CCLXX.—*Researches on Residual Affinity and Co-ordination. Part XXVII. Ethylenediammine Copper Salts.*

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AMONG acidic radicals which favour the reversion of copper to its fundamental univalency are the cyanide, iodide, thiocyanate, and xanthate, so that cupric salts of these radicals pass spontaneously into cuprous compounds even in aqueous media at the ordinary temperature. This change of valency can, however, be hindered by certain addenda of crystallisation or co-ordination which tend to retain the metallic atom in the alternative condition of bivalency.

In accordance with the electronic conception of atomic structure and chemical combination, this change from univalent to bivalent copper corresponds with a displacement of an electron from a complete inner sub-group to the outermost group of valency electrons: Cu^{I} 2. 224. 22446. **1** to Cu^{II} 2. 224. 22445. **2** (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323). The latter arrangement is less symmetrical as regards inner electrons and suggests a strained condition manifested generally by the appearance of visible colour.

The experiments described below indicate the extent to which cupric iodide and cyanide can be stabilised by means of ethylenediamine.

I. *Amminated Cupric Iodides.*

It was already known that ammonia had a stabilising effect on cupric iodide and several ammino-derivatives have been described. Monoaquotetramminocupric iodide, $[Cu,4NH_3,H_2O]I_2$, has been prepared by a variety of processes (Berthelot, *J. Pharm.*, 1830, **15**, 445; Rammelsberg, *Pogg. Ann.*, 1839, **48**, 162; Saglier, *Compt. rend.*, 1886, **102**, 1554; Pozzi Escot, *ibid.*, 1900, **130**, 90; Horn, *Amer. Chem. J.*, 1908, **39**, 204). A polynuclear compound, decamminocupric iodide, $3CuI_2,10NH_3$, has also been obtained (Richards and Oenslager, *Amer. Chem. J.*, 1895, **17**, 302; Saglier, *loc. cit.*; Kohlschütter and Pudschies, *Ber.*, 1904, **37**, 1153; Ephraim, *Ber.*, 1919, **52**, 940). A readily dissociable hexamminocupric iodide, $[Cu,6NH_3]I_2$, has been studied by Richards and Oenslager, Horn, and Ephraim (*loc. cit.*), and the last-mentioned investigator has indicated a pentammine, $CuI_2,5NH_3$, and a diammine, $CuI_2,2NH_3$.

In earlier researches on ethylenediamminocupric salts Grossman and Schück (*Z. anorg. Chem.*, 1906, **50**, 15), who prepared the chloride and bromide of the general formula CuX_2,en,H_2O, also isolated a bromide, $CuBr_2,2en,2H_2O$, corresponding with the chloride, $CuCl_2,2en,2H_2O$, already produced by Werner and Spruck (*ibid.*, 1899, **21**, 234), but in neither of these investigations was any derivative of cupric iodide obtained.

By operating in aqueous solutions, *diaquobisethylenediamminocupric iodide* (I) has now been prepared as a well-defined crystalline substance quite stable in air. When left over sulphuric acid, this salt loses half its combined water and passes into *monoaquobisethylenediamminocupric iodide* (II), which undergoes no further change in dry air even up to 110°, although in a moist atmosphere it reverts to the dihydrate.

$$\text{(I.)}\quad [2H_2O,Cu,2en]I_2 \rightleftharpoons [H_2O,Cu,2en]I_2 \quad \text{(II.)}$$

The dehydration is accompanied by a change of colour from deep purple to lilac or mauve. This monohydrate corresponds in type with the methyl alcoholate $[CH_4O,Cu,2en]I_2$ and alcoholate $[C_2H_6O,Cu,2en]I_2$ described on pp. 2023, 2028.

Comparative experiments on the chloride and bromide $[Cu,2en,2H_2O]X_2$ showed that these salts are not converted into monohydrates when left over sulphuric acid.

