CCXCIX.—*Researches on Ammines.   Part IV.   Cuprammine Salts of Monobasic Acids.*

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ALTHOUGH a number of ammines of bivalent copper containing fewer than four molecules of the base in the co-ordination complex have been described, no evidence has been adduced as to whether the acid radicals are ionised.

Further examination of these compounds seemed desirable, in order to ascertain whether, in such complex kations, as in the more stable kations derived from tervalent metals, acid radicals can replace molecules of ammonia or pyridine, with formation of acido-ammines sufficiently stable for their existence to be detected in aqueous solution.

If this were so, aqueous solutions of triamminocupric salts should

contain one univalent acid radical in the ionised and one in the un-ionised condition. $Cu(NH_3)_3(NO_3)_2,2H_2O$, described by Bhaduri (*Z. anorg. Chem.*, 1913, **81**, 406), was found not to exist, the method given for its formation yielding tetramminocupric nitrate. Tri-ammino- and tripyridino-cupric formates, described by Grossmann and Jäger (*ibid.*, 1912, **73**, 48), were also unobtainable by the methods given, which yielded instead *tetrammino-* and *monohydrated dipyridino-cupric formates*.

Triamminocupric aceto-halides (Richards, *Amer. Chem. J.*, 1893, **15**, 642; 1895, **17**, 145, 297) and *tripyridinocupric o-nitrobenzoate* (see p. 2315) were unsuitable for further investigation, being insoluble in, or decomposed by, water and other solvents. The remaining cases recorded are triamminocupric trichloroacetate (Grossmann and Jäger, *loc. cit.*) and tripyridinocupric nitrate (Pfeiffer and Pimmer, *Z. anorg. Chem.*, 1905, **48**, 98). The chemical individuality of the former is not well established. Obtained by exposing the higher ammine to the air till it attained constant weight, it did not at any concentration give a clear solution with water, and it could not be recrystallised. When shaken with an aqueous solution containing 1 mol. of ammonium picrate, it yielded an impure cuprammine picrate which contained only half the original copper and no trichloroacetic acid, indicating that both the trichloroacetate radicals were ionised. Tripyridinocupric nitrate was obtained by Pfeiffer and Pimmer by repeated recrystallisation from alcohol of a mixture of the dipyridino- and tetrapyridino-salts. Its chemical individuality, however, is supported by the results of molecular-weight determinations. When its aqueous solution was treated with a solution containing 1 mol. of ammonium picrate, only half the copper was precipitated and the product contained no nitrate radical. It will be seen from Table II that van't Hoff's factor i for this compound in aqueous solutions of concentrations 0.025—$0.25M$ falls from 3.79 to 2.41, so that its value is always of the order required for the tri-ionic salt, $[Cu(C_5H_5N)_3](NO_3)_2$, while the possible alternative formulæ $[Cu(C_5H_5N)_3NO_3]NO_3$ and $[Cu(C_5H_5N)_6][Cu(NO_3)_4]$ would require i values somewhat lower than 2 and 1 respectively. Although both acid radicals are attached by electrovalent links in aqueous solution, it is probable that in the solid state both links are covalent. It appears preferable, in cases where solution in water is not known to effect any change other than the conversion of covalent into electrovalent links, to follow Werner's method of formulating a complex compound in accordance with its condition in aqueous solution, so that the formula reveals the ordinary reactions of the substance. This compound is then tripyridinocupric nitrate, $[Cu(C_5H_5N)_3](NO_3)_2$. It is possible that solution of the salt in

water involves, in addition to ionisation, the co-ordination of molecules of water, but there is no evidence of this, and no justification for any assumption as to the number of water molecules co-ordinated.

Attempts to prepare other triammines from cupric salts of acids which readily enter the co-ordination complex of tervalent cobalt or chromium were unsuccessful. Thus, *tetramminocupric acetate*, when treated in alcoholic solution with 1 mol. of glacial acetic acid, yielded a crystalline precipitate of the diammine. The only compound already described in which it appeared possible that the acidotriamminocupric ion was present was decamminotricupric iodide, obtained from aquotetramminocupric iodide by exposure to air or by treating its aqueous solution with excess of potassium iodide. Kohlschütter formulated this compound as

