CCCXVII.—*Action of Ammonium Nitrate and of Aqueous Ammonia on Copper. Properties of Cupric Tetrammine Nitrite and Nitrate.*

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THAT solutions of ammonia or ammonium salts rapidly attack copper is well known. The case of the attack by ammonium nitrate in aqueous solution assumed considerable interest in connexion with the use of copper or alloys of copper in the manufacture of ammunition. When these were used in conjunction with high explosives containing ammonium nitrate, corrosion was liable to occur sooner or later whenever absorption of moisture by the explosive allowed aqueous exudations therefrom to come into contact with the copper or copper alloy. Such corrosion rarely occurred except in situations where some air at least was present, indicating that atmospheric oxygen was essential to the process, as is normally the case in the corrosion of metals by salt solutions. Striking dark blue and green products, resulting from contact of ammonium nitrate with copper, immediately directed attention to the action. It became necessary to examine these products, as indeed many others, to see whether they were likely to prove dangerous or harmful. Into the full details of this aspect of the matter it is not necessary to enter, but a few points bearing on the chemistry of copper are now recorded.

It was at once recognised that the dark blue, prismatic crystals formed in the corrosion of copper by ammonium nitrate consisted of cupric tetrammine nitrate, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$, whilst the green sub-

stance also present was the basic nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$. Both of these are well-known compounds and can readily be prepared in a pure state. The corrosion products also contained small amounts of other substances, notably of nitrite, and the main interest from the chemical point of view centred round the question as to the form in which this was present.

Although not giving a true picture of the course of the reaction, the equation

probably represents fairly well the net result of the main reactions occurring between copper and ammonium nitrate in presence of air and water. The products of corrosion actually found in practice do not as a rule contain the basic nitrate and the tetrammine in equimolecular proportions, and this for two reasons: First, because the concentrated solution of the highly soluble tetrammine nitrate is separated, by diffusion and by capillary action, from the basic nitrate, which is deposited in the solid state; secondly, because hydrolysis occurs in situations where the tetrammine is exposed to moist air and causes it slowly to revert to the basic nitrate with loss of ammonia. Thus it was often noticed that a green crust of the basic nitrate was in contact with the metal, the blue tetrammine deposit overlying it, but in some cases the latter deposit was separated by some distance from the former. Where the corrosion occurs in presence of much water, the blue tetrammine may never be in a condition to separate in the solid state and is ultimately converted entirely into the basic nitrate. Analyses I and II illustrate the sort of corrosion products met with in practice. Corrosion I consisted chiefly of deep blue, prismatic crystals mixed with a moderate amount of green material. It was obtained from a piece of ammunition filled with 40/60 amatol. When this munition was first opened for the purpose of sampling the filling, there was no corrosion, but when next opened, in three weeks' time, much corrosion was found on those parts of the copper where amatol had been scattered during excavation of the sample. The lead present is derived from solder. The corrosion was washed with acetone before analysis in order to remove any trinitrotoluene.

Corrosion II, which consisted almost entirely of dark blue crystals, was obtained from the top of a tinned copper can on which a bag of ammonium nitrate had been lying for several weeks.

	CuO.	PbO.	SnO ₂ .	NH ₃ .	N ₂ O ₅ .	N ₂ O ₃ .	H ₂ O and loss, etc. (by diff.).
I.	35.6	2.1	trace	16.6	32.0	1.9	11.8 per cent.
II.	30.8	—	0.9	21.0	38.8	0.5	7.1 per cent.

No. II contained more than 80 per cent. of the tetrammine; a trace of carbonate was also present.

Action of Ammonium Nitrate Solution on Copper.

When fine copper gauze is immersed in a saturated solution of ammonium nitrate with free access of air at the ordinary temperature, the solution acquires a blue colour in a very short time and after about twenty-four hours a green solid begins to separate. If too much gauze has not been used, the metal will have completely disappeared in about a fortnight and there will be a copious green precipitate in a deep blue solution. The green solid, after filtration and washing with cold water, is found to be identical in composition and behaviour with the basic nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, prepared by heating a solution of copper nitrate to which sodium nitrite has been added (see Dammer, "Handbuch der anorganischen Chemie," II, 2, 716). If portions of solid ammonium nitrate crystals or copper gauze projected above the solution, capillary action and subsequent evaporation gave rise to the formation of blue crystals, $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$, identical with those obtained in the usual way and also with those obtained in corrosions I and II.