II. *Amminated Cupric Cuprocyanides.*

The co-ordination theory affords a simple explanation of the chemical constitutions of complex copper cyanides, including their combinations with alkali cyanides and with ammonia. This clue to the structure of these copper compounds is based on the view that cuprous cyanide itself is a highly associated molecule, $[Cu_x(CN)_x]$, which becomes more or less depolymerised when combining with alkali cyanides to form such soluble double cyanides as $K[Cu_2(CN)_3]$ and $K[Cu(CN)_2]$. These alkali derivatives are salts of hypothetical dicuprocyanic and cuprocyanic acids, $HCu_2(CN)_3$ and $HCu(CN)_2$, belonging to a series containing the minimum proportion of cation (meta-acids and salts). Other alkali salts containing a larger proportion of cation are known such as $K_2[Cu(CN)_3]$, $K_3[Cu(CN)_4]$ and $Rb_2[Cu_3(CN)_5]$. Complex derivatives of the hypothetical acids $H_2Cu(CN)_3$, $H_3Cu(CN)_4$, and $H_2Cu_3(CN)_5$ are classified below.

1. *Derivatives of* $H[Cu_2(CN)_3]$. The olive-yellow cupric dicuprocyanide, $Cu^{II}[Cu_2(CN)_3]_2,H_2O$, and its ammines fall into this group. Of the latter, the following have been isolated: The diammine, $[Cu,2NH_3,H_2O][Cu_2(CN)_3]_2$ (Monthiers, *J. Pharm.*, 1847, **11**, 257), and the anhydrous compound (Treadwell and Girsewald, *Z. anorg. Chem.*, 1904, **39**, 87); the tetrammine, $[Cu,4NH_3][Cu_2(CN)_3]_2$, and its dihydrate (Hilkenkamp, *Annalen*, 1856, **97**, 221); *pentamminocupric dicuprocyanide*, $[Cu,5NH_3][Cu_2(CN)_3]_2$, obtained in insoluble green scales by one of us (G. T. M.) and J. W. Porter (unpublished research, 1914) by adding to concentrated ammoniacal copper

sulphate half the amount of 15% aqueous potassium cyanide required to decolorise the solution *; the hexammine,

$$[Cu,6NH_3][Cu_2(CN)_3]_2,$$

prepared by Schiff and Bechi (*Compt. rend.*, 1865, **60**, 33).

It has now been found that ethylenediamine furnishes a very stable derivative of this series, namely, *bisethylenediamminocupric dicuprocyanide*, $[Cu,2en][Cu_2(CN)_3]_2$, obtained in pink crystals which differ markedly in colour from both the blue anhydrous tetrammine and its green dihydrate.

2. *Derivatives of* $H[Cu(CN)_2]$. The siskin-green cupric cuprocyanide, $Cu[Cu(CN)_2]_2$, and a numerous series of ammines containing two, three, four, and six molecular proportions of ammonia: the blue hexammine, $[Cu,6NH_3][Cu(CN)_2]_2$, readily dissociating into the green tetrammine, $[Cu,4NH_3][Cu(CN)_2]_2$. Similar compounds have been obtained from mono-, di-, and tri-methylamines, while pyridine furnishes complexes containing 2, 3, and 5 molecules of the base.

A stable *monoaquobisethylenediamminocupric cuprocyanide*, $[Cu,2en,H_2O][Cu(CN)_2]_2$, crystallising in well-defined, dark purple needles has now been obtained by several methods of preparation which leave no doubt as to its constitution. It loses its characteristic colour on dehydration, but the brown anhydrous compound regains the molecular proportion of water on exposure to the atmosphere.

3. *Derivatives of* $H_2[Cu(CN)_3]$. Although the cupric salt of this acid has not been identified, yet two ammines have been described: $[Cu,2NH_3,H_2O][Cu(CN)_3]$ and $[Cu_2,2NH_3,3H_2O][Cu(CN)_3]_2$ (Bouveault, *Bull. Soc. chim.*, 1890, **4**, 640; Fleurent, *Compt. rend.*, 1892, **114**, 1060).

