ART. X.—*On a Series of New Combinations of Ammonia, Picric Acid and Metallic Bases*; by M. CAREY LEA.

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IN a paper published in this Journal, vol. xxvi, 379, for 1858, I described two compounds of picric acid and ammonia with copper and nickel respectively, and mentioned their instability and the great difficulty of obtaining them in a state of tolerable purity. Since then I have found that many other metals form compounds of a similar nature, and have succeeded in obtaining several of them sufficiently pure for approximate analysis. The results obtained are given below—other investigations are in progress and I hope to communicate them hereafter.

When a metallic salt is precipitated by ammonia, and a large excess of the precipitant added, a more or less complete solution of the precipitate is frequently obtained, especially if a considerable quantity of ammoniacal salt be present. I have found that these ammoniacal solutions when treated with an alkaline picrate, for the most part yield an immediate precipitate containing

the elements of a metallic picrate united with those of ammonia. These precipitates are often very beautiful, they are generally yellow or yellowish, somewhat soluble in the mother liquid, or in strong ammoniacal solutions by aid of heat, nearly insoluble in water and decomposed by it very readily, especially if it be present in quantity, or heat be applied. Thrown on a filter and washed, the picric acid, ammonia, and some portion of undecomposed salt in solution pass through, while the greater part of the metallic oxyd remains on the filter and with sufficient washing is perfectly freed from picric acid and ammonia, and presents the appearance of a pure hydrate.

The analyses of these substances were made in the following manner. It was found desirable that before the ammonia and metallic oxyd were determined, the whole of the picric acid should first be removed. This was effected by adding chlorhydric acid to a weighed quantity of the substance carefully dried, and evaporating to dryness at a gentle heat. Ether, which must be anhydrous or nearly so, was added in the proportion of 15 to 18 grammes to '6 or '7 gms. of the salt used, detaching the dry crust and breaking it up to powder with a glass rod that every part might be brought thoroughly in contact with the ether. After standing ten minutes the ether was poured off, a fresh quantity added, and a larger beaker was inverted over that which contained the substance undergoing analysis. After a lapse of three or four hours the liquid was poured off, a third, and, if necessary, a fourth, quantity added in the same way. The decantation is effected with the greatest ease, as, if the ether is sufficiently strong, the chlorids remain nearly or quite dry at the bottom. It was found that by this means the picric acid could be separated with sufficient exactness to afford a tolerably correct estimation of its quantity, a careful trial with a weighed quantity of perfectly pure picric acid showed that the result fell a little under the truth by reason of a small loss arising from minute portions of the acid remaining undissolved. On the other hand, no chlorids are dissolved when the operation is properly performed: the ethereal solution evaporated to dryness, and the residue dissolved in water was not troubled by solution of nitrate of silver.

The operation requires nice manipulation, otherwise the loss of picric acid is considerable, and if the ether be not sufficiently anhydrous, portions of the chlorids may be removed by it.

In this manner the quantity of picric acid was determined, and from it was calculated the quantity of the group $C_{12}H_2N_3O_{14}$, or picric acid minus the equivalent of hydrogen which is replaceable by a metallic oxyd; in other words, the group which by union with a base forms a picrate, or by union with hydrogen forms picric acid. From the residue undissolved by the ether, the ammonia was determined either by distillation with solution of caustic soda, or by precipitation with bichlorid of platinum.

From another portion the metallic oxyd was found by appropriate means.

As far as examined, the ammonia-picrates all contain more than one equivalent of ammonia, and are represented either by the formula:—

Ammonia-picrate of silver.

Nitrate of silver dissolved in water and treated first with excess of ammonia, and the resulting clear solution mixed with cold saturated solution of picrate of ammonia gives immediately an abundant highly crystalline light yellow precipitate of ammonia-picrate of silver, which is to be thrown upon a filter, thoroughly washed with dilute ammonia, and dried in vacuo over sulphuric acid.

It is to be observed that in the formation of this, as well as of all the other salts here described, the metallic solution must invariably be in excess to check as far as possible the precipitation of picrate of ammonia together with the compound sought. I have shown in a paper intended to be read at the same time as this,* that if an alkaline picrate be poured into an alkaline solution, a precipitate of alkaline picrate takes place. When the alkaline solution is strong the precipitate is immediate, and in the ammoniacal solutions used in the preparation of these salts any excess of alkaline picrate would fall with the ammonia-picrate. Even with every precaution, it is difficult and in some cases apparently impossible to obtain the ammonia-picrate perfectly free from this impurity.

