689. *A Violet Water-soluble Copper Cyanide.*

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The conditions for the production of a violet solution of cupric cyanide were investigated. Some reactions of this solution are reported and it is suggested that formulating the ion as $[Cu(CN)_4,HCN]''$ describes the composition of this complex. It seems probable that the violet colour is typical of all penta-co-ordinated cupric complexes.

On the addition of potassium cyanide to a neutral or slightly alkaline solution of a cupric salt an intense transient violet colour is often observed. The literature contains several references to such coloured compounds : Lallemand (*Compt. rend.*, 1864, **58**, 750) mentions a " wine-red " solution obtained on the addition of copper salts to a potassium cyanide solution. Moles and Izaguirre (*Anal. Fis. Quim.*, 1921, **19**, 33) produced a violet solution at temperatures below 0° and, on the evidence of viscosity and melting point depressions, put forward the formula $K_2Cu[Cu(CN)_4]_2$. Treadwell and Girsewald (*Z. anorg. Chem.*, 1904, **38**, 92; **39**, 87) separated crystalline violet compounds to which they gave the formulæ $Cu[Cu_2(CN)_3(NH_3)_2]_2$ and $Cu[Cu_2(CN)_4(NH_3)_2]$, containing both univalent and bivalent copper. Morgan and Burstall (*J.*, 1926, 2018) prepared several such coloured salts, which were also mixed cupric–cuprous complexes, but two crystalline iodides were given the formulæ

$$\underset{\text{deep purple}}{[Cu,2\,en,2H_2O]I_2} \;\underset{\text{moist atm.}}{\overset{\text{over } HS_2O_4}{\rightleftharpoons}}\; \underset{\text{lilac}}{[Cu,2\,en,H_2O]I_2}$$

(en = ethylenediamine) and were supposed to contain only cupric copper. Kruger, Bussem, and Tschirch (*Ber.*, 1936, **69**, 1601; 1941, **74**, 1378) studied the composition of violet copper thiocyanate precipitates produced in the presence of very small amounts of an iodide; analytically these precipitates could not be differentiated from the well-known white cuprous thiocyanate, but the examination of *X*-ray diagrams showed some additional lines; the authors therefore attributed the violet colour to the adsorption of a cupric complex by the original cuprous precipitate. Further Spacu and Grecu (*Bul. Soc. Stiinte Cluj*, 1931, **5**, 422) precipitated the dark-violet [Cu en$_2$][Ag(CNS)$_3$] and the mauve [Cu en$_2$][Zn(CNS)$_4$], [Cu en$_2$][Hg(CNS)$_4$], and [Cu en$_2$]$_3$[Cr(CNS)$_6$]$_2$ complex amines. A violet solution was produced (Tartarini, *Gazzetta*, 1933, **63**, 597) on addition of excess of *o*-phenanthroline to cupric sulphate, and on addition of potassium iodide or thiocyanate this gives a violet-blue precipitate.

Thus clearly there is a whole array of violet copper compounds which contain seemingly bivalent copper. We have attempted to clarify the conditions under which violet copper cyanide may be produced and to obtain some knowledge about its composition. Our preliminary results are summarised as follows.

(1) On the gradual addition of potassium cyanide to a neutral solution of a cupric salt, a green precipitate is first obtained, which later becomes brown; then a weak violet colour appears in the solution when about 4 molecular proportions of cyanide have been added. The precipitate as well as the violet colour disappear on a further small addition of cyanide, to yield a clear colourless or yellow solution.

(2) In alkaline solution we obtained the violet colour only if the alkalinity was very low.

(3) In a solution acidified with sulphuric acid, the violet colour appeared when in addition to the four moles of potassium cyanide (necessary for the production of the colour in neutral solution) another two moles of cyanide were added for each mole of sulphuric acid.

(4) When the amount of sulphuric acid was increased whilst the molar ratio $CuSO_4 : H_2SO_4 : KCN = 1 : x : (4 + 2x)$ was retained, the intensity of the violet colour increased up to one-half mole of sulphuric acid for each mole of copper sulphate, *i.e.*, up to the molar ratio $CuSO_4 : H_2SO_4 : KCN = 1 : 0{\cdot}5 : 5$. On further increase of x, the intensity of the colour was not altered.

(5) Approximate colorimetric and photometric measurements in the visual range showed that the solutions had a maximum extinction at a wave-length of about 500 mμ. and that the optical density increased almost linearly with x up to $x = 0{\cdot}5$, remaining constant at this maximum value (see Table I).

TABLE I.

Relative optical density of the violet copper cyanide solutions, Cu = 0·0333M.

M-KCN	0·133	0·148	0·159	0·167	0·181	0·200
M-H_2SO_4	0·0000	0·0075	0·0128	0·0167	0·0240	0·0333
Relative optical density	—	(1)	2·14	4·53	4·28	3·81

(6) Addition of potassium cyanide to more than the ratio stated decolorised the violet solution; an excess of one mole of cyanide sufficed to produce a colourless solution, which later became yellow, or orange in the presence of very great excess of cyanide.

(7) Addition of sulphuric acid to the violet solution gave a white precipitate, and the filtrate therefrom was free from copper, whilst the precipitate smelled strongly of cyanogen. About one mole of sulphuric acid per atom of cupric copper was required for complete precipitation and decolorisation. If treated within a short time, the white precipitate could be dissolved in potassium cyanide with the re-production of the violet solution. If the potassium cyanide was added 10—15 minutes after precipitation, only a colourless solution was obtained.

(8) On filtration of the white precipitate as quickly as possible, followed by the determination of the cyanide, in solutions which had originally the molar composition $CuSO_4 : H_2SO_4 : KCN = 1 : 1 : 6$, at least 38·1% of the original amount of cyanide introduced into the mixture remained in solution. This percentage increased when the filtration was delayed, up to 52%.

