

CCCXLVIII.—*Researches on Ammines. Part III.*  
*Derivatives of Cupric Nitrite.*

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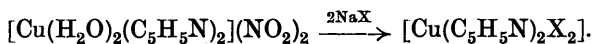
WHEN solutions of copper salts and nitrites are mixed, green solutions are obtained which probably contain normal cupric nitrite, a salt which has never been isolated in the solid state. As Pélégot (*Compt. rend.*, 1861, **53**, 209) claimed to have prepared solid cupric nitrite by maintaining tetramminocupric nitrite for some days at 100°, the action of heat on this salt was reinvestigated. On heating at 85°, complete conversion into diamminocupric nitrite occurred in 2 hours with no loss of oxides of nitrogen. On continued heating at 85° in a vacuum, gradual diminution in the weight of the diammine occurred, amounting in 14 hours to 9%. An ammonia estimation showed that one-half of this loss was due to decomposition of the nitrite radicals. No analyses were recorded by Pélégot, and his product was evidently a basic nitrite, still containing ammonia.

When a mixture of equivalent solutions of potassium nitrite and copper sulphate is precipitated with alcohol, a deep green aqueous-alcoholic filtrate is obtained, from which, on removal of the alcohol by evaporation, van der Meulen's basic nitrite separates (*Ber.*, 1879, **12**, 758). When, however, the green solution was filtered into pyridine, aniline, or a solution of *p*-toluidine or  $\beta$ -naphthylamine, no basic nitrite was obtained, the precipitate consisting of normal cupric nitrite stabilised by two molecular proportions of the base. These results support the view that the green solution contains normal cupric nitrite. It was not found possible by the action of heat, or by leaving them over sulphuric acid in a vacuum, to remove the stabilising base from any of these compounds and so obtain cupric nitrite. In the cases where the base was an aromatic amine, deflagration occurred on warming. When *dipyridinocupric*

*nitrite* was heated in a vacuum at 85°, the diminution in weight after 12 hours amounted to 31%. A nitrite estimation showed a loss of 15%; therefore, on the assumption that this had been lost as nitrogen trioxide, 40% of the total loss was due to decomposition of the nitrite radicals. Another sample of dipyridinocupric nitrite, after standing in a vacuum over sulphuric acid for 3 months, had diminished in weight by 2.5% : 36% of this loss was due to decomposition of the nitrite radicals.

Copper is usually considered to have a principal co-ordination number of 4, and in accordance with this view, cupric diammines are frequently formulated as diamminodiacydo-derivatives,  $[R_2CuX_2]$ , where R is a molecule of ammonia, pyridine, etc., and X is a monobasic acid radical. In nearly all cases the diammines are insoluble in or decomposed by water, so that the correctness of this assumption cannot be tested. Of the compounds here described, *dianilino-*, *di-p-toluidino-*, and *di-β-naphthylamino-cupric nitrites* were insoluble in water, alcohol, and ether. Dipyridinocupric nitrite, however, was sparingly but completely soluble in water, and this solution, when treated with a solution of sodium picrate, gave an immediate precipitate of anhydrous *dipyridinocupric picrate*, in analytically pure condition. Similarly, sodium benzoate gave a precipitate of anhydrous *dipyridinocupric benzoate*. These results support for dipyridinocupric nitrite the formula  $[Cu(C_5H_5N)_2](NO_2)_2$  rather than  $[Cu(C_5H_5N)_2(NO_2)_2]$ .

An alternative possibility is that non-ionic  $[Cu(C_5H_5N)_2(NO_2)_2]$  dissolves in water, forming diaquodipyridinocupric nitrite, and that both picrate and benzoate radicals expel the co-ordinated water from the complex :



These assumptions seem unlikely, and there is no experimental evidence that diaquodipyridinocupric nitrite exists, dipyridinocupric nitrite being obtained in the anhydrous form even when recrystallised from water.

Although a number of compounds are known in which a copper atom with co-ordination number 5 forms the centre of a complex anion, complex kations in which the copper atom has this co-ordination number are somewhat rare. To the small number on record must be added *pentapyridinocupric picrate*, which separated from a concentrated solution of dipyridinocupric picrate in pyridine.

Since the compounds in which cupric nitrite is stabilised by two molecular proportions of a primary aromatic amine contain equivalent proportions of amine and nitrite radical, it appeared likely that they would give improved yields in syntheses ordinarily

carried out by diazotisation. It was found that dianilino- and di-*p*-toluidino-cupric nitrites dissolved readily in dilute acids without noticeable evolution of nitrous fumes, and that on steam distillation the phenols passed over, leaving no tar. From 30 g. of the two compounds, 73% and 76% yields of redistilled phenol and *p*-cresol were obtained. The availability of these compounds in organic syntheses is being further investigated.