The analogous product with ethylenediamine has the composition $2Cu(CN)_2,Cu_2(CN)_2,2en,H_2O$ and may be regarded as *monoaquobisethylenediamminodicupric cuprocyanide*,

$$[\mathrm{en}\cdot\cdot Cu\cdot\cdot H_2O\cdot\cdot Cu\cdot\cdot \mathrm{en}][Cu(CN)_3]_2.$$

The water present is held very tenaciously and is only partly eliminated after prolonged heating at 110°.

This ethylenediamine derivative, which contains equal atomic proportions of univalent and bivalent copper, represents probably the extent to which the diamine stabilises cupric cyanide. It is significant that both ammonia and ethylenediamine stop short of complete stabilisation at the same stage.

4. *Derivatives of* $H_2[Cu_3(CN)_5]$. The rubidium, cæsium, and calcium salts of this hypothetical acid have been described (Gross-

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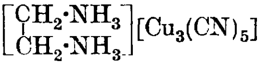
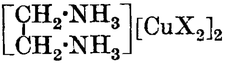
* Found: Cu, 56·5; NH_3, 15·3; CN, 28·9. $C_6H_{15}N_{11}Cu_5$ requires Cu, 56·9; NH_3, 15·2; CN, 27·9%.

mann and Van der Forst, *Z. anorg. Chem.*, 1905, **43**, 94) and we have now prepared the corresponding salt of ethylenediamine (III), obtaining it in both hemihydrated and anhydrous forms.

(III.) 

$$\left[\begin{matrix}CH_2\cdot NH_3\\ | \\ CH_2\cdot NH_3\end{matrix}\right][Cu_3(CN)_5]$$

 (IV.)

$$\left[\begin{matrix}CH_2\cdot NH_3\\ | \\ CH_2\cdot NH_3\end{matrix}\right][CuX_2]_2$$

The alkali salts of cuprochloric acid exhibit similar complications in regard to the anion as, for example, in $(NH_4)_2Cu_3Cl_5$ and $Cs_3Cu_2Cl_5$, but on combining ethylenediamine with cuprous chloride and bromide in the presence of the respective halogen hydride *ethylenediammonium cuprochloride* and *cuprobromide* of the simplest type (IV) were isolated, the latter being much the more stable of the two salts.

Co-ordination Numbers of Bivalent Copper.

In the preceding communication of this series (this vol., p. 914) it was pointed out that, owing to the electronic structure of the metallic radical, a co-ordination number 5 should be characteristic of bivalent copper, and the present investigation supplies further evidence on this point.

A survey of the extremely varied types of co-ordination compounds presented by copper suggests the operation of two opposing sets of forces. One set of forces, partly or wholly external to the copper atom, tends to marshal the associating units into symmetrical positions in the co-ordination complex so that, when these forces preponderate, co-ordination numbers of 4 and 6 are manifested. But to these forces making for symmetry is opposed another set arising from within the copper atom and depending upon the number and orientation of its chemically effective electrons. When these forces prevail, less symmetrical aggregates are produced and among such the system containing five associating units is predominant.

During this investigation two new co-ordinated cupric salts have been obtained: *tetra-aquoethylenediamminocupric perchlorate*, $[Cu,en,4H_2O](ClO_4)_2$, and a complex cupric cyanate,

$$Cu(CNO)_2,2en,2CH_3\cdot OH,4H_2O,$$

which on account of its excessive solubility in water only crystallises on addition of methyl alcohol. On the assumption that its organic addenda are associated with the metallic atom, this salt may be formulated as $[Cu,2en,2CH_3\cdot OH](CNO,2H_2O)_2$.

