in liquid ammonia are obviously strictly analogous. In the one case a weak aquo acid, zinc hydroxide, acts upon an aquo base to form an aquo salt; in the other, an ammonio salt is formed by the action of an ammonio acid on an ammonio base.

The existence of an ammonia analog of aquozincate of potassium thus established it seemed almost a matter of course that an ammonioaluminate and an ammonioplumbite of potassium should be capable of existence, more especially in view of the fact that the precipitates formed by the action of potassium amide on liquid ammonia solutions of salts of aluminium and lead were found to be readily soluble on excess of the precipitant.

As was expected, the solution obtained by dissolving lead imide in a liquid ammonia solution of potassium amide was found to contain an ammonioplumbite of potassium. The compound,<sup>1</sup> formed in accordance with the equation



separates from concentrated solution in the form of beautiful crystals of sharply definite composition, a behavior which is

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such as zinc amide must be assumed to be, could be replaced by potassium in the presence of ammonia is of course remote.

Fitzgerald obtained a beautifully crystallized dipotassium salt of the empirical composition  $\text{ZnN}_4\text{H}_8\text{K}_2$ , which may be formulated as an ammoniated dipotassium salt as represented by the formula  $\text{Zn}(\text{NHK})_2 \cdot 2\text{NH}_3$ , or it may be looked upon as a "molecular compound" of zinc amide and potassium amide and given the formula  $\text{Zn}(\text{NH}_2)_2 \cdot 2\text{KNH}_2$ . According to Werner (*Neu. Anschau. Geb. anorg. Chem.* 3te. Aufl., 123 (1913)) the formation of salts by the action of potassium hydroxide on the hydroxides of tin (stannic), lead zinc, aluminium, platinum, gold, etc., does not consist in the substitution of acid hydrogen by the alkali metal but in the direct union (*Anlagerung*) of the basic hydroxide with the central atom of the heavy metal hydroxide as represented by the formula  $[\text{Zn}(\text{OH})_2]\text{Na} \cdot 2\text{H}_2\text{O}$  for the compound obtained by Comey and Jackson and by Förster and Günther from solutions of zinc hydroxide in aqueous sodium hydroxide. Such compounds Werner calls hydroxo salts. Analogously our potassium ammoniozincate is an amido salt and, according to Werner, should be given the formula  $[\text{Zn}(\text{NH}_2)_2]\text{K}_2$ . Potassium ammoniozincate loses ammonia on being heated but a well-defined deammonation product has not been obtained.

<sup>1</sup> *Jour. Phys. Chem.*, 15, 509 (1911).

in marked contrast with water solutions of the aquo plumbite.<sup>1</sup>

The ammonia analog of aquoaluminate of potassium is undoubtedly formed when potassium amide is added in excess to a liquid ammonia solution of aluminium iodide but attempts to isolate the salt have been unsuccessful.<sup>2</sup>

Although strictly analogous compounds, the behavior of the aquozincate and aquo plumbite of potassium on the one hand, and the corresponding ammonio salts on the other, towards the respective solvents, water and ammonia, is in striking contrast. The ammonio salts are easily obtained pure in the form of beautiful crystals which show no apparent tendency to undergo ammonolysis in contact with liquid ammonia, whereas the aquo salts are highly hydrolyzed in aqueous solution even in the presence of a large excess of potassium hydroxide, and are isolable with difficulty or not at all.

In explanation of this striking difference in behavior it seems reasonable to assume that the ammonolyzing power of liquid ammonia is comparatively weak compared with the hydrolyzing power of water, an assumption which is supported by the fact that pure liquid ammonia is a very much poorer conductor of electricity<sup>3</sup> than is pure water. It follows, therefore, as a result of the very low concentration of amide ions in liquid ammonia as compared with the concentration of hydroxyl ions in water, that acids entirely too weak to form stable salts, even with strong bases, in water solution will, in liquid ammonia solution, form salts which undergo but slight ammonolysis.

Such considerations as these, together with the very satisfactory outcome of the work described above and with early observations showing that salts of a number of metals, such as silver, copper and thallium, in solution in liquid ammonia, when treated with potassium amide, give precipitates

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<sup>1</sup> Potassium plumbite is unknown except as it exists in the solution formed by dissolving lead hydroxide in potassium hydroxide.

<sup>2</sup> Jour. Am. Chem. Soc., 27, 849 (1905); 37, 847 (1915).