Analysis.

·4245 substance gave	·2632 picric acid.
·5865 " "	·3600 " "
·4245 " "	·1577 chlorid of silver.
·5865 " "	·2177 " "
·3788 " "	·4932 chloroplatinate of ammonia.

This leads to the formula:—

Dried over sulphuric acid in vacuo:—

	Calculated.	Found.		Mean.
		1.	2.	
$\text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$ - - -	61·62	61·73	61·11	61·42
Ag - - - - -	29·19	27·96	27·94	27·95
2NH_3 - - - - -	9·19	9·93		9·93
	100·00	99·62		99·30

* See page 75.

The silver falls below, and the ammonia exceeds the calculated amount in consequence of the impossibility of obtaining the salt quite free from admixed picrate of ammonia.

This beautiful salt appears to be one of the most permanent of this very unstable class of substances. It dissolves readily in hot water containing ammonia, sparingly in cold, and crystallizes in fine needles from the hot solution. Heated on platinum foil it detonates and leaves a brilliant spot of metallic silver.

Ammonia-picrate of copper.

A cold saturated solution of picrate of ammonia added to an ammoniacal solution of sulphate or nitrate of copper, immediately throws down an abundant precipitate which after washing with strong solution of carbonate of ammonia and afterward with dilute ammonia exhibits a beautiful pale greenish yellow color with a shade of red through it. It is in fine scales and much resembles the dust of the wings of butterflies.

Analysis gave for this salt a constitution similar to that of the silver salt.

·6059	gms. substance gave	·4652	picric acid.
·9310	" "	"	·1279 oxyd of copper.
1·4240	" "	"	·1577 metallic copper.
·6059	" "	"	·2190 chlorhydrate of ammonia.

The copper was determined in the one case by precipitating the cupric solution while boiling with hyposulphite of soda, dissolving in aqua regia, evaporating to dryness, redissolving in dilute chlorhydric acid, and precipitating with distilled zinc and estimating as metallic copper—in the other by precipitating at 212° by caustic soda.

These results lead to the formula:—

Dried over sulphuric acid in vacuo:—

	Calculated.	Found.		Mean.
		1.	2.	
$\text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$	77·63	76·44		76·44
Cu	10·79	10·97	11·07	11·02
2NH_3	11·58	11·52		11·52
	100·00			98·98

In an experiment to ascertain whether all the moisture was removed by drying in vacuo over SO_3 , a quantity of about two grammes by exposure to a temperature of 210° to 212° for 9 hours in the exsiccator lost a little less than one and a half milligrammes.

Heated on platinum foil the ammonia picrate of copper explodes with some violence and with a dazzling light.

Ammonia-picrate of Cobalt.

To a solution of protochlorid of cobalt prepared from chlorid of purpureo-cobalt in the manner recommended by Gibbs and Gent in their interesting and valuable paper on the ammonia-cobalt bases, a large excess of ammonia was added, and to the filtrate, cold saturated solution of picrate of ammonia. An abundant highly crystalline precipitate falls at once, which after drying is yellowish green: while moist decomposes with great facility with separation of cobaltous oxyd.

·6293 substance gave	·4784 picric acid.
·6075 " "	·4594 " "
·6067 " "	·1641 protosulphate of cobalt.
·5416 " "	·1475 " " "
·6075 " "	·2065 chlorhydrate of ammonia.

which results lead to the formula:—

	Calculated.	Found.		Mean.
		1.	2.	
$\text{C}_{12}\text{H}_2\text{N}_3\text{O}_{14}$	75·87	75·69	75·29	75·49
Co	9·82	10·13	10·29	10·21
2NH_3	11·32	10·81		10·81
HO	2·99			
	100·00			

This salt is much more unstable than the foregoing, and undergoes a commencement of decomposition in washing: even when this part of the operation is performed with great care, using carbonate of ammonia and dilute liquid ammonia, a portion of picrate of ammonia is washed through, and as cobaltous oxyd is not easily soluble in ammoniacal solutions, it is not easily removed by washing with such. It is also probable that more or less cobaltous oxyd is thrown down with the precipitate, as the latter at the first moment crystalline, becomes quickly more and more curdy—and ammoniacal solution of cobalt by mere dilution with water throws down a bright green precipitate. In the preparation of the ammoniacal solution, it is better to drop a strong solution of cobaltous chlorid into a large excess of ammonia.