The foregoing perchlorate * and cyanate together with the

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* Cupric perchlorate has also been combined with the following addenda: $4H_2O$, $2Cu(OH)_2$, $8NH_3$, $4NH_3$, $3NH_3 + H_2O$, $Cu(OH)_2 + 6NH_3 + 2H_2O$, and $Cu(OH)_2 + 4NH_3 + 2H_2O$ (Salvadori, *Gazzetta*, 1912, **42**, i, 458); $Cu(ClO_4)_2,4NH_3,2H_2O$, having been previously described by Roscoe (*Annalen*, 1862, **121**, 355).

most highly amminated iodides, $[Cu,6NH_3]I_2$, and cuprocyanides, $[Cu,6NH_3][Cu(CN)_2]_2$ and $[Cu,6NH_3][Cu_2(CN)_3]_2$, represent the symmetrical octahedral arrangement, but these hexammines are easily decomposed even at the ordinary temperature into penta- and tetra-ammines. Compounds exhibiting a co-ordination value of 5 such as $[Cu,4NH_3,H_2O]I_2$ and $[Cu,2en,H_2O][Cu(CN)_2]_2$ are more stable, but there is also a tendency to furnish the lower symmetrical arrangement of four associating units as in $[Cu,2en][Cu_2(CN)_3]_2$, which separates in this anhydrous form from aqueous solutions.

Moreover, the opposing tendencies are plainly seen on considering the bisethylenediamminocupric halides $[Cu,2en,2H_2O]X_2$. The chloride and bromide persist in the symmetrical dihydrated form whereas the iodide, although obtainable in this condition, passes readily into a monohydrate, monoalcoholate, and monomethyl-alcoholate, these three derivatives demonstrating a descent from 6 to 5 in the co-ordination number.

EXPERIMENTAL.

I. *Ethylenediammino-derivatives of Cupric Iodide.*

Cuprous iodide (1 mol. Cu_2I_2) and ethylenediamine (2 mols.) were shaken together in water containing a small amount of iodine. An intense violet coloration was developed immediately, although but little cuprous iodide dissolved. The mixture was heated to 60° while air was bubbled through it; the cuprous salt then passed into solution with the deposition of an orange-brown precipitate containing cuprous hydroxide and copper. The filtered solution was concentrated until intensely purple, tabular crystals slowly separated. On recrystallisation from water the purple salt was obtained in large, compact, prismatic crystals which, when dried on a porous plate and subsequently over anhydrous calcium chloride, retained their colour (Found: Cu, 13·6; I, 53·9; C, 10·0; H, 4·2; N, 12·0. $C_4H_{20}O_2N_4I_2Cu$ requires Cu, 13·4; I, 53·6; C, 10·1; H, 4·25; N, 11·8%). These numbers indicate the *dihydrate. Diaquobisethylenediamminocupric iodide* (I) was extremely soluble in water, sparingly so in methyl alcohol and insoluble in ether, acetone, benzene, or chloroform. In aqueous solution it was unaffected by caustic soda or potassium iodide, even on warming, but with cold silver nitrate, a quantitative precipitation of silver iodide occurred, thus indicating that the iodine was entirely ionised in an aqueous solution of the cupric salt.

On heating, this complex iodide darkened at 90° and melted with decomposition at 240° to a green liquid. In moist air the dihydrate was somewhat hygroscopic, but when left over concentrated sulphuric acid it lost half its water in 48 hours and thereafter the residue remained of constant weight (Found : H_2O, 3·7. Calc. for one H_2O, 3·8%). This partial dehydration was accompanied by a change of colour from deep purple to pale mauve or lilac.

The *monohydrate* (II), which resembled the dihydrate in its chemical reactions, gave the following data : Cu, 14·0 ; I, 55·9 ; C, 10·5 ; H, 4·1 ; N, 12·5. $C_4H_{18}ON_4I_2Cu$ requires Cu, 13·95 ; I, 55·7 ; C, 10·5 ; H, 4·0 ; N, 12·3%).

Monoaquobisethylenediamminocupric iodide (II) is quite stable in a stoppered bottle or at 110°, but on exposure to moist air it reverts quantitatively to the dihydrate.