#### EXPERIMENTAL.

Tetramminocupric nitrite was obtained by Bassett and Durrant (J., 1922, **121**, 2635) by spontaneous evaporation of a solution of van der Meulen's basic nitrite in concentrated aqueous ammonia. This method proved inconvenient, and the pure compound was readily obtained in quantity from dianilino-cupric nitrite (see p. 2597). This salt (30 g.) was triturated with a little ammoniacal alcohol, which converted it into a blue powder. More alcohol was added, and ammonia gas was passed into the suspension for 10 minutes. The blue product was collected, washed with ammoniacal alcohol and ether, and left in a vacuum over soda-lime (yield, 62%) (Found:  $\text{NH}_3$ , 30.5. Calc.:  $\text{NH}_3$ , 30.45%).

When tetramminocupric nitrite was exposed to dry air, free from acid vapours, for 5 days, the deep violet diammine obtained by Bassett and Durrant (*loc. cit.*) remained [Found:  $\text{NH}_3$ , 17.9. Calc. for  $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ :  $\text{NH}_3$ , 18.0%]. The diammine was quickly decomposed by water, giving a pale blue precipitate. After standing in a vacuum over sulphuric acid for 3 months, it had lost only 3.7% of its ammonia.

The green aqueous-alcoholic solution containing cupric nitrite, used in preparing the stabilised cupric nitrites described below, was obtained by treating a cold saturated solution of copper sulphate with solid potassium nitrite (2 mols.), adding an equal volume of alcohol, and removing the copious precipitate of potassium sulphate and copper hydroxide. From the concentrated filtrate thus obtained, the basic nitrite was quickly deposited on standing, even at the ordinary temperature. (If considerably diluted with water, it remained clear indefinitely.) An analysis of a typical sample of the solution showed that it contained seven nitrite radicals in association with two copper atoms.

*Dipyridinocupric Nitrite.*—The green solution prepared as above from 30 g. of crystallised copper sulphate was filtered into 25 c.c. of pyridine; after 12 hours, 17 g. of greenish-black, large, monoclinic prisms had separated. The product was washed with a little alcohol and ether and left over-night in a vacuum over soda-lime. (Unless otherwise stated, the other compounds described below

were similarly treated before analysis.) The compound was sparingly but completely soluble in water and in alcohol, to deep green solutions. It dissolved readily in aqueous or liquid ammonia to a deep blue solution of tetramminocupric nitrite. It was practically insoluble in ether, but dissolved very readily in cold pyridine, giving a dark green solution from which, on spontaneous evaporation, it crystallised unchanged, m. p.  $155^{\circ}$  (decomp.) (Found : Cu, 20.4;  $C_5H_5N$ , 50.6;  $NO_2$ , 29.5.  $[Cu(C_5H_5N)_2](NO_2)_2$  requires Cu, 20.3;  $C_5H_5N$ , 50.4;  $NO_2$ , 29.3%). Nitrite was estimated with permanganate, after the compound had been dissolved in aqueous ammonia and neutralised with sulphuric acid. The compound was recrystallised from water, containing a few drops of pyridine, at  $60^{\circ}$ , and the air-dried product again proved to be anhydrous *dipyridinocupric nitrite*.

*Interaction of Dipyridinocupric Nitrite and Sodium Picrate.*—The nitrite (1 g.), dissolved in 200 c.c. of water at room temperature, was added to a solution of 1.46 g. (2 mols.) of picric acid, converted into the sodium salt. An immediate precipitate of bright green, microscopic plates was obtained in 76% yield (Found : Cu, 9.5; N, 16.6;  $C_5H_5N$ , 23.3.  $[Cu(C_5H_5N)_2]\{C_6H_2O_7N_3\}_2$  requires Cu, 9.4; N, 16.5;  $C_5H_5N$ , 23.3%). No diminution in weight occurred on heating for 3 hours at  $100^{\circ}$ . The compound was insoluble in water, alcohol, and ether. *Dipyridinocupric picrate* was readily obtained in quantity as follows. A solution of 5 g. of cupric chloride was treated with 20 g. of pyridine, and the deep blue suspension was shaken with 14.7 g. of picric acid (*i.e.*, 10% excess), converted into the ammonium salt, in 1300 c.c. of water. *Dipyridinocupric picrate* separated in 93% yield (Found : Cu, 9.6%).