$$2[Cu(NH_3)_3I]I,[Cu(NH_3)_4]I_2,$$
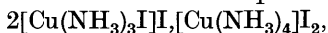
considering $[Cu(NH_3)_3I]I$ to be the primary product of the reaction (*Ber.*, 1904, **37**, 1153). However, treatment of *pentamminocupric iodide* with 2 mols. of aqueous hydriodic acid gave an equimolecular mixture of *diammine* and *tetrammine*, while trituration of hexamminocupric iodide with 3 mols. of an alcoholic solution of hydriodic acid resulted in complete decomposition, with liberation of iodine. Evidently $Cu(NH_3)_3I_2$ does not exist, so Kohlschütter's formula for the decammine seems very improbable. *Decamminotricupric picrate*, $Cu_3(NH_3)_{10}\{C_6H_2O_7N_3\}_6$, has now been obtained by treatment of tetramminocupric formate with excess of sodium formate and precipitation with ammonium picrate.

It was shown in Part III (J., 1929, 2593) that, while all cupric diammines containing ammonia in the complex are insoluble in or decomposed by water, dipyridinocupric nitrite dissolved in water without decomposition as the ionic salt $[Cu(C_5H_5N)_2](NO_2)_2$. Monohydrated dipyridinocupric formate has proved more readily soluble than the nitrite, and from it, by double decomposition in aqueous solution, anhydrous dipyridinocupric benzoate and the monohydrated o-*nitrobenzoate* were obtained. Even at a concentration of $0·15M$, the highest obtainable, dipyridinocupric formate gave an i value of $2·12$, which is inconsistent with the presence of a non-polar compound. These results support the conclusion that in aqueous solution the compound is $[Cu(C_5H_5N)_2](H·CO·O)_2$. Here again it is possible that solution is accompanied by co-ordination of water molecules, but there is no evidence that this occurs.

Diamminocupric acetate, although decomposed by water, dissolved in boiling absolute alcohol, without decomposition, to the extent of about 2%. The elevation of the boiling point of the alcohol was only $0·035°$, whence $M = ca.$ 624 [Calc. for

$\{Cu(NH_3)_2(CH_3 \cdot CO \cdot O)_2\}_3$: M, 647]. Nevertheless, diammino-cupric acetate and potassium thiocyanate interacted in hot alcoholic solution, with precipitation of diamminocupric thiocyanate.

Cuprammine salts differ from ammines of tervalent cobalt and chromium in that the former melt at comparatively low temperatures, indicating that, in the solid state, the valency linkages are non-polar. The m. p.'s previously recorded have been those of the ammine stable at the temperature of fusion. By carrying out the determinations in sealed tubes, individual m. p.'s for the various cuprammine salts of a given acid have now been obtained (see Table I). The m. p.'s of tetra- and hexa-pyridinocupric nitrates

TABLE I.

Melting points (uncorr.) in sealed tubes.

$Cu(C_5H_5N)_6(NO_3)_2$	171°	$Cu(NH_3)_4(H \cdot CO \cdot O)_2$ ...	157° (decomp.)
$Cu(C_5H_5N)_4(NC_3)_2$	168·5	$Cu(NH_3)_2(H \cdot CO \cdot O)_2$ ...	152 (decomp.)
$Cu(C_5H_5N)_2(NO_3)_2$	161	$Cu(NH_3)_4(CH_3 \cdot CO \cdot O)_2$	194
		$Cu(NH_3)_2(CH_3 \cdot CO \cdot O)_2$	189 (decomp.)

are only 7·5° and 10° higher than that of dipyridinocupric nitrate, while those of tetramminocupric acetate and formate are 5° higher than the values for the corresponding diammines. These figures suggest that the co-ordination of further molecules of ammonia or pyridine is accompanied by no fundamental change in the type of linkage, all the compounds, from diammine to hexammine, being non-polar in the solid state.

Aqueous solutions of ammino- or pyridino-cupric salts smell of the base at all concentrations, but the only evidence available as to the extent to which dissociation of the complex ion occurs is that of Dawson (J., 1906, **89**, 1666), who extracted ammoniacal solutions of copper sulphate with chloroform, to obtain a measure of the free ammonia, and calculated the molecular ratio of combined ammonia to metal. Values have now been obtained for the number of mols. of ammonia or pyridine associated with each g.-atom of copper in aqueous solutions of hexammino-, tetrammino-, hexa-pyridino-, and tetrapyridino-cupric nitrates, at concentrations between 0·025 and 0·25M, by attributing the excess freezing-point depressions of these salts in aqueous solution over those of cupric nitrate at equivalent concentrations to free ammonia or pyridine, the concentration of which could then be calculated (see Table III). While rigid accuracy is not claimed for these values, which involve the assumption that the complex nitrates ionise similarly to cupric nitrate, they are considered to represent fairly closely the condition of the salts in aqueous solution, and they agree well with the results of Dawson, where comparison is possible. Thus the value 3·51 was