Methanolbisethylenediamminocupric Iodide $[CH_3{\cdot}OH,Cu,2en]I_2$.—On adding excess of pure methyl alcohol to a concentrated aqueous solution of hydrated bisethylenediamminocupric iodide bluish-purple glistening leaflets separated. These were purified by redissolution in water with addition of more methyl alcohol (Found : C, 12·65 ; H, 4·2 ; N, 12·0 ; I, 53·9 ; Cu, 13·65. $C_5H_{20}ON_4I_2Cu$ requires C, 12·8 ; H, 4·3 ; N, 11·9 ; I, 54·0 ; Cu, 13·5%). This cupric iodide derivative was very soluble in water, sparingly so in methyl or ethyl alcohol, and insoluble in ether or non-hydroxylic solvents. Blackening occurred at 100° and melting with decomposition to a blue liquid at 225—230°.

II. *Ethylenediammino-derivatives of Cupric Cuprocyanides.*

Monoaquobisethylenediamminocupric Cuprocyanide, $[Cu,2en,H_2O][Cu(CN)_2]_2$.—To the dark blue solution containing copper sulphate (1 mol.) and ethylenediamine (2 mols.) was added half the amount of 10% aqueous potassium cyanide required for complete decolorisation. The liquid was concentrated and allowed to cool ; lustrous, deep purple needles then separated. Further evaporation produced another crop of these crystals, which dissolve only sparingly in cold water, are more soluble in warm water but insoluble in alcohol and other organic media (Found : Cu, 43·8 ; C, 22·2 ; H, 4·2 ; N, 26·2 ; CN, 23·2. $C_8H_{18}ON_8Cu_3$ requires Cu, 44·1 ; C, 22·2 ; H, 4·2 ; N, 25·9 ; CN, 24·0%).

This complex monocuprocyanide was also obtained by the two following methods : (1) As the main product, separating in well-defined, dark purple needles, in the double decomposition between barium cyanide and bisethylenediamminocupric sulphate in aqueous solution (Found : Cu, 43·8 ; N, 26·2%). (2) An aqueous solution of potassium cuprocyanide, $KCu(CN)_2$, prepared by decomposing the siskin-green, cupric cuprocyanide, $Cu[Cu(CN)_2]_2$, with the calculated amount of potassium hydroxide, was added to bisethylenediamminocupric sulphate ; a portion of the product then separated immediately as a pale mauve, microcrystalline powder and a further crop crystallised in dark purple needles on concentrating the mother-liquor (Found : Cu, 43·9 ; N, 26·0%). On heating to 110°, the purple monohydrated cuprocyanide lost its water and passed into brown bisethylenediamminocupric cuprocyanide, $[Cu,2en][Cu(CN)_2]_2$ (Found : Cu, 45·7 ; loss, 4·1. Calc. : Cu, 45·9 ; 1 mol. H_2O, 4·2%). The anhydrous salt reverted to the purple monohydrate on exposure to moist air. On heating to 210—240° the brown compound melted with decomposition to a red liquid.

The purple cuprocyanide dissolved to a colourless solution in aqueous potassium cyanide, and when warmed with water or aqueous caustic soda this salt dissolved respectively to a purple or a deep blue solution from which, on rapid cooling, the following dicuprocyanide separated as a pink, crystalline precipitate.

Bisethylenediamminocupric Dicuprocyanide, $[Cu,2en][Cu_2(CN)_3]_2$.—In addition to the foregoing mode of formation, this dicuprocyanide was prepared by the following reactions : (1) Double decomposition between bisethylenediamminocupric sulphate and a solution of potassium dicuprocyanide, $KCu_2(CN)_3$, prepared by warming aqueous potassium cyanide with excess of cuprous cyanide (Found : Cu, 53·3 ; N, 24·0%). (2) Freshly precipitated cuprous cyanide was boiled with excess of aqueous ethylenediamine and hydrocyanic acid ; the cyanide dissolved to a purple solution from which the complex dicuprocyanide separated as a pink, crystalline precipitate (Found : Cu, 53·5 ; C, 19·7, 19·6 ; H, 2·85, 2·9 ; N, 23·95 ; CN, 25·8. $C_{10}H_{16}N_{10}Cu_5$ requires Cu, 53·5 ; C, 20·2 ; H, 2·7 ; N, 23·6 ; CN, 26·25%).