Cupric tetrammine nitrate, when quite dry, is remarkably stable. On heating in a dry tube, it melts at about 210° , bubbles rapidly for a while, and then explodes vigorously at about 212° , leaving a residue of black cupric oxide. If any basic nitrate is present in the tetrammine, melting seems to begin at a much lower temperature, even as low as 150° , owing no doubt to some solution being formed from the water contained in the basic salt. At 120° in a vacuum, the tendency of the dry tetrammine to lose ammonia is negligible, and even after heating for two hours at 160 – 190° in a current of dry air the total loss of ammonia was only 3.16 per cent. or less than one-eighth of the total amount present. In moist air, even at the ordinary temperature, the salt is slowly hydrolysed with formation of the basic nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$.

The Corrosion of Copper by Aqueous Ammonia.

The mechanism of the reaction which gives rise to the nitrite in the corrosion of copper by ammonium nitrate is of interest. From our investigations we have come to the conclusion that little or no reduction from nitrate to nitrite is brought about by copper under the above conditions,* but that the nitrite is produced by the oxida-

* *Spongy* copper can slowly reduce alkaline nitrate solutions to nitrite in absence of air (Müller and Weber, *Z. Elektrochem.*, 1903, **9**, 965) and we have found that this also applies to solutions of ordinary neutral ammonium nitrate.

tion of ammonia (resulting from hydrolysis of the tetrammine nitrate) in presence of copper, which acts as a positive catalyst. Thus, when copper was left in 2*N*- and in 8*N*-ammonia in absence of nitrate but exposed to the air, considerable quantities of nitrite were formed which obviously resulted from atmospheric oxidation; 25 and 23.9 molecules of CuO were formed in the two experiments for each molecule of N₂O₃; which seems, on the whole, to indicate that the oxidation of the ammonia is merely catalysed by the copper or copper salts and is not directly "coupled" with the oxidation of the copper.

The precise course of events in the corrosion of copper gauze by solutions of ammonia depends on several rather ill-defined factors. The first solid product of the reaction is normally cupric hydroxide (loss on ignition—found 18.6 per cent.; calc. 18.4 per cent.), which begins to change into the oxide in the course of a few days. When this occurs, corrosion proceeds comparatively rapidly. In other cases, owing to the intervention of atmospheric carbon dioxide, a very compact and adherent coating of malachite, CuCO₃.Cu(OH)₂, is formed which protects the copper from further attack far more effectively than does the cupric oxide. When this occurs, corrosion proceeds very slowly. Whether the malachite is the first product formed or whether it is preceded by a small amount of the hydroxide, which later on becomes carbonated, is undecided. We have obtained corrosion products containing nearly 98 per cent. of malachite by leaving copper gauze and 2*N*-ammonia exposed to the air. The relative proportions of the copper and ammonia oxidised in the two cases do not seem to differ greatly.

The compositions of the blue solutions formed also differ in the two cases. When cupric oxide has formed and corrosion been rapid, about half the copper in solution is present as cupric tetrammine nitrite and half as cupric diammine carbonate. When, however, malachite has formed and corrosion has been slow, most of the copper in solution is present as the diammine carbonate and only about 5 per cent. as the tetrammine nitrite. It is evident, therefore, that atmospheric carbon dioxide plays an important part in the changes which occur when copper and ammonia are exposed to the air.

Péligot (*Compt. rend.*, 1861, **53**, 209) showed that a vigorous reaction occurred between strong ammonia solution, finely divided copper, and air with formation of ammonium nitrite, oxides of copper, and a blue solution.* By evaporating the blue solution to

* We also find that ammonia acts vigorously on finely divided copper (reduced from solution by means of zinc). After nine days, no metallic copper remained and all blue tetrammine salts originally formed had separ-

dryness on the water-bath and extracting with hot alcohol saturated with ammonia, he isolated violet-blue crystals, to which, merely on the strength of a copper estimation, he assigned the formula $\text{Cu}(\text{NO}_2)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$. It has been conclusively shown that these violet-blue crystals consist of cupric tetrammine nitrite and several alternative methods of preparing this compound have been worked out. As will be seen, the most satisfactory method (III) involves the previous preparation of van der Meulen's basic nitrite, a salt exactly analogous to the basic nitrate. Since the present paper was written, the formation of nitrite during the action of air and ammonia on copper has been noticed by Joyner (this vol., p. 1513).

Preparation of Cupric Tetrammine Nitrite.

The five methods employed are given in Roman numerals, which appear also at the head of the analysis columns referring thereto.