(9) When kept in an open vessel, the violet solution decomposed during a few hours to give a yellow solution, whilst in closed full vessels the colour faded only slowly during a few days. Ethanol did not stabilise the solution.

(10) The violet solution decomposes hydrogen peroxide with the production of a brown precipitate.

(11) It was advisable to carry out the reactions by mixing the solutions in the desired ratio in closed bottles. It was impossible to titrate an acid solution of copper sulphate with potassium cyanide, as the copper cyanide decomposed in less time than was required for a titration. The addition of copper sulphate as the last reagent (*i.e.*, in the order KCN, H_2SO_4, $CuSO_4$) was more advantageous.

(12) When the solutions were mixed, gases were evolved unless the mixture had the exact composition given above for the production of intensely coloured solutions; under these conditions no gas bubbles were seen and no pressure was exerted on the stopper of the flask.

(13) Similar results were obtained with cupric chloride and hydrochloric acid. All the

results were independent of the absolute concentration of the mixtures (in the concentration range of 0·025—0·125M-copper sulphate).

(14) The reagents used were : copper sulphate pentahydrate, Prolabo, R.P.; sulphuric acid, Kahlbaum p.A.; and potassium cyanide, Prolabo, R.P. They were not further purified. The copper concentrations of the various stock solutions were determined by electrolysis, and potassium cyanide concentrations by titration with standard silver nitrate.

Some additional experiments were made with reagents of various sources, such as : copper sulphate pentahydrate B.D.H. "AnalaR"; sulphuric acid, May and Baker, B.P.; sodium potassium cyanide, May and Baker, 98/100% potassium cyanide. They gave qualitatively and quantitatively identical results.

DISCUSSION.

The violet complex is formed from cupric salts; its formation precedes reduction to the cuprous state, and no evolution of gas is observed when the solutions are mixed in proportions required to produce maximum intensity of colour. The copper in this complex is therefore very probably in the bivalent state.

The stoicheiometric ratios requisite for the formation of the violet complex are $Cu^{++} : 5CN^- : H^+$, which favour the formula $[Cu(CN)_4,HCN]''$, with a penta-co-ordinated bivalent copper nucleus, for the ion. Morgan and Burstall (*loc. cit.*) consider that such unstable copper complexes should exist, as for example in the lilac iodide $[Cu,2\ en,H_2O]I_2$. Thus the violet colour may plausibly be typical of the penta-co-ordinated cupric complexes. Clearly such unusual co-ordination complexes may be formed only under well-defined conditions, in conformity with our experiments. As a matter of fact, the tetra- or hexa-co-ordinated cupric complexes are formed more easily and under a variety of conditions, but the violet cyanide is the less readily decomposed to the cuprous state than any other cupric cyanide. The rather rapid decomposition of the other cyanides explains why the violet complex could not be produced by titrating slowly an acid cupric sulphate solution with potassium cyanide.

The violet complex decomposed slowly, presumably thus

$$\underset{\text{violet solution}}{2[Cu(CN)_4,HCN]''} \longrightarrow \underset{\text{yellow solution}}{2[Cu(CN)_3]''} + 2HCN + (CN)_2;$$

in closed bottles where the gaseous products could not escape, even this slow decomposition was retarded.

Addition of an excess of potassium cyanide had an effect similar to that produced by adding alkali : it caused replacement of the hydrogen cyanide molecule in the violet complex by a cyanide ion, followed by transformation into the hexa- and tetra-co-ordinated copper complexes.

On the other hand, acids precipitate a white crystalline substance. Now for each mole of copper sulphate one mole of sulphuric acid was necessary for complete precipitation, and of *six* moles of potassium cyanide (including one mole of hydrogen cyanide in excess) a minimum of 2·28 remained in the solution. Therefore this reaction should be written :

$$\underset{\text{violet complex}}{[Cu(CN)_4,HCN]''} + 2H^+ \longrightarrow \underset{\text{white precipitate}}{[Cu(CN)_2,(HCN)_2]} + HCN \quad . \quad . \quad . \quad . \quad . \quad (1)$$

followed by

$$2[Cu(CN)_2,(HCN)_2] \longrightarrow 2CuCN + (CN)_2 + 4HCN \quad . \quad . \quad . \quad . \quad (2)$$

Reaction (2) is complete in about 10—15 minutes. During this time the violet colour may be partly restored by the addition of a cyanide :

$$\underset{\text{white precipitate}}{[Cu(CN)_2,(HCN)_2]} + 2CN' \longrightarrow \underset{\text{violet solution}}{[Cu(CN)_4,HCN]''} + HCN.$$

Reaction (2) explains also the facts that the filtered solution contained always slightly more than one-third of the original amount of cyanide (working with an excess of one mole of hydrogen cyanide present in the solutions) and that this ratio increased if the filtration was delayed.

The production of the violet colour in neutral solution is accounted for by partial decomposition of the cupric cyanide, followed by the hydrolysis of the cyanogen giving some hydrogen cyanide :

$$2Cu(CN)_2 + H_2O \longrightarrow 2CuCN + HCN + HCNO$$

In connexion with the catalytic decomposition of hydrogen peroxide by the violet complex it should be noted that cupric hydroxide and alkaline copper solutions catalyze this decomposition whereas acid solutions do not. The pH of the violet solution, measured with glass electrodes, was about 5·4; therefore the catalytic effect of the violet complex should also be attributed to its labile penta-co-ordination.

Owing to unfavourable circumstances we were unable to follow up our preliminary results, but we hope to do so later.

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