Like the foregoing this salt explodes by heat.

Ammonia-picrate of Zinc.

To a solution of pure sulphate of zinc, chlorhydric acid was added in sufficient quantity to prevent precipitation by the sub-

sequent addition of ammonia in excess. To the clear solution, a hot, strong solution of picrate of ammonia was added. Immediately the whole became nearly solid with beautiful yellow needles and scales—the beaker was rapidly cooled by cold water, the contents thrown on a filter, and washed first with a solution of carbonate of ammonia mixed with caustic ammonia, and finally with dilute caustic ammonia alone.

The splendid gold yellow mass of interlaced needles and scales, was more or less decomposed, even by the most careful washing, so that the brightest and purest parts only could be taken for analysis, nor were even these satisfactory.

$C_{12}H_2N_3O_{14}$	mean of 5 determinations,	81.26
NH_3	“ 3 “ “	9.06
Zn	“ “ “ “	10.08
		<hr/> 100.30

The formula $3NH_3 \cdot 2 \left[ZnO \cdot C_{12} \frac{H_2}{3NO_4} \right] O$ requires:—

$2C_{12}H_2N_3O_{14}$	-	-	-	-	79.692
$3NH_3$	-	-	-	-	8.913
$2Zn$	-	-	-	-	11.395
					<hr/> 100.00

The salt examined may be either this compound containing admixed picrate of ammonia, or may be a mixture of:—

The fact that when a strongly acid solution of zinc-chlorid is supersaturated with ammonia, the compounds $2NH_3 \cdot ZnO \cdot HCl$ and $NH_3 \cdot ZnO \cdot HCl$ successively crystallize out, speaks in favor of the latter hypothesis.

Ammonia-picrate of Cadmium.

The cadmium salt is obtained and purified in exactly the same manner as the zinc, which it nearly resembles: it is however not so bright in color, but pure canary yellow. Like the zinc salt it redissolves in its mother liquid by heat without decomposition, but like almost all the compounds here described, when washed with pure water on a filter, the picric acid and ammonia wash through. A greyish white residue of oxyd of cadmium remains behind.

Heated on platinum foil, the salt deflagrates with a beautiful green light.

·7170	substance gave	·5247	picric acid.
·6622	"	·4877	" "
1·1459	"	·8452	" "
·6496	"	·1653	sal ammoniac.
1·1459	"	·2945	" "
·6045	"	·6289	chlorplatinat of ammonia.
·7321	"	·1501	cadmium oxyd.

These results lead to the formula:—

	Calculated.	1.	2.	Found.	3.	Mean.
2(C ₁₂ H ₂ N ₃ O ₁₄)	73·67	73·44	72·86	73·31		73·20
3NH ₃	8·24	8·10	8·17	7·93		8·07
2Cd	18·09	17·94				17·94
	100·00					99·24

It seems however not improbable that this substance may be a mixture in nearly equivalent quantities of the salts:—

for reasons similar to those mentioned in the case of the zinc salt.

Ammonia-picrate of Chromium.

This salt is easily obtained from an ammoniacal solution of chromoxyd which may be prepared in the following manner:

Three grammes of potash chrome alum are dissolved in water by boiling, the solution removed from the fire and 14 c. c. of pure concentrated sulphuric acid and 90 c. c. of liquid ammonia added. A strongly alkaline beautiful purple solution is thus obtained which may be preserved in well stopped vessels quite filled, for a considerable time.*

To a solution prepared in this manner, a strong hot solution of picrate of ammonia, not in excess, is to be added. Some precipitation follows at once which increases very much as the solution cools. The precipitate is thrown on a filter and washed with dilute liquid ammonia. It consists of splendid green metallic looking scales which if heated with a considerable quantity of water, even strongly ammoniacal, are decomposed with

* While studying the chromium salt, I met with Frémy's "Investigation of the salts of chromium." In it the author states that the salts of chromoxyd modified by boiling (green modification) are insoluble in ammonia except after having been boiled in acid and precipitated by ammonia. It will be observed that the above process is not in conformity with the opinion of M. Frémy, as it is there shown that the green modification, produced by boiling, is rendered soluble in ammonia by the simple addition of sulphuric acid and without any application of heat. The solution in ammonia is always complete, and the process never fails.

precipitation of chromoxyd. On cooling, picrate of ammonia crystallizes out. Even with very careful washing the salt is always partly decomposed, with separation of green oxyd of chromium.