obtained for $0.05M$-hexamminocupric nitrate, whereas Dawson gives 3·55 for $0.05M$-copper sulphate containing 6 mols. of ammonia. For $0.1M$-tetramminocupric nitrate, the value 3·46 was obtained, as compared with 3·43 for $0.1M$-tetramminocupric sulphate as found by Dawson. His other results were obtained in presence of excess of ammonia, and are somewhat higher than those now recorded for the pure salts.

<div align="center">EXPERIMENTAL.</div>

Unless otherwise stated, the compounds described were prepared for analysis by being washed successively with alcohol and ether, and left over-night in a vacuum over soda–lime.

Acetates.—Foerster (*Ber.*, 1892, **25**, 3416) and Horn (*Amer. Chem. J.*, 1908, **39**, 206) prepared the anhydrous diammine, and from it, by the action of liquid ammonia, the latter obtained the tetrammine, which has now been prepared in a crystalline condition by a modification of Horn's method for preparation of the diammine. 20 G. of copper acetate were treated with 150 c.c. of ammoniacal alcohol and dry ammonia gas was passed through the suspension for an hour. The ice-cold, filtered solution was treated with an equal volume of ammoniacal ether, whereupon large hexagonal blue plates separated rapidly {Found : NH_3, 27·1. Calc. for $[Cu(NH_3)_4](CH_3 \cdot CO \cdot O)_2 : NH_3$, 27·3%}. The compound was readily soluble in water and in alcohol. After $\frac{1}{2}$ hour, even when kept in an ammoniacal atmosphere, surface loss of ammonia had occurred, and exposure to dry air for 2 days resulted in complete conversion into the violet diammine, which was decomposed by even a little water, forming a blue jelly. When equivalent solutions of diamminocupric acetate and potassium thiocyanate in hot absolute alcohol were mixed, greyish-blue needles of diamminocupric thiocyanate separated immediately in 60% yield (Found : Cu, 29·9; NH_3, 16·1. Calc. : Cu, 29·7; NH_3, 15·9%).

Formates.—The existence of tetramminocupric formate was detected by Ephraim and Bolle (*Ber.*, 1915, **48**, 1770). Anhydrous *tetramminocupric formate* has now been prepared by treating finely powdered tetrahydrated cupric formate with liquid ammonia. The deep blue product was extremely soluble in water and sparingly soluble in alcohol and in liquid ammonia {Found : Cu, 28·9; NH_3, 30·6. $[Cu(NH_3)_4](H \cdot CO \cdot O)_2$ requires Cu, 28·7; NH_3, 30·7%}. The tetrammine was also obtained as large hexagonal plates by passing ammonia gas into an alcoholic suspension of cupric formate, filtering the product and precipitating the salt with ether.

Action of Excess of Sodium Formate on Tetramminocupric Formate. —When saturated aqueous solutions of sodium formate (20 g.) and tetramminocupric formate (2 g.) were mixed, ammonia was liber-

ated. The deep blue, filtered solution was aerated for 2 hours, to remove free ammonia, and then added to a solution of ammonium picrate [from 4·2 g. (2 mols.) of picric acid] in 350 c.c. of water. The precipitate of *decamminotricupric picrate* (microscopic green needles) was collected and washed with water [Found : Cu, 11·0; NH_3, 10·1; N, 22·6. $Cu_3(NH_3)_{10}\{C_6H_2O_7N_3\}_6$ requires Cu, 11·0; NH_3, 9·9; N, 22·7%]. The same product was obtained when 3 mols. of picric acid were employed. The compound lost no ammonia when heated for 3 hours at 100°.

Cobalt-blue *diamminocupric formate* [Found : Cu, 34·0; NH_3, 18·1. $Cu(NH_3)_2(H\cdot CO\cdot O)_2$ requires Cu, 33·9; NH_3, 18·2%] was obtained by leaving the tetrammine under an open bell-jar in presence of soda–lime for 3 days; no dark blue particles of tetrammine then remained. The compound was insoluble in alcohol and decomposed by water. It lost 5% of its ammonia in 3 hours at 90°.