Method I. A Modification of Pélégot's Method, Gauze replacing finely divided Copper.—The blue solution obtained by the combined action of aqueous ammonia and air on gauze was evaporated to dryness in a warm cupboard and the residue extracted several times on the water-bath with alcohol previously saturated with ammonia gas. The extraction must be done rapidly or otherwise all the ammonia is driven off and very little copper salt dissolves. The hot alcoholic extract was rapidly filtered and on cooling deposited deep blue crystals, which were filtered with suction and air-dried. During drying, they became more purple as though slight superficial decomposition had occurred. The yield by this method is poor; only 0.4 gram of the blue crystals was obtained from the corrosion of 6 grams of copper gauze. This was doubtless due to decomposition of ammonium nitrite during the evaporation of the original aqueous solution or during extraction with hot alcoholic ammonia.

Methods II and III. From the Basic Nitrite, $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$.—Since Pélégot's method gives very poor yields and involves the preliminary preparation of a somewhat indefinite mixture, it seemed simpler to deal with the definite compound, $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$, first prepared by van der Meulen (*Ber.*, 1879, **12**, 758). Method II was to extract from this compound with alcoholic ammonia as in

ated from the solution as basic salts. Analysis of the green solid product corresponded with a mixture of $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$ (1.5), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ (3.0), $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (51.5), and $\text{Cu}(\text{OH})_2$ (44.0 per cent.).

This would be the kind of mixture which Pélégot extracted with alcoholic ammonia, and it seems probable that the ammine nitrite he obtained was contaminated with nitrate. We have only observed the formation of nitrate when using the finely divided reduced copper. With copper gauze, the oxidation of ammonia seems to proceed only as far as nitrous acid.

Péligot's method, and method III to extract with aqueous ammonia (d 0.880).

Method II is somewhat tedious, as repeated extraction is necessary. Several grams of cupric tetrammine nitrite were prepared in this way and dried over a mixture of calcium chloride and its hexammine to minimise decomposition. As, however, the yield by this method was only 40 per cent. of the theoretical, and the extracted residue was practically free from nitrite, it is clear that considerable decomposition of nitrite occurs in this process.

Method III gives excellent results and we recommend it for the preparation of the tetrammine nitrite in quantity. The readily prepared basic nitrite is treated with the minimum amount of ammonia (d 0.880) at the ordinary temperature, the deep blue solution filtered through asbestos from black cupric oxide, and allowed to evaporate and crystallise at the ordinary temperature over quicklime to which a few drops of ammonia (d 0.880) have been added. If less than the theoretical amount of ammonia is used, the pure salt may be obtained after one evaporation, but the yield will be smaller (IIIa gives the analysis). The theoretical yield may be very nearly reached by using rather more ammonia, but this extraction will deposit a dark stain on the dish when evaporation has nearly finished, and the resulting crystals must be redissolved in a small quantity of ammonia and the solution again evaporated—possibly the operation may have to be repeated (IIIb gives the analysis).

Two more direct methods were attempted :

Method IV.—The action of strong ammonium nitrite solution containing excess of ammonia on cupric hydroxide.

Method V.—The action of the gases, evolved from arsenious oxide and nitric acid, on cupric hydroxide suspended in ammonia (d 0.880). Blue solutions were obtained in both cases which on evaporation over quicklime yielded deep blue crystals. These were invariably a mixture (apparently mixed crystals) of cupric tetrammine nitrite and nitrate and it does not appear possible to obtain the pure nitrite by these methods.

Analyses of Preparations Obtained by the Foregoing Five Methods.

The nitrite was estimated by standard permanganate, ammonia by distillation with sodium hydroxide into standard acid, any nitrate by further distillation after reduction over-night with Devarda's alloy, the amount of nitrate being calculated from the excess of ammonia over that due to reduction of nitrite. The copper was either precipitated and weighed as oxide or estimated by Rose's method.

	Percentages found by methods						Calculated.	
	I.	II.	III.		IV.	V.	Péligot's formula.	$\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$
			a.	b.				
CuO	39.4	37.2	35.5	35.9	33.4	35.7	35.4	35.6
NH_3	26.0	27.9	30.3	30.3	27.9	29.8	15.2	30.4
N_2O_3	32.9	33.8	33.8	33.9	17.8	29.9	33.8	34.0
N_2O_5	not determined		none	none	20.7	4.1		
H_2O (diff.)	1.7	1.1					15.6	
	100.0	100.0	99.6	100.1	99.8	99.5	100.0	100.0