The portions that were least decomposed were selected, but were not sufficiently pure to give any satisfactory result, although a number of specimens were analyzed.

1.	.6949	substance	gave	.5864	picric acid.
2.	.5537	"	"	.4735	" "
3.	.4446	"	"	.3709	" "
4.	.4446	"	"	.0179	sesq. ox. chromium.
5.	.6949	"	"	.0271	" "

These numbers correspond to

1.	$C_{12}H_2N_3O_{14}$	84.02	per cent.
2.	"	85.14	" "
3.	"	83.06	" "
4.	Cr	2.78	" "
5.	"	2.63	" "

results which do not lead to any satisfactory conclusion, but show that the quantity of ammonia salt necessary to keep the chromoxyd in solution, throws down picrate of ammonia simultaneously with the ammonia-picrate of chromium. This salt is very beautiful, its lustre is remarkable.

Ammonia-picrate of Manganese.

If ammonia be added to a solution of manganous sulphate, previously rendered strongly acid with chlorhydric or nitric acid, a considerable quantity of manganese escapes precipitation, an extremely unstable solution is obtained, which in a few minutes, even before filtration is ended, becomes cloudy again. To give the solution more stability, the presence of a very large quantity of ammonia salt is necessary, a circumstance very unfavorable for the production of a pure ammonia-picrate, as by a solution so strongly saline, picrate of ammonia (as already observed) is at once precipitated. The following were the observations made:—

A. If a cold solution of picrate of ammonia be poured into an ammoniacal solution of manganese prepared by adding to a concentrated solution of manganous sulphate an equal volume of dilute chlorhydric acid, and then ammonia in large excess, there falls a precipitate of brilliant satiny scales, mixed however with precipitated manganous oxyd, which is readily distinguishable on the filter.

B. If the ammoniacal solution is added to a hot moderately strong solution of picrate of ammonia and the whole be rapidly

filtered, the liquid passes through before complete precipitation takes place, and on cooling, granular crystals are obtained which rapidly turn brown in the air. Heated on platinum foil, they turn brown, melt and deflagrate sharply with a brilliant white light.

Neither A, nor B, yield a salt sufficiently pure for analysis. A, always contains admixed manganous oxyd and B, picrate of ammonia. A, bears considerable resemblance to the chrome salt just described.

1·0115 of B gave ·9115 picric acid.

So large a percentage of picric acid corresponding to 89·72 per cent of the molecule $C_{12}H_2N_3O_{14}$ probably indicates a large admixture of picrate of ammonia, which cannot be removed. The formula

Ammonia-picrate of Iron.

An ammonia-picrate of protoxyd of iron appears to exist. If solution of protosulphate of iron be mixed with one of salammoniac, and then with liquid ammonia, be rapidly filtered, and the filtrate be treated with picrate of ammonia, a dark green crystalline precipitate is obtained: thrown upon a filter a red liquid passes through containing a portion of the picrate of ammonia reduced by the ferrous oxyd. The precipitate, when heated on platinum foil, deflagrates with scintillations. Heated with solution of salammoniac and caustic ammonia, it does not appear to dissolve, but ferric oxyd is thrown down and picrate and picramate of ammonia remain in solution. It was found impossible to obtain this salt in a condition to admit of even an approximate determination of its constitution.

If acetate of lead be treated with ammonia in excess, and if to the clear solution be added picrate of ammonia, a curdy precipitate, at first pale yellow, gradually deepening to orange color falls. Heated on platinum foil it detonates with violence. Boiled with caustic alkali, it disengages no ammonia. The result of an analysis showed it to be Marchand's penta-basic picrate of lead, $4PbO PbO C_{12}H_2N_3O_{14} \} O$. The above described salts containing ammonia are all highly crystalline. The lead compound just mentioned is amorphous.

Other ammonia picrates exist which I propose to examine hereafter.

Philadelphia, July 14, 1860