A solution of cupric formate in aqueous ammonia was left in a vacuum over soda–lime for 2 weeks. The violet needles thus obtained proved to be the tetrammine (Found : NH_3, 30·1%). After exposure to dry air for 3 days, they had been completely converted into diammine (Found : NH_3, 18·1%). Grossmann and Jäger (*loc. cit.*) stated that they obtained triamminocupric formate by this method, and that it remained unchanged after standing in air for 12 weeks.

Monohydrated Dipyridinocupric Formate.—This *compound* {Found : Cu, 19·4; N, 8·5; H_2O, 5·4. $[Cu(C_5H_5N)_2](H\cdot CO\cdot O)_2, H_2O$ requires Cu, 19·3; N, 8·5; H_2O, 5·5%} was obtained when pyridine was heated to boiling with cupric formate. The filtrate deposited bright blue needles, which were washed with pyridine and left overnight in a pyridine atmosphere over soda–lime. If the boiling was continued for more than a few minutes, decomposition occurred. By heating at 85° for 4 hours, the whole of the water and slightly more than one mol. of pyridine were removed, leaving a bright green powder. (Water in the compound was determined by finding the loss in weight at 85°, and estimating nitrogen in the residue, so that loss of pyridine could be allowed for.) Grossmann and Jäger stated that they obtained tripyridinocupric formate by this method.

Reaction with sodium benzoate. The formate (2 g.), dissolved in 30 c.c. of water, was shaken with 1·1 g. (2 mols.) of sodium benzoate, giving a precipitate of dipyridinocupric benzoate (1·4 g.) (Found : Cu, 13·7; N, 5·9. Calc. : Cu, 13·7; N, 6·0%. See Part III).

Reaction with ammonium o-nitrobenzoate. The aqueous solution of the formate (2 g.) was added to 2·5 g. (2·5 mols.) of *o*-nitrobenzoic

acid converted to the ammonium salt in 10 c.c. of water. An imme-
diate pale blue precipitate of *dipyridinocupric o-nitrobenzoate mono-
hydrate* was obtained. It was washed with water, alcohol, and ether
[Found : Cu, 11·2 ; N, 9·7 ; H_2O, 3·1. $Cu(C_5H_5N)_2\{C_7H_4O_4N\}_2,H_2O$
requires Cu, 11·1 ; N, 9·8 ; H_2O, 3·2%].

Iodides.—Hexamminocupric, monohydrated tetramminocupric,
and decamminotricupric iodides have been obtained by various
investigators. Ephraim (*Ber.*, 1919, **52**, 940) detected the existence
of the pentammine and diammine, both of which are now
described ; but he obtained no indication of the existence of an
anhydrous tetrammine, so the monohydrated tetrammine should
probably be formulated $[Cu(NH_3)_4,H_2O]I_2$.

Horn (*Amer. Chem. J.*, 1908, **39**, 184) stated that he prepared this
compound by treating mixed solutions of copper sulphate, potassium
iodide, and ammonia with ammonia gas. This method was found,
however, to yield a product largely contaminated with potassium
sulphate, from which it was separated by treatment with liquid
ammonia. The potassium sulphate did not dissolve, and deep
violet crystals of hexamminocupric iodide were obtained from the
filtrate.

Pentamminocupric iodide hemihydrate, $[Cu(NH_3)_5]I_2,\frac{1}{2}H_2O$. When
a solution of hexamminocupric iodide in ammonia (*d* 0·880) was
saturated with ammonia gas, a precipitate of small blue plates,
lighter in colour than the hexammine, was obtained. The product
was readily soluble in water, but insoluble in alcohol (Found : Cu,
15·5 ; NH_3, 21·0 ; I, 61·6 ; H_2O, 2·2. $[Cu(NH_3)_5]I_2,\frac{1}{2}H_2O$ requires
Cu, 15·5 ; NH_3, 20·7 ; I, 61·7 ; H_2O, 2·2%).

When the *compound* was left in a vacuum over sulphuric acid for
a week, the water and $1\frac{2}{3}$ mols. of ammonia were removed, leaving
a black residue of decamminotricupric iodide. The same hemi-
hydrate was also prepared by recrystallising decamminotricupric
iodide from 5 parts of warm ammonia (*d* 0·880) (Found : NH_3,
20·7%).