The dicuprocyanide darkened at 200° and decomposed at 240°, giving a red liquid ; it was insoluble in water or organic media but dissolved in aqueous sodium cyanide to a colourless solution. When warmed with aqueous caustic soda, it dissolved to a blue solution from which the original pink precipitate separated on cooling.

Monoaquobisethylenediamminodicupric Cuprocyanide,

$[en{\cdot\cdot}Cu{\cdot\cdot}OH_2{\cdot\cdot}Cu{\cdot\cdot}en][Cu(CN)_3]_2$.

—To a 20% solution of cupric sulphate (1 mol.) and ethylenediamine (1 mol.) was added half the amount of 10% aqueous potassium cyanide required for complete decolorisation ; a dull bluish-green, microcrystalline precipitate then separated which was insoluble in water or alcohol but dissolved in aqueous caustic soda to a blue solution from which black cupric oxide was precipitated on boiling. With sodium cyanide the compound dissolved to a blue solution which became colourless on warming (Found : Cu, 46·7; C, 21·7; H, 3·35; N, 25·25; CN, 27·8. $C_{10}H_{18}ON_{10}Cu_4$ requires Cu, 46·35; C, 21·9; H, 3·3; N, 25·5; CN, 28·4%). On heating at 110° for several hours, the compound lost only 80% of its contained water.

This substance was also produced by the following methods: (1) On adding bisethylenediamminocupric sulphate to a warm solution of potassium cuprocyanide, $KCu(CN)_2$, containing hydrocyanic acid (Found: Cu, 46·9; C, 21·5; H, 3·2; N, 25·4%). (2) When purple aquobisethylenediamminocupric cuprocyanide was warmed with aqueous hydrogen cyanide, these crystals assumed a green tint.

The Compound $C_{25}H_{80}O_6N_{24}Cu_5$.—Freshly prepared cuprous cyanide was mixed with strong hydrocyanic acid, and ethylenediamine was added with stirring until the cuprous compound had dissolved. The solution, which had warmed appreciably on the addition of the diamine, was cooled and filtered. The dark blue, oily filtrate, after evaporation to a small bulk on the water-bath, was left for some days in a desiccator. Compact, prismatic, saxe-blue crystals separated very slowly and were dried over sulphuric acid (Found: Cu, 28·1; C, 26·5; H, 7·1; N, 29·7; CN, 13·6. $C_{25}H_{80}O_6N_{24}Cu_5$ requires Cu, 28·1; C, 26·5; H, 7·1; N, 29·7; CN, 13·8%). These data correspond with the formula

$$Cu_5(CN)_6,9C_2H_4(NH_2)_2,H_2CO_3,3H_2O,$$

carbon dioxide having been slowly absorbed from the atmosphere. The substance was decomposed on prolonged exposure to air with formation of more highly carbonated products. It dissolved readily in water or alcohol, but not in ether, chloroform or benzene. It darkened at 70° and melted at 125° to a deep blue liquid. Not affected by aqueous alkalis, it was decolorised by alkali cyanide. Mineral acids precipitated cuprous cyanide with evolution of hydrogen cyanide. Its aqueous solution reduced silver nitrate but not Fehling's solution.

III. *Ethylenediammonium Cupro-salts.*

Ethylenediammonium Tricuprocyanide Hemihydrate (III).—Freshly precipitated cuprous cyanide and copper foil were boiled with an aqueous solution of ethylenediamine containing excess of hydrocyanic acid. The filtrate, from which a pink precipitate of dicuprocyanide separated, was again boiled with excess of hydrocyanic acid to insure a colourless solution. On cooling, small glistening plates of the tricuprocyanide separated (Found: Cu, 48·8; C, 21·4; H, 3·1; N, 25·25; CN, 31·9. $C_{14}H_{22}ON_{14}Cu_6$ requires Cu, 48·8; C, 21·5; H, 2·6; N, 25·1; CN, 33·3%). When quite dry, this tricuprocyanide was stable in air, but was readily decomposed by water, yielding cuprous cyanide. It was insoluble in all organic media, darkened on heating at 100° and decomposed at 240°. When maintained at 110°, the salt loses its combined water (Found: loss, 2·3. Calc. for $\frac{1}{2}H_2O$: loss, 2·3%. Found: Cu in residue, 50·2. $C_7H_{10}N_7Cu_3$ requires Cu, 49·95%).