<sup>3</sup> Cf. Ibid., 27, 191 (1905).

which dissolve on adding the precipitant in excess led to a series of investigations planned to determine the extent to which the formation of salts by the action of potassium amide on the amides, imides and nitrides of other metals might be carried. The result of these investigations has been to show that a large number of metallic amides, including those of such strongly positive metals as magnesium, barium, strontium and calcium, react with potassium amide just as zinc amide does to form compounds which must be looked upon as salts in which these metals play the same part as zinc, lead and aluminium do in the compounds formed by the action of potassium hydroxide on the hydroxides of these metals.<sup>1</sup>

It will be shown below that the formation of this class of salts does not stop with the amides of the alkaline earth metals but extends even to the amides of sodium and lithium. These latter amides acting as ammono acids react with the strongly basic amides of potassium and rubidium to form salts which, it would seem, are properly designated by the names potassium ammonosodiate, potassium ammonolithiate, rubidium ammonosodiate and rubidium ammonolithiate.

A list of the compounds which have been prepared is given in the table which follows. Each compound is formulated first as an ammono salt of potassium containing "ammonia

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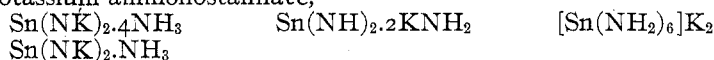
<sup>1</sup> It has probably frequently been assumed that the well-known solubility of many metallic oxides in fused potassium hydroxide is accompanied by salt formation. Certainly the existence of the list of ammono salts tabulated below lends considerable support to the view that in these fusions the aquo analogs of our ammono salts are present.

Some observations on the solubility of metallic oxides in fused potassium hydroxide gave the following results:

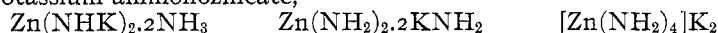
The oxides of barium, strontium, calcium, magnesium, zinc, cadmium, mercury, and silver dissolve to clear, colorless solutions. Metallic magnesium and calcium dissolve in fused potassium hydroxide with vigorous evolution of hydrogen. Cupric oxide gives a solution blue at lower temperatures and brown at higher. Nickel oxide gives a purple solution which changes to brown at high temperatures. Ferric oxide gives a purple solution when dilute, more concentrated solutions are very dark. Bismuth oxide dissolves abundantly to form a deep orange-colored solution. Metallic platinum gives a clear, yellow solution. Palladium dissolves from the palladium gold alloy known as "palau" to form a green solution, leaving the interior of the crucible yellow from exposed gold.

of crystallization." A second formulation is given the majority of them in accordance with which they are represented as "molecular compounds" of potassium amide with the acid or less basic amide. Finally, in so far as practicable, they are given formulas as amido salts, that is, as salts related to ammonia as Werner's hydroxo salts are related to water.

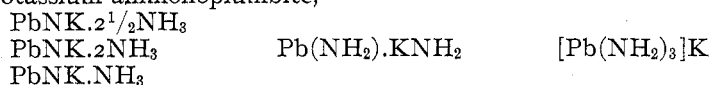
Potassium ammonostannate,<sup>1</sup>



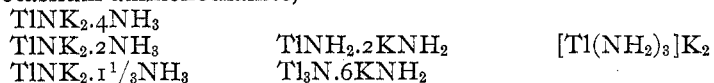
Potassium ammonozincate,<sup>2</sup>



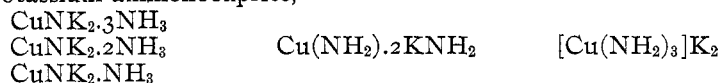
Potassium ammonoplumbite,<sup>3</sup>



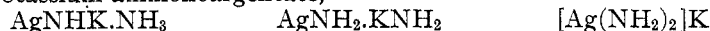
Potassium ammonothallite,<sup>4</sup>



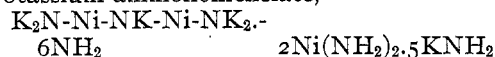
Potassium ammonocuprite,<sup>5</sup>



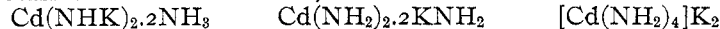
Potassium ammonoargentate,<sup>6</sup>



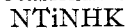
Potassium ammononickelate,<sup>7</sup>



Potassium ammonocadmiate,<sup>8</sup>



Potassium ammonotitanate,<sup>9</sup>



<sup>1</sup> Jour. Am. Chem. Soc., **29**, 1693 (1907).

<sup>2</sup> Ibid., **29**, 660, 1274 (1907).