Diamminocupric iodide. In an unsuccessful attempt to prepare
triamminocupric iodide, the solid pentammine (2 g.) was shaken with
9·8 c.c. (2 mols.) of *N*-hydriodic acid. Chocolate-brown *diammino-
cupric iodide* (1 g.), which was formed immediately, was filtered off,
leaving a deep blue filtrate [Found : Cu, 18·0 ; NH_3, 9·7 ; I, 72·7.
$Cu(NH_3)_2I_2$ requires Cu, 18·1 ; NH_3, 9·7 ; I, 72·2%]. The filtrate,
on treatment with excess of a solution of ammonium picrate, gave
a precipitate of tetramminocupric picrate equivalent to 40% of the
original copper (Found : NH_3, 11·4. Calc. : NH_3, 11·6%. See
p. 2315) ; hence the mechanism of the reaction is $2[Cu(NH_3)_5]I_2,H_2O$
$+ 4HI = [Cu(NH_3)_4(H_2O)]I_2 + Cu(NH_3)_2I_2 + 4NH_4I$.

4 I

Diamminocupric iodide was also obtained when the hexammine was kept in a vacuum over sulphuric acid for a month (Found : Cu, 17·9; NH$_3$, 9·7%). The compound was insoluble in and decomposed by water. It was not decomposed by cold concentrated sulphuric acid, iodine being liberated only on warming. When the diammine was kept in a vacuum over sulphuric acid, continuous slow liberation of iodine occurred, indicating that 2 mols. of ammonia are the minimum number capable of stabilising the cupric iodide molecule.

Hexapyridinocupric iodide. When hexamminocupric iodide (5 g.) was boiled gently for 10 minutes with 50 c.c. of pyridine, the ammonia was displaced and the dark brown filtered solution deposited, on cooling, 7·5 g. of large, irregular, black plates. The product was washed successively with pyridine and ether, and transferred immediately to a stoppered bottle (Found : Cu, 8·3; C$_5$H$_5$N, 60·2; I, 32·5. [Cu(C$_5$H$_5$N)$_6$]I$_2$ requires Cu, 8·0; C$_5$H$_5$N, 59·9; I, 32·1%). The *compound* dissolved completely in ammonia to a deep blue solution. It was insoluble in water and in cold alcohol. Hot alcohol decomposed it with liberation of iodine and precipitation of cuprous iodide.

Tetrapyridinocupric iodide. After exposure to dry air free from acid vapours for 4 days, powdered hexapyridinocupric iodide had been converted into a moss-green *compound* (Found : Cu, 10·1; C$_5$H$_5$N, 49·5; I, 40·2. [Cu(C$_5$H$_5$N)$_4$]I$_2$ requires Cu, 10·0; C$_5$H$_5$N, 49·9; I, 40·1%). It was not found possible to obtain cupric iodide by keeping the tetrapyridino-derivative in a vacuum over sulphuric acid, as both pyridine and iodine were gradually lost. After six weeks, 0·8 mol. of pyridine and 1·5 g.-atoms of iodine remained in association with each g.-atom of copper, the residue being a brownish-yellow powder.

Nitrobenzoates.—*Cupric o-nitrobenzoate* was precipitated by mixing aqueous solutions of ammonium *o*-nitrobenzoate and the calculated amount of copper sulphate. The air-dried product was bright green and was practically insoluble. There was no loss in weight on heating at 100° [Found : Cu, 16·1; N, 7·0. Cu(C$_7$H$_4$O$_4$N)$_2$ requires Cu, 16·1; N, 7·0%].

Tetramminocupric o-nitrobenzoate. By treating cupric *o*-nitrobenzoate with liquid ammonia, a cobalt-blue ammine, insoluble in liquid ammonia, was first obtained, but this was unstable at air temperature, being completely converted in a few hours into the purple tetrammine, even if kept in a strongly ammoniacal atmosphere (Found : Cu, 14·0; NH$_3$, 14·8; N, 17·9. [Cu(NH$_3$)$_4$]{C$_7$H$_4$O$_4$N}$_2$ requires Cu, 13·7; NH$_3$, 14·7; N, 18·1%). The *tetrammine* dissolved readily in water, and less readily in alcohol, giving bright blue

solutions. On exposure to dry air for 6 days, 1 mol. of ammonia was lost, leaving a greyish-blue powder which was decomposed by water.