*Pentapyridinocupric picrate* was obtained by dissolving the above salt in four parts of boiling pyridine. The filtered deep green solution was left in a vacuum over concentrated sulphuric acid over-night; large, very deep green plates had then separated. The compound was washed with a little pyridine and dried in a vacuum over soda-lime. It was quantitatively reconverted into *dipyridinocupric picrate* on being heated for  $1\frac{1}{2}$  hours at  $85^{\circ}$  (Found : Cu, 6.9;  $[Cu(C_5H_5N)_2]\{C_6H_2O_7N_3\}_2$ , 74.0.  $[Cu(C_5H_5N)_5]\{C_6H_2O_7N_3\}_2$  requires Cu, 6.95;  $[Cu(C_5H_5N)_2]\{C_6H_2O_7N_3\}_2$ , 74.1%).

*Interaction of Dipyridinocupric Nitrite and Sodium Benzoate.*—The nitrite (2 g.) was dissolved in 400 c.c. of water and added to an aqueous solution of 2.6 g. ( $2\frac{1}{2}$  mols.) of sodium benzoate, giving an immediate precipitate (2.5 g.) of bright blue, microscopic needles, insoluble in water, alcohol, and ether (Found : Cu, 13.7; N, 5.8;  $C_7H_5O_2$ , 51.9.  $[Cu(C_5H_5N)_2]\{C_7H_5O_2\}_2$  requires Cu, 13.7; N, 6.0;  $C_7H_5O_2$ , 52.2%).

*Dipyridinocupric benzoate* was also obtained by treating anhydrous cupric benzoate with pyridine, and recrystallising the blue product from boiling pyridine, so that, under ordinary conditions, cupric benzoate appears to be incapable of combining with more than two molecular proportions of pyridine.

*Dianilinocupric Nitrite*.—The green solution from 30 g. of copper sulphate was filtered into 34 g. of aniline (3 mols.). A voluminous precipitate (23.5 g.) of very thin, green plates was obtained [Found : Cu, 18.7; N, 16.2; NO<sub>2</sub>, 27.1. Cu(C<sub>6</sub>H<sub>5</sub>·NH<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> requires Cu, 18.6; N, 16.4; NO<sub>2</sub>, 26.9%].

The compound was decomposed immediately by sodium hydroxide solution, with liberation of aniline and precipitation of copper hydroxide. After boiling to remove aniline, the nitrite radical in the filtrate was estimated with permanganate. The compound deflagrated on warming, even at 85°, and also on treatment with liquid ammonia or with cold concentrated sulphuric acid. No diminution in weight occurred on keeping for 3 months in a vacuum over sulphuric acid.

*Di-p-toluidinocupric Nitrite*.—The green solution from 30 g. of copper sulphate was filtered into 38.5 g. (3 mols.) of *p*-toluidine, dissolved in alcohol. An immediate moss-green precipitate (26 g.) of thin microscopic plates was obtained, closely resembling the aniline derivative in colour and properties [Found : Cu, 17.1; N, 15.1; NO<sub>2</sub>, 24.5. Cu(C<sub>7</sub>H<sub>7</sub>·NH<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> requires Cu, 17.2; N, 15.15; NO<sub>2</sub>, 24.9%].

*Di-β-naphthylaminocupric Nitrite*.—The ice-cooled green solution from 10 g. of copper sulphate was filtered into an ice-cooled acetone solution containing 11.5 g. (2 mols.) of β-naphthylamine. The precipitate of greenish-brown microscopic plates was quickly collected and washed with ether. It was insoluble in water and in ether, but somewhat soluble in acetone [Found : Cu, 14.6; N, 12.6; NO<sub>2</sub>, 20.6. Cu(C<sub>10</sub>H<sub>7</sub>·NH<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> requires Cu, 14.4; N, 12.7; NO<sub>2</sub>, 20.8%]. The compound was immediately decomposed by a little cold aqueous ammonia with separation of β-naphthylamine. Nitrite was estimated in the deep blue filtrate after acidification. If the solutions used were not cooled, or if the precipitate was not rapidly collected, evolution of nitrogen occurred with formation of a red tarry mass. When α-naphthylamine was used, rapid evolution of nitrogen occurred immediately the compound was precipitated.

Copper in all the above compounds was estimated as the anhydrous sulphate, after decomposition by evaporation with dilute or concentrated sulphuric acid.