<sup>3</sup> Ibid., **27**, 842 (1905); Jour. Phys. Chem., **15**, 509 (1911).

<sup>4</sup> Jour. Phys. Chem., **16**, 682 (1912).

<sup>5</sup> Jour. Am. Chem. Soc., **34**, 1501 (1912).

<sup>6</sup> Ibid., **37**, 852 (1915).

<sup>7</sup> Jour. Phys. Chem., **19**, 559 (1915).

<sup>8</sup> Ibid., **19**, 542 (1915).

<sup>9</sup> Jour. Am. Chem. Soc., **34**, 1497 (1912).

Potassium ammonobariate, <sup>1</sup>		
BaNK <sub>2</sub> .2NH <sub>3</sub>	Ba(NH <sub>2</sub> ) <sub>2</sub> .KNH <sub>2</sub>	[Ba(NH <sub>2</sub> ) <sub>3</sub> ]K
Potassium ammonostrontiate, <sup>1</sup>		
SrNK <sub>2</sub> .2NH <sub>3</sub>	Sr(NH <sub>2</sub> ) <sub>2</sub> .KNH <sub>2</sub>	[Sr(NH <sub>2</sub> ) <sub>3</sub> ]K
Potassium ammonocalciate, <sup>1</sup>		
CaNK <sub>2</sub> .2NH <sub>3</sub>	Ca(NH <sub>2</sub> ) <sub>2</sub> .KNH <sub>2</sub>	[Ca(NH <sub>2</sub> ) <sub>3</sub> ]K
Potassium ammonosodiate,		
NaNK <sub>2</sub> .2NH <sub>3</sub>	NaNH <sub>2</sub> .2KNH <sub>2</sub>	[Na(NH <sub>2</sub> ) <sub>3</sub> ]K <sub>2</sub>
Potassium ammonolithiate,		
LiNK <sub>2</sub> .2NH <sub>3</sub>	LiNH <sub>2</sub> .2KNH <sub>2</sub>	[Li(NH <sub>2</sub> ) <sub>3</sub> ]K <sub>2</sub>
Rubidium ammonosodiate,		
NaNHRb.NH <sub>3</sub>	NaNH <sub>2</sub> .RbNH <sub>2</sub>	[Na(NH <sub>2</sub> ) <sub>2</sub> ]Rb
NaNRb <sub>2</sub> .2NH <sub>3</sub>	NaNH <sub>2</sub> .2RbNH <sub>2</sub>	[Na(NH <sub>2</sub> ) <sub>3</sub> ]Rb <sub>2</sub>
Rubidium ammonolithiate,		
LiNHRb.NH <sub>3</sub>	LiNH <sub>2</sub> .RbNH <sub>2</sub>	[Li(NH <sub>2</sub> ) <sub>2</sub> ]Rb

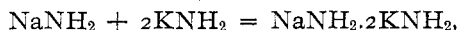
### Experimental

In the pages following is given a description of the manipulative details together with the analytical data which establish the existence of the four salts named in the title of this paper.

The reader is reminded that the reactions involved in the preparation of these salts are carried out in liquid ammonia solutions and entirely out of contact with air and water.

*Di-Potassium Ammonosodiate, NaNK<sub>2</sub>.2NH<sub>3</sub>, or NaNH<sub>2</sub>.2KNH<sub>2</sub> or (Na(NH<sub>2</sub>)<sub>3</sub>)K<sub>2</sub>.*—Experiments described in detail below show that this compound is formed by the action of potassium amide in solution in liquid ammonia on sodium amide;<sup>2</sup> by the addition of a soluble salt of sodium, such as sodium iodide, to an excess of potassium amide in solution in liquid ammonia; and by allowing a solution containing metallic sodium and potassium amide, the latter in large excess, to stand in contact with a small quantity of platinum black.

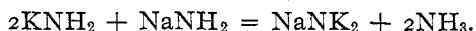
The reaction which takes place between potassium amide and sodium amide may be explained as resulting in the formation of a simple addition product in accordance with the equation



<sup>1</sup> Jour. Am. Chem. Soc., 37, 2295 (1915).

<sup>2</sup> Sodium amide is very slightly soluble in liquid ammonia.

or it may be interpreted as the interaction of an acid and a base to form a salt as represented by the equation



The salt formed separates from solution with two molecules of ammonia of crystallization.