Tripyridinocupric o-nitrobenzoate. Cupric *o*-nitrobenzoate turned blue when treated with pyridine. The product was recrystallised from pyridine, collected, washed with a little pyridine, and kept in a vacuum over soda–lime over-night. It was insoluble in and not decomposed by water or alcohol [Found : Cu, 10·3; N, 11·0. $Cu(C_5H_5N)_3\{C_7H_4O_4N\}_2$ requires Cu, 10·1; N, 11·1%].

Tetramminocupric m-*nitrobenzoate.* Cupric *m*-nitrobenzoate reacted with liquid ammonia similarly to the *o*-compound, the highest stable ammine being the lilac *tetrammine* (Found : Cu, 13·5; NH_3, 14·9; N, 18·0. $[Cu(NH_3)_4]\{C_7H_4O_4N\}_2$ requires Cu, 13·7; NH_3, 14·7; N, 18·1%). On exposure to dry air for 7 days, the ammonia content diminished to 7·3% (Calc. for the diammine : NH_3, 7·9%). The tetrammine was moderately soluble in water to a bright blue solution, and sparingly soluble in alcohol.

Picrates.—*Tetramminocupric picrate* was prepared by double decomposition between aqueous solutions of monohydrated tetramminocupric sulphate and the calculated amount of sodium picrate. The precipitate of greenish-yellow microscopic needles was washed with water and dried over soda–lime in a vacuum (Found : Cu, 10·5; NH_3, 11·4; N, 23·7. $[Cu(NH_3)_4]\{C_6H_2O_7N_3\}_2$ requires Cu, 10·8; NH_3, 11·6; N, 23·8%). On heating at 100°, no loss in weight occurred. The tetrammine dissolved in liquid ammonia to a red solution, from which, as the ammonia evaporated, a reddish-brown solid separated. As removal of the excess ammonia continued, the residue became green and finally the greenish-yellow tetrammine remained, being the highest ammine stable at room temperature. This is remarkable, as the higher co-ordination number 5 is exercised in pentapyridinocupric picrate (see Part III). Other picrates have been described in Part III (*loc. cit.*) and on p. 2312.

Trichloroacetates.—Hexahydrated cupric trichloroacetate was described by Judson (*Ber.*, 1870, **3**, 783). It is readily soluble in ether and was conveniently obtained as a dihydrate by the following method. An ethereal solution of 50 g. of trichloroacetic acid was treated with 15 c.c. of water and 25 g. of copper carbonate. After evolution of carbon dioxide had ceased, the mixture was kept for an hour, and the excess carbonate then removed. The filtrate was left for 10 days in a vacuum over sulphuric acid, and bright green crystals remained (Found : Cu, 15·2. Calc. : Cu, 15·0%).

Pentammino- and triammino-cupric trichloroacetates were described by Grossmann and Jäger (*loc. cit.*) but no evidence of the existence of the former has been obtained in this work.

Tetramminocupric trichloroacetate. Dihydrated cupric trichloro-acetate was treated with liquid ammonia, in which it dissolved very readily to a deep blue solution. The excess ammonia was allowed to evaporate from the filtered solution, leaving bluish-violet rectangular plates. The compound, which was readily soluble in water and in alcohol, was left for 2 days in a vacuum over soda–lime in an ammoniacal atmosphere, and proved to be the anhydrous *tetrammine* (Found : Cu, 13·9; NH_3, 14·9; Cl, 46·2. $[Cu(NH_3)_4]\{CCl_3 \cdot CO \cdot O\}_2$ requires Cu, 13·9; NH_3, 14·9; Cl, 46·6%).

Grossmann and Jäger's triammine was obtained by exposing the tetrammine to dry air for 5 days (Found : NH_3, 11·8. Calc. : NH_3, 11·6%).

Diquinolinocupric trichloroacetate. 5 G. of dihydrated cupric trichloroacetate in 15 c.c. of ether were added to 10 c.c. of quinoline. Small bluish-violet triangular prisms separated, and were freed from excess quinoline by washing with ether. The product was sparingly soluble in and decomposed by water. It was somewhat soluble in absolute alcohol, giving a clear light blue solution [Found : Cu, 9·8; N, 4·5. $Cu(C_9H_7N)_2\{CCl_3 \cdot CO \cdot O\}_2$ requires Cu, 9·8; N, 4·3%].