The figures for I and II correspond approximately with the presence of 13 and 8 per cent., respectively, of basic nitrite, $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$, probably formed by hydrolysis and decomposition during crystallisation of the hot solutions. It is also probable that some cupric diammine nitrite was formed at these comparatively high temperatures, as indicated by the purple coating observed on the crystals (this diammine nitrite is described later on). IV and V correspond with mixtures of the tetrammine nitrite with 47.8 and 9.8 per cent., respectively, of the tetrammine nitrate. The deficit in IIIa must have been due to a trace of water retained by the crystals. If allowance is made for this, the agreement is excellent. The slight excess of copper in IIIb was due to a trace of cupric oxide still held in the crystals and corresponding to 0.34 per cent. It is to be noted that the recrystallisations of this specimen had extended over two months. There was no nitrate, however, showing that no auto-oxidation or atmospheric oxidation had occurred. It will be noticed that the ammonia content calculated from Péligot's formula is just half what was found in IIIa and IIIb, and is much less than the amount found in any of the other specimens.

Properties of Cupric Tetrammine Nitrite.

As Péligot described it, this salt forms needle-shaped prisms of a beautiful violet-blue colour. We have obtained crystals more than 1 cm. in length by slow deposition from aqueous ammonia. The pure salt is exceedingly soluble in water and yields a perfectly clear, dark blue solution. This becomes a test of purity as regards contaminating hydroxide. A specimen proved to contain 6.5 per cent. of hydroxide immediately gave a pale blue deposit on the addition of a few drops of water. A deposit occurs slowly when excess of water is added to the pure salt, but if a little ammonia is then added the solution becomes and remains perfectly clear. Such solutions were used in the nitrite estimations and were slowly delivered from the burette into standard permanganate, previously warmed with excess of sulphuric acid. The dry salt, when slowly heated, first gives off ammonia, later on it evolves red fumes accom-

panied by steam and leaves a residue of cupric oxide. This reaction appears to have afforded the only estimation in Pélégot's analysis. His percentage of CuO agrees with the formula $\text{Cu}(\text{NO}_2)_2 \cdot 2\text{NH}_3 \cdot 2\text{H}_2\text{O}$, but almost equally well with the formula $\text{Cu}(\text{NO}_2)_2 \cdot 4\text{NH}_3$. He found it necessary to mix the powdered salt with silica in order to avoid explosion. We find that the pure salt may be heated either slowly or rapidly without any explosion, but all specimens containing nitrate are apt to explode towards the end of the heating process. The action of heat on pure cupric tetrammine nitrate has been recorded in this paper. The explosion at 212° was so vigorous that the apparatus was broken; the loss of ammonia after two hours at 200° in a continuous current of air was only 3 per cent., whereas the corresponding nitrite loses more than 15 per cent. at temperatures below 100° , and this without any current of air. It appears, therefore, that ammonia is held firmly in the nitrate, but not in the nitrite, and that in mixtures the nitrite is quietly decomposed by heat, final explosion being due to subsequent action on the nitrate.

Cupric Diammine Nitrite, $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$.

This derivative was obtained as a purple powder by heating finely powdered blue tetrammine nitrite for twenty-four hours at 97° in a tube provided with a loose glass stopper. The percentage losses per time were :

Hours	1.3	2.3	3.55	4.8	6.8	9.3
Per cent. loss	3.37	4.9	7.12	8.5	10.56	11.56
Hours	12.9	16.5	19.7	21.9	23.9	
Per cent. loss	13.17	13.7	14.54	15.58	15.58	

These figures present an asymptotic curve.

The loss calculated for removal of 2NH_3 is 15.2 per cent. The extra 0.38 per cent. must have been due to some absorption of moisture during the process of powdering and transference to the tube.

This purple powder readily dissolves in ammonia to form a perfectly clear blue solution, and on exposing the powder to an atmosphere containing dry ammonia at the ordinary temperature, the violet-blue tetrammine nitrite was re-formed.

The Effect of Moist Air on Cupric Tetrammine Nitrite.

A finely powdered sample of the tetrammine nitrite, protected from dust, was exposed to moist air for about three months. The dry grey powder was then analysed, with the following percentage results :

CuO 48.23; N_2O_3 35.28; NH_3 14.49; H_2O (by diff.) 2.00.
4 U*

These figures correspond very closely with those required by a mixture of 80 per cent. of cupric diammine nitrite, $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$, and 20 per cent. of the basic nitrite, $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$. It appears, therefore, that in moist air the tetrammine nitrite loses half its ammonia, yielding the diammine nitrite, which then very slowly gives place to the basic nitrite through hydrolysis. No nitrate had been formed.