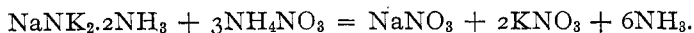
When solutions of potassium amide and sodium iodide are brought together in equivalent amounts, or when the latter is in excess, a crystalline precipitate of sodium amide is formed in accordance with the equation



An equivalent of sodium iodide is mixed with an amount of potassium amide greater than one and less than three equivalents gives a precipitate which is a mixture of sodium amide and potassium ammonosodiate, while one equivalent of the salt added carefully to three or more equivalents of potassium amide results in the formation of pure potassium ammonosodiate. By the careful addition of sodium iodide to an excess of potassium amide the salt may be obtained in the form of beautifully developed crystals.

When a liquid ammonia solution containing metallic sodium and a large excess of potassium amide is allowed to stand in contact with a small quantity of platinum black the metallic sodium is rapidly converted into sodium amide which, instead of crystallizing out as such, reacts with the potassium amide to form the potassium salt of sodium amide.

The salt does not lose ammonia at 100° in vacuum. At higher temperatures it melts, loses ammonia and attacks the glass container, for which reason attempts have not been made to obtain definite deammonation products. The compound is decomposed by liquid ammonia solutions of acids with the formation of salts of sodium and potassium. For example, the action of ammonium nitrate<sup>1</sup> is represented by the equation




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<sup>1</sup> Ammonium salts in liquid ammonia solution show the characteristic properties of acids.

It is vigorously attacked by water giving as hydrolytic products the hydroxides of sodium and potassium and ammonia.

Preparatory to analysis the compound is decomposed in vacuum by the action of water vapor, after which the hydrolytic products are dissolved in water and converted into chlorides by the addition of a slight excess of hydrochloric acid. The analytical procedure from this stage is the simple one of determining potassium, sodium, and ammonia in an aqueous solution containing potassium, sodium and ammonium chlorides. A description of this procedure is unnecessary.

*Preparation I.*—A liquid ammonia solution of potassium amide in large excess was poured from one leg of a reaction tube<sup>1</sup> upon pure sodium amide, prepared from about 150 milligrams of metallic sodium, in the other. Mere standing of the potassium amide solution in contact with the very slightly soluble sodium amide would undoubtedly, in the course of time, result in the complete conversion of the latter into potassium ammonosodiate. However, in the absence of any adequate evidence of complete reaction, it seemed advisable to recrystallize the product, a process which, because of the slight solubility of the salt, turned out to be a rather tedious task. Recrystallization was accomplished as follows: The solution containing the excess of potassium amide and saturated with the reaction product was poured into the second leg of the reaction tube and the tube was then so disposed, with the one leg immersed in tepid water and the other in an ice bath, that the ammonia from the solution was distilled back upon the reaction product. After boiling away the greater portion of the solvent a promising quantity of well-formed crystals had separated. The mother liquor was then poured over into the leg containing the distillate and the original reaction product. After saturating with the latter the solution was again transferred to the second leg of the reaction tube and again evaporated. A second portion of the pure compound was thus added to the first small crop of crystals. The operations thus described were repeated un-

<sup>1</sup> These tubes have been described in earlier papers cited above.



til the whole of the reaction product was transferred to the second leg of the apparatus. The preparation, consisting of well-formed crystals, was washed several times with small quantities of solvent and dried in vacuum at  $20^{\circ}$  preparatory to analysis.

One-fourth of the specimen which weighed 0.9152 g gave 0.5595 g mixed  $\text{KCl-NaCl-NH}_4\text{Cl}$ , 0.3176 g mixed  $\text{KCl-NaCl}$  and 0.7508 g  $\text{K}_2\text{PtCl}_6$ . Another fourth gave 0.0650 g N.

*Preparation II.*—This experiment was in all essential respects a repetition of the preceding. A crop of beautiful crystals was obtained. One-fourth of the specimen which weighed 0.5929 g gave 0.3661 g mixed  $\text{KCl-NaCl-NH}_4\text{Cl}$ , 0.2078 g mixed  $\text{KCl-NaCl}$  and 0.4912 g  $\text{K}_2\text{PtCl}_6$ . Another fourth gave 0.0406 g N.

*Preparation III.*—A liquid ammonia solution of sodium iodide, contained in one leg of a reaction tube, was added very slowly to a solution of approximately four equivalents of potassium amide contained in the second leg. Early in this procedure crystals began to separate on the walls and bottom of the tube. With the exercise of care in mixing the solutions a crop of beautiful crystals was obtained which was washed several times with small quantities of liquid ammonia and dried in vacuum at  $20^{\circ}$  for analysis. The specimen weighed 0.1667 g. One-half gave 0.2052 g mixed  $\text{KCl-NaCl-NH}_4\text{Cl}$  and 0.1157 g mixed  $\text{KCl-NaCl}$ .<sup>1</sup> A test made of the other half of this preparation showed it to be free from iodine.