Molecular-weight Determinations.—Ebullioscopic method. In the Beckmann apparatus, 0·3998 g. of diamminocupric acetate ($M = 215·7$) raised the b. p. of 21·05 g. of anhydrous alcohol by 0·035°, giving an apparent molecular weight of about 624. The alcohol was dried by refluxing it twice with barium oxide and twice with calcium turnings and redistilling it after each operation.

Cryoscopic method. The Beckmann apparatus was used, with water as solvent. Hexamminocupric nitrate solutions were obtained by mixing the calculated amounts of tetramminocupric nitrate, ammonia solution, and water, and for tripyridinocupric nitrate, equivalent quantities of the dipyridino- and tetrapyridino-salts were mixed. In all other cases, solutions of the pure salts were employed. The pyridinocupric nitrates were prepared as described by Pfeiffer and Pimmer (*loc. cit.*).

In the tables, M indicates the calculated molecular weight, C the concentration (in g. mols./1000 g. water), Δt the depression of the freezing point, and i the osmotic factor, which was obtained from the formula $i = \Delta t(1 + 0·0055\Delta t)/1·858C$ (see Noyes and Falk, *J. Amer. Chem. Soc.*, 1910, **32**, 1011). In Table III, a and b represent the ratio of combined ammonia or pyridine (as the case may be) to copper, the former value being calculated as explained below, and the latter on the assumption that cupric nitrate dissolves in water as $[Cu(H_2O)_6](NO_3)_2$.

Table IV gives the freezing-point depressions for cupric nitrate,

ammonia, and pyridine, which have been used in calculating these ratios. Thus, for hexamminocupric nitrate and cupric nitrate at a concentration of $0.15M$, the values of Δt are $1.242°$ and $0.751°$, respectively; the difference of $0.491°$ corresponds to a free ammonia concentration of 0.242 (by extrapolation from the observed depression of $0.498°$ obtained at a concentration of 0.245); hence the molar concentration of free ammonia is $0.242 \div 0.15 = 1.61$, and that of

TABLE II.

$[Cu(C_5H_5N)_2](H\cdot CO\cdot O)_2$. $M = 311.8$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175		
Δt...	0.150°	0.271°	0.365°	0.440°	0.512°	0.591°	—		
i ...	3.23	2.92	2.63	2.37	2.21	2.12	—		

$[Cu(C_5H_5N)_2](NO_3)_2$. $M = 345.7$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	0.160°	0.281°	0.385°	0.505°	0.605°	0.707°	0.805°	0.913°	1.122°
i ...	3.45	3.03	2.77	2.73	2.61	2.55	2.49	2.47	2.43

$[Cu(C_5H_5N)_3](NO_3)_2$. $M = 424.8$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	0.176°	0.295°	0.412°	0.519°	0.632°	0.732°	0.829°	0.930°	1.113°
i ...	3.79	3.18	...2.96	2.80	2.73	2.64	2.56	2.52	2.41

$[Cu(NH_3)_5]I_2$. $M = 402.6$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	0.238°	0.440°	0.581°	0.742°	0.893°	1.020°	1.112°	1.211°	1.453°
i ...	5.13	4.75	4.18	4.01	3.86	3.68	3.44	3.28	3.15

	$M.$	$C.$	$\Delta t.$	$i.$
$[Cu(C_5H_5N)_2](NO_2)_2$	313.7	0.025	0.150°	3.23
$[Cu(NH_3)_4]\{CH_3\cdot CO\cdot O\}_2$	249.8	0.075	0.482	3.47

TABLE III.

$[Cu(NH_3)_4](NO_3)_2$. $M = 255.7$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	—	—	0.475°	0.611°	0.715°	0.820°	0.912°	1.010°	—
i ...	—	—	3.42	3.29	3.09	2.96	2.81	2.73	—
a ...	—	—	3.37	3.46	3.65	3.77	3.89	3.98	—
b ...	—	—	3.35	3.44	3.62	3.73	3.84	3.92	—

$[Cu(C_5H_5N)_4](NO_3)_2$. $M = 503.9$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	0.215°	0.345°	0.481°	0.612°	0.725°	0.830°	0.945°	1.050°	1.234°
i ...	4.63	3.72	3.45	3.30	3.13	2.99	2.92	2.84	2.68
a ...	2.74	3.22	3.42	3.53	3.66	3.77	3.82	3.89	—
b ...	2.74	3.21	3.40	3.51	3.63	3.73	3.78	3.85	3.97

$[Cu(NH_3)_6](NO_3)_2$. $M = 289.8$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	
Δt...	0.278°	0.506°	0.706°	0.895°	1.085°	1.242°	1.420°	—	
i ...	6.00	5.46	5.09	4.84	4.70	4.49	4.40	—	
a ...	3.27	3.51	3.85	4.07	4.18	4.39	4.49		
b ...	3.27	3.50	3.83	4.05	4.15	4.35	4.44		

$[Cu(C_5H_5N)_6](NO_3)_2$. $M = 662.0$.