Ethylenediammonium Cuprochloride (IV).—Freshly prepared uprous chloride (3·9 g.) was digested with excess of hydrochloric acid, ethylenediamine (2·3 g.), and copper foil, the mixture being boiled in a stream of carbon dioxide until the solution was colourless. On cooling, large colourless plates of the cuprochloride were deposited; these were recrystallised from hot dilute hydrochloric acid (Found: Cu, 38·3; C, 7·1; H, 3·0; N, 9·0; Cl, 42·5. $C_2H_{10}N_2Cl_4Cu_2$ requires Cu, 38·4; C, 7·2; H, 3·0; N, 8·5; Cl, 42·8%). When quite dry, the cuprochloride was stable, but with a trace of moisture it rapidly oxidised in air, becoming yellow and then green. The compound blackened at 120° and decomposed at 210° into a black liquid. It was dissociated by water in the cold into its component chlorides; boiling aqueous caustic alkalis gave cuprous oxide.

Ethylenediammonium cuprobromide (IV), prepared in a similar manner to the cuprochloride, crystallised from hydrobromic acid in long, colourless lamellæ (Found: Cu, 25·1; C, 4·8; H, 1·6; N, 5·8; Br, 62·8. $C_2H_{10}N_2Br_4Cu_2$ requires Cu, 25·0; C, 4·7; H, 2·0; N, 5·5; Br, 62·8%). The cuprobromide was much less readily oxidised than the cuprochloride; it melted with slight blackening at 235°.

IV. *Tetra-aquoethylenediamminocupric Perchlorate,* $[Cu,en,4H_2O][ClO_4]_2$.

We are indebted to Dr. G. R. Davies for the preparation of the perchlorate obtained by concentrating an aqueous solution of cupric perchlorate and ethylenediamine in molecular proportions. The salt crystallised in dark bluish-violet needles (Found: Cu, 16·4; ClO_4, 49·8; en, 15·8. $C_2H_{16}O_{12}N_2Cl_2Cu$ requires Cu, 16·1; ClO_4, 50·4; en, 15·2%).

This perchlorate, although slightly hygroscopic, was stable in air at the ordinary temperature. About 0·8 g., heated in a porcelain crucible over a Méker burner, decomposed quietly, but in an attempt to burn 0·2 g. in oxygen for the determination of carbon and hydrogen the substance exploded with extreme violence. A similar quantity mixed with copper oxide and heated in carbon dioxide for a nitrogen estimation exploded vigorously.

The perchlorate was readily soluble in water to a dark purple solution, but practically insoluble in alcohol and other organic media. Aqueous caustic soda gave a blue solution stable even on boiling, whereas the alcoholic alkali decomposed the salt, yielding cupric oxide.

V. *Ethylenediammino-derivative of Cupric Cyanate.*

A concentrated aqueous solution of potassium cyanate was added to a saturated solution of copper sulphate or acetate. The light green precipitate, after being washed successively with aqueous potassium cyanate and alcohol, was added to an aqueous solution of ethylenediamine until no more of the insoluble cyanate dissolved. The deep purple solution was evaporated to dryness over sulphuric acid, potassium cyanate being separated from time to time. The final residue was dissolved in hot methyl alcohol; the solution on evaporation deposited acicular crystals (Found: Cu, 15·7; C, 24·0; H, 7·6; en, 29·3. $C_8H_{32}O_8N_6Cu$ requires Cu, 15·7; C, 23·8; H, 8·0; en, 29·7%). This result corresponds with the composition of *bismethanolbisethylenediamminocupric cyanate tetrahydrate*, $[Cu,2en,2CH_3{\cdot}OH](CNO)_2,4H_2O$.

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