*Preparation IV.*—A second experiment conducted as above described gave an even more beautiful specimen of the salt which, dried in vacuum at  $20^{\circ}$ , weighed 0.2254 g. One-half gave 0.1560 g mixed  $\text{KCl-NaCl}$ ,<sup>1</sup> the other half gave 0.0320 g N.

<sup>1</sup> To establish the composition of the compound formed in this and the preceding experiment it was not deemed necessary to separate the potassium from the mixed chlorides as potassium chlorplatinate. Dependence was placed upon the determinations of the nitrogen content and the weight of the mixed potassium sodium chlorides.

In a further experiment a solution of potassium amide was run carefully into an excess of sodium iodide in solution in liquid ammonia in order to determine whether sodium amide is formed under these conditions. A crystalline precipitate was formed which analysis showed to consist of pure sodium amide. The analytical data are not given for the reason that sodium amide is a known compound.

The composition of potassium ammonosodiate calculated from the above given analytical data follows:

	Calculated for $\text{NaNK}_{2.2}\text{NH}_3$	Found			
		I	II	III	IV
K	52.3	52.7	53.2	....	....
Na	15.4	15.0	15.1	....	....
N	28.8	27.7-28.4	27.4-28.1	28.1	28.4
KCl-NaCl	139.1	138.8	140.0	138.8	138.8

*Mono-Rubidium Ammonosodiate.*  $\text{NaNHRb.NH}_3$ ,  $\text{NaNH}_2\text{-RbNH}_2$  or  $[\text{Na}(\text{NH}_2)_2]\text{Rb}$ .—With the existence of an ammonosodiate of potassium established one may assume almost as a matter of course, that a similar compound of rubidium would be formed by treating sodium amide with a liquid ammonia solution of rubidium amide. Experiments described below show that certainly one, and probably two, definite compounds may be so prepared. The compound whose existence has been definitely established differs from the potassium salt in that the latter contains two equivalents of potassium to each equivalent of sodium, whereas in the former the rubidium and sodium are present in equivalent quantities. The second compound whose existence is less certain corresponds in composition to that of potassium ammonosodiate. If it is legitimate to look upon the action between sodium amide and rubidium amide as that of an acid on a base, and it has been shown earlier in this paper that such a view is a reasonable one, then, since sodium amide or ammono sodic acid is a di-basic acid it should be capable of forming two salts by

interaction with rubidium amide which is a monacid base. The one may be called acid or mono-rubidium ammonosodiate, the other normal or di-rubidium ammonosodiate. Both these salts are readily soluble in liquid ammonia. The di-rubidium salt is apparently incapable of existence in solution excepting in the presence of a large excess of rubidium amide. They are acted on violently by water giving as hydrolytic products rubidium and sodium hydroxides and ammonia and are decomposed by acids in ammonia solution just as is the corresponding potassium salt.

*Preparation I.*—Into the two legs of the familiar reaction tube were introduced, respectively, 93 milligrams of metallic sodium and 800 milligrams of metallic rubidium, each with a minute portion of platinum black which, it will be remembered, very greatly accelerates the conversion of the metals into the amides. When the solution of the readily soluble rubidium amide was poured into the leg containing the very slightly soluble amide of sodium the latter was found to dissolve much more readily than it does in a solution of potassium amide. By slowly evaporating the solvent from the concentrated solution a crop of beautiful crystals was obtained which was dissolved in fresh solvent and the solution thus obtained again evaporated to crystallization. The crop of crystals obtained was drained of mother liquor and washed several times with small quantities of solvent to insure its purity. The salt was dried in vacuum at  $50^{\circ}$ , hydrolyzed by exposure to water vapor and converted into a mixture of rubidium chloride, sodium chloride and ammonium chloride for analysis. The specimen weighed 0.1684 g. Two-fifths gave 0.0131 g N. Three-fifths gave 0.1289 g mixed  $\text{RbCl-NaCl}$  and 0.2059 g  $\text{Rb}_2\text{PtCl}_6$ .