C ...	0.025	0.05	0.075	0.1	0.125	0.15	0.175	0.2	0.25
Δt...	0.280°	0.488°	0.667°	0.832°	1.013°	1.141°	1.292°	1.420°	1.629°
i ...	6.04	5.27	4.81	4.50	4.39	4.12	4.01	3.85	3.54
a ...	3.47	3.75	4.08	4.29	4.37	4.62	4.74	4.89	5.19
b ...	3.47	3.74	4.05	4.26	4.34	4.58	4.69	4.83	5.12

TABLE IV.

Cu(NO$_3$)$_2$.

C ...	0·025	0·05	0·075	0·1	0·125	0·15	0·175	0·2	0·25
Δt...	0·144°	0·257°	0·383°	0·506°	0·629°	0·751°	0·875°	1·002°	1·247°

(These figures were used in calculating the values of a.)

[Cu(H$_2$O)$_6$](NO$_3$)$_2$.

C ...	0·025	0·05	0·075	0·1	0·125	0·15	0·175	0·2	0·25
Δt...	0·144°	0·256°	0·380°	0·501°	0·621°	0·740°	0·859°	0·980°	1·215°

(These figures were extrapolated from those recorded above for cupric nitrate and were used in calculating the values of b.)

Ammonia.

C ...	0·006	0·02	0·05	0·0667	0·111	0·149	0·186
Δt...	0·013°*	0·039°*	0·098°*	0·131°	0·220°	0·298°	0·375°
C ...	0·226	0·245	0·285				
Δt...	0·454°	0·498°	0·588°				

Pyridine.

C ...	0·0341	0·0491	0·0740	0·103	0·157	0·179	0·208
Δt...	0·077°	0·111°	0·159°	0·211°	0·308°	0·340°	0·392°

combined ammonia is 6·00 − 1·61 = 4·39.   The values in Table IV indicated by an asterisk are taken from International Critical Tables, Vol. IV, p. 254, and the others were determined experimentally.   The cupric nitrate solution was stirred for 2 days with copper carbonate, filtered, standardised, and diluted for use.

Blanks in the tables indicate that the compound separated on cooling or was decomposed by water.

Discussion of Results.

While the osmotic factors recorded for the dipyridino-compounds indicate the presence of a tri-ionic salt, they diminish somewhat more rapidly with increasing concentration than would be expected, and between concentrations of 0·1 and 0·25M the freezing-point depressions are lower than the corresponding values for cupric nitrate.

The differences are greater than would be expected to result from hydration of the cupric ion, and suggest that to a small extent co-ordination of acid radicals has occurred. This is the only evidence of co-ordination that has been obtained.

Comparatively little increase in the osmotic factor takes place on passing from dipyridino- to tripyridino-cupric nitrate, and the difference diminishes with increasing concentration until at a concentration of 0·25M the two salts produce the same depression. The results can best be accounted for by supposing that a small proportion of the tripyridino-salt is present as an acido-ammine.

The slight differences between the a and b values (Table III) indicate that no considerable modification is produced by ionic hydration and

that, at all events up to a concentration of 0·1, the effect of any probable degree of hydration of the cupric ion is negligibly small.

The stability of the salts of a complex kation in the solid state has not necessarily much relation to their stability in aqueous solutions. For instance, tetramminocupric nitrate can be heated at 85° without loss of ammonia, while tetramminocupric acetate loses ammonia in a few minutes at air temperature, but the freezing-point depressions at a concentration of 0·075M are very close, viz., 0·475° and 0·482° respectively.

The ratios combined NH_3/Cu and combined C_5H_5N/Cu at the same concentrations are practically identical for tetramminocupric and tetrapyridinocupric nitrates, but the latter ratio is 5—6% higher in the case of the hexammines.

In the solid state, both tetrammines are very stable, but whilst hexapyridinocupric nitrate is readily obtained pure and can be kept indefinitely in a closed vessel, hexamminocupric nitrate readily loses ammonia unless strongly cooled.

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