Preparation of van der Meulen's Basic Nitrite, $\text{Cu}(\text{NO}_2)_2 \cdot 3\text{Cu}(\text{OH})_2$.

The method of preparation (van der Meulen, *loc. cit.*) is to add alcohol to an aqueous solution containing equivalent amounts of copper sulphate and potassium nitrite. After filtering from the heavy precipitate, the dark green alcoholic solution is evaporated on the water-bath until nearly colourless. Alcohol and ethyl nitrite are given off and the basic nitrite separates as a bluish-green, crystalline deposit. The best yield obtainable seems to be about half the theoretical, but it is often half that, and experiments were made to find the best conditions for a good yield and also to examine the nature of the products formed, as the information given by van der Meulen on these points is rather vague. The best results were obtained when the temperature during the first stage in the preparation was kept below 15° . At temperatures exceeding this, there is considerable loss of ethyl nitrite during the addition of alcohol. The proportion of alcohol to water should be in the ratio 5 : 4 by volume at least. The precipitate formed on the addition of alcohol is of a complex nature and its composition varies considerably with the temperature, proportion of alcohol added, lapse of time between precipitation and filtration, etc. Of the total, air-dried solid, from 50 to 60 per cent. consists of potassium sulphate and more than 10 per cent. may consist of the double sulphate, $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, which is often obtained as large, green crystals, especially if some time has been allowed to elapse before filtration; otherwise, copper sulphate pentahydrate, with no double sulphate, appears to be formed. Cupric hydroxide is always present, sometimes apparently as such (exceeding 11 per cent.), but in other cases only in the form of basic copper sulphate. Lastly, the air-dried solid contains 0.7 per cent. or less of cupric nitrite, probably as basic nitrite.

It is of course owing to this co-precipitation of copper salts with potassium sulphate that the yield of basic nitrite is so poor.

The final filtrate from which the basic copper nitrite crystallises still contains from 20 to 24 per cent. of the original potassium nitrite and a trace—or sometimes more—of copper. This trace of copper nevertheless imparts a strong green colour to the solution, and migration experiments proved that it is present as a complex anion—

probably as $\text{Cu}(\text{NO}_2)_6'''$. The colouring power of this anion is about equal to that of the blue complex kation, $\text{Cu}(\text{NH}_3)_4^{++}$, of the tetrammine salts.

In view of the formation of nitrite when copper dissolves in aqueous ammonia it was of interest to see whether any oxidation of ammonia occurred when oxygen was absorbed by copper gauze in presence of the mixed solution of ammonium hydroxide and carbonate as recommended by Hempel for gas analysis ("Gas Analysis," p. 125 of the English edition, 1892). The dissolution of copper in this mixture is very rapid if air is slowly bubbled through it. Thus 100 c.c. of the mixture dissolved 3 grams of copper gauze in less than sixteen hours, and 1.8 per cent. of the dissolved copper was present as nitrite. On evaporation over quicklime, the deep blue solution deposited large crystals of the very soluble salt, $\text{Cu}(\text{NH}_3)_2\text{CO}_3$, whilst the trace of nitrite remained in the mother-liquor as $\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$, which is still more soluble. The colour of these two compounds is practically identical. The stability of this diammine carbonate is very remarkable; our experiments fully confirm the composition and properties as described by Favre, its discoverer (*Ann. Chim. Phys.*, 1844, [iii], 10, 116).

Sensitiveness to Shock of some of the Compounds dealt with.

In view of the manner in which these experiments originated, it is of interest to record the sensitiveness to shock of some of the compounds dealt with. This was determined by means of a falling-weight instrument (Robertson, T., 1921, 119, 16). Basic cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$, was found to be quite insensitive and the corresponding nitrite nearly so. For other compounds, the figures of insensitiveness (taking that of picric acid as 100) were as follow :

$\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$	89
$\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$ (prepared by method III)	89
Mixed crystals containing $\left\{ \begin{array}{l} 11 \text{ per cent. of } \text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2 \\ 89 \text{ per cent. of } \text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2 \end{array} \right\}$	55
$\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$ —another sample prepared by method I or II. Possibly it contained a little nitrate or basic nitrite }	55
$\text{Cu}(\text{NH}_3)_2\text{CO}_3$	greater than 120

The greater sensitiveness of the mixed tetrammine nitrate and nitrite is possibly connected with the higher oxygen content of the former in conjunction with the readier loss of ammonia by the latter.

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