*Preparation II.*—The mother liquor from the preceding experiment was transferred<sup>1</sup> to a new reaction tube in which it was evaporated to crystallization. The crop of crystals was washed three times with small portions of pure solvent

<sup>1</sup> A description of the manner in which such transfers are made has been described in another place. Jour. Am. Chem. Soc., 36, 1460 (1915).

preparatory to analysis. Dried in vacuum at  $20^{\circ}$  the specimen weighed 0.1284 g. One-fifth gave 0.00508 g N. Four-fifths gave 0.2097 g mixed  $\text{RbCl-NaCl-NH}_4\text{Cl}$ , 0.1316 g mixed  $\text{RbCl-NaCl}$  and 0.2116 g  $\text{Rb}_2\text{PtCl}_6$ .

*Preparation III.*—A repetition of the procedure described above for making Preparation I, in which 40 milligrams of metallic sodium and 400 milligrams of metallic rubidium were used, gave a product which dried at  $20^{\circ}$  in vacuum weighed 0.1419 g. One-half gave 0.1446 g mixed  $\text{RbCl-NaCl-NH}_4\text{Cl}$ , 0.0907 g mixed  $\text{RbCl-NaCl}$  and 0.1457 g  $\text{Rb}_2\text{PtCl}_6$  and 0.0353 g  $\text{Na}_2\text{SO}_4$ .

*Preparation IV.*—In the preceding experiments, excepting the first, the solutions worked with contained a large excess of rubidium amide. For certain reasons it seemed desirable to undertake the preparation of a specimen of the salt from a solution containing approximately equivalent quantities of the amides. Accordingly a solution of slightly more than one equivalent of rubidium amide was poured upon the sodium amide formed from 122 milligrams metallic sodium. The sodium amide dissolved readily and completely. On cooling the concentrated solution a good crop of crystals was obtained which, when washed and dried, that is, freed from solvent in vacuum at  $20^{\circ}$ , weighed 0.2409 g. Three-fifths gave 0.2930 g mixed  $\text{RbCl-NaCl-NH}_4\text{Cl}$  and 0.1845 g  $\text{RbCl-NaCl}$ .

*Preparation V.*—The mother liquor from the preceding preparation was concentrated and cooled to  $-33^{\circ}$ . The crop of crystals formed was dissolved in pure solvent and the solution thus obtained evaporated to crystallization. The new crop was again dissolved and recrystallized and the final product thus obtained was washed with pure solvent and dried for analysis. The beautiful specimen weighed 0.2244 g. Two-fifths gave 0.01755 g N. Three-fifths gave 0.2718 g mixed  $\text{RbCl-NaCl-NH}_4\text{Cl}$  and 0.1716 g mixed  $\text{RbCl-NaCl}$ . In neither this nor the preceding experiment was it considered necessary to separate the sodium and rubidium in order to establish the composition of the compound.

The percentage composition of mono-rubidium ammonosodiate calculated from data given above follows:

	Calculated for $\text{NaNHRb}_4\text{NH}_3$	Found				
		I	II	III	IV	V
Na	16.4	16.6	16.5	16.7-16.1	...	...
Rb	60.8	60.3	60.8	60.7	...	...
N	19.9	19.5	19.8-19.9	19.9	19.7	19.5-19.5
RbCl-NaCl						
NaCl	127.7	127.5	128.0	127.9	127.6	127.6

**Di-Rubidium Ammonosodiate,  $\text{NaNRb}_2.2\text{NH}_3$  or  
 $\text{NaNH}_2.2\text{RbNH}_2$  or  $[\text{Na}(\text{NH}_2)_3]\text{Rb}_2$**

The mother liquors from preparations 2 and 3 which contained a very large excess of rubidium amide were transferred to a reaction tube and evaporated to crystallization at a low temperature with the object in view of determining whether under these conditions a di-rubidium salt might be formed. The crystals were distinctly different in appearance from those of the mono-rubidium salt and they seemed to be distinctly more soluble. The product was not recrystallized but was simply drained of the concentrated mother liquor and washed twice with small quantities of the pure solvent. The specimen dried in vacuum at  $20^\circ$  weighed 0.4716 g. One-fifth gave 0.01555 g N. Another fifth gave 0.01563 g N. Three-fifths gave 0.5270 g mixed RbCl-NaCl- $\text{NH}_4\text{Cl}$ , 0.3474 g mixed RbCl-NaCl and 0.6807 g  $\text{Rb}_2\text{PtCl}_6$ .

Calculated for	Na	Rb	N
$\text{NaNRb}_2.2\text{NH}_3$	9.5	70.7	17.3
Found	8.7	71.1	16.6-16.6

It should perhaps be said that the evidence for the existence of the di-rubidium salt is not entirely conclusive. The exhaustion of the supply of metallic rubidium prevented a repetition of this experiment.

**Di-Potassium Ammonolithiate,  $\text{LiNK}_2 \cdot 2\text{NH}_3$ ,  $\text{LiNH}_2 \cdot 2\text{KNH}_2$  or  $[\text{Li}(\text{NH}_2)_3]\text{K}_2$** 

Because of the very slight solubility of potassium ammonolithiate several attempts to prepare the salt by the action of liquid ammonia solutions of potassium amide on lithium amide led to unsatisfactory results. The attempt was first made to obtain a specimen of the salt by transferring successive small portions to the second leg of the reaction tube in the manner described above for the first preparation of potassium ammonosodiate. The salt was found to be insufficiently soluble to make this procedure practicable. It was then decided to allow the solution of potassium amide to stand in contact with the practically insoluble lithium amide for several days, with occasional shaking, in the hope that thus the conversion of the latter into potassium ammonolithiate might be completed. The result, however, was unsatisfactory, for analyses of two specimens made in this manner showed them to be mixed with considerable amounts of lithium amide. Following these unsuccessful attempts to prepare specimens of potassium ammonolithiate the pure compound was obtained by the action of potassium amide on lithium iodide and also by allowing a mixed solution of the two metals in liquid ammonia to stand in the presence of platinum black.

The salt was obtained in the form of minute colorless crystals by the first method, slightly grayish by the second from the presence of platinum black. It is practically insoluble in liquid ammonia. Acids, that is, acid amides and ammonium salts of oxygen and halogen acids, decompose it with the formation of the corresponding salts of lithium, potassium and ammonium. It is energetically acted upon by water giving as hydrolytic products lithium and potassium hydroxides and ammonia. For the determination of the composition of the salt a weighed specimen was hydrolyzed in vacuum by water vapor. The potassium and lithium hydroxides and ammonia formed were dissolved in an excess of dilute hydrochloric and the aqueous solution of mixed chlorides analyzed by the well-known methods.

*Preparation I.*—A dilute solution of lithium iodide formed by the action of a liquid ammonia solution of ammonium iodide on metallic lithium was added in successive small portions to a large excess of potassium amide solution. After the addition of each portion of iodide it was thoroughly mixed with the concentrated solution of potassium amide before adding the next portion, thus avoiding the formation of lithium amide, which, once precipitated, is slowly converted into the double amide.

The crystalline precipitate obtained was washed well with pure solvent and dried in vacuum at  $20^{\circ}$ . The specimen weighed 0.2080 g. Three-tenths gave 0.0191 g N, one-half gave 0.1486 g mixed KCl-LiCl, 0.3721 g  $K_2PtCl_6$  and 0.0451 g  $Li_2SO_4$ . Iodine was tested for and found to be absent.

*Preparation II.*—A third method for the preparation of potassium ammonolithiate was based on the hypothesis that the simultaneous conversion of metallic lithium and metallic potassium, the latter in large excess, in solution in liquid ammonia into their amides would result in the direct separation of the compound in view. Accordingly, the two metals, together with a minute portion of platinum black, were introduced into one leg of a reaction tube, ammonia was then distilled in upon the metals and the apparatus set aside until the reaction between the metals and the solvent was complete. A surprisingly small quantity of salt was found, a result due, as was realized later, to an error in using a much smaller quantity of lithium than had been intended. The crystalline product was grayish in color from the presence of platinum black. Well washed and dried in vacuum at  $20^{\circ}$  the specimen weighed 0.0479 g. The platinum black recovered weighed 0.0004 g. One-half gave 0.00758 g N. The other half gave 0.0341 g mixed KCl-LiCl.

*Preparation III.*—A repetition of the procedure described above, using 37 milligrams of lithium and 410 milligrams of potassium, gave a grayish but well-crystallized product which weighed 0.5323 g. From the specimen

0.0046 g Pt was recovered. One-fifth of the specimen gave 0.0332 g N. Another fifth gave 0.1517 g mixed KCl-LiCl and 0.3819 g  $K_2PtCl_6$  and 0.0386 g LiCl. One-tenth gave 0.01668 g N, another tenth gave 0.0761 g KCl-LiCl and 0.1923 g  $K_2PtCl_6$ .

*Preparation IV.*—A fourth specimen of potassium ammonolithiate, made by the action of potassium amide on lithium iodide, gave on analysis the results found under IV below. The analytical data were not available when this paper was written.

	Calculated for $LiNK_{2.2}NH_3$	Found			
		I	II	III	IV
Li	5.3	5.5-5.5	....	5.5	5.3
K	58.7	57.6	....	58.3	58.6
N	31.5	30.6	31.9	31.5	31.6
LiCl-KCl	143.8	143.0	143.6	143.7	144.1

**Mono-Rubidium Ammonolithiate,  $LiNHRb.NH_3$  or  
 $LiNH_2.RbNH_2$  or  $[Li(NH_2)_2]Rb$**

A pure specimen of this salt was prepared by the action of a solution of rubidium amide in excess on metallic lithium in the presence of platinum black in the following described manner:

Into the one leg of a reaction tube were introduced 500 mg of metallic rubidium together with a small quantity of platinum black, and into the other 20 mg of metallic lithium. Ammonia was then distilled into the apparatus to bring the metals into solution. After the lapse of a few minutes the rubidium was completely converted into the amide while the amount of lithium amide simultaneously formed in the absence of the accelerator was entirely negligible. As soon as the blue color of the rubidium solution had disappeared the solution of metallic lithium was poured into the leg containing the rubidium amide and platinum black. The metallic lithium was then generally converted into the amide in the



presence of a large excess of rubidium amide, a condition which insured complete action between the two amides. The grayish<sup>1</sup> crystalline product was found to be so slightly soluble that no attempt was made to recrystallize it. It was simply washed several times with pure solvent to free it from mother liquor and dried in vacuum at 20° preparatory to analysis.

For analysis the compound was hydrolyzed by water vapor and then dissolved in dilute hydrochloric acid. In the aqueous solution of chlorides thus obtained the rubidium lithium and nitrogen were determined by the usual methods. The specimen weighed 0.3380 g. The platinum black filtered from the acidified aqueous solution of the mixed chlorides weighed 0.0026 g. One-fifth of the specimen gave 0.0148 g N. Three-tenths gave 0.0223 g N. One-half gave 0.2192 g mixed RbCl-LiCl, 0.3878 g Rb<sub>2</sub>PtCl<sub>6</sub> and 0.0762 g Li<sub>2</sub>SO<sub>4</sub>.

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Calculated for			
LiNHK.NH <sub>3</sub>	Li 5.6	Rb 68.7	N 22.5
Found	5.6-5.8	68.4	22.1

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It is interesting to note in passing that of the 20 mg of lithium used 19 mg were recovered in the preparation obtained while of the 500 mg of rubidium about 270 mg remained in the mother liquor as rubidium amide.

The existence of this compound was not confirmed by the preparation and analysis of a second specimen for the reason that our limited supply of metallic rubidium was exhausted.

Rubidium ammonolithiate has been obtained as a crystalline precipitate very slightly soluble in liquid ammonia. As do the other double amides described in this paper, it dissolves in liquid ammonia solution of acids and is vigorously attacked by water.

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<sup>1</sup> From intermixture of platinum black.

**Isomorphous Mixtures of Rubidium Amide and Potassium Amide**

Four unsuccessful attempts were made to separate a definite compound from solutions containing rubidium amide and potassium amide, both of which, it should be noted, are very soluble in liquid ammonia. From solutions of the mixed amides good crops of crystals were obtained on cooling the concentrated solutions nearly to the freezing point of ammonia, but in no case were rubidium and potassium present in these crystals in atomic ratios. Products containing the amides in ratios approximately represented by the formulas  $\text{KNH}_2.3\text{RbNH}_2$ ,  $\text{KNH}_2.2.5\text{RbNH}_2$ ,  $\text{KNH}_2.1.5\text{RbNH}_2$ , and  $\text{KNH}_2.\text{RbNH}_2$  were obtained. It must therefore be concluded that these two amides form isomorphous mixtures. It is interesting to note that the crystals are obtained relatively richer in rubidium than the solutions from which they are deposited. In one experiment recrystallization repeated three times gave a preparation which was nearly pure rubidium amide from a solution containing relatively a large quantity of potassium amide.

**Summary**

In the introductory part of this paper attention is called to the existence of a considerable number of potassium salts of metallic amides which are related to ammonia as the alkali zincates, plumbites and aluminates are related to water. A list of the compounds which have been prepared is given.

In the experimental part is given a description of the manipulative details together with the analytical data which establish the existence of the four salts named in the title of this paper.

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