

# COORDINATION COMPOUNDS OF COPPER.

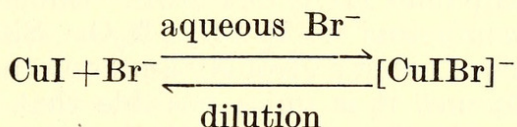
## PART II. COMPOUNDS DERIVED FROM COPPER (I) IODIDE.

By C. M. HARRIS.

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Copper (I) halides readily dissolve in boiling concentrated solutions of the corresponding alkali or ammonium halides to form complex halogeno-cuprates (I). Recently the author employed this reaction (Harris, 1948) to isolate tetrammine and bis-ethylenediamine copper (II) dihalogeno-cuprates (I) of the general formula  $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{X}_2]_2$  ( $\text{A}=\text{NH}_3$ ;  $2\text{A}=\text{C}_2\text{H}_4(\text{NH}_2)_2$  and  $\text{X}=\text{Br}$  and  $\text{I}$ ). With the chloro-complexes the ammonia compound was obtained as the monohydrate  $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$  and the ethylenediamine compound possessed the formula  $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}_3\text{Cl}_5]$ .

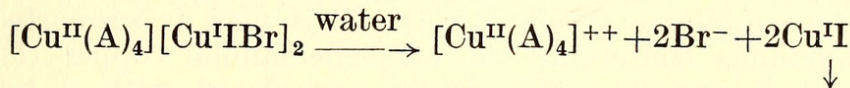
It has since been found that copper (I) iodide dissolves in a boiling concentrated solution of alkali or ammonium bromide forming a colourless solution presumably containing the bromo-iodo-cuprate (I) ion.



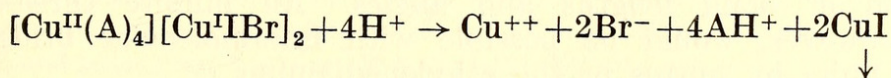
Dilution decomposes the complex ion causing copper (I) iodide to be precipitated. That this solution does contain such an ion and is not merely a mixture of the dibromo- and diiodo-cuprate (I) ions is supported by its reactions with ammonia and ethylenediamine described later.

Addition of a solution containing the bromo-iodo-cuprate (I) ion to a solution containing tetrammine copper (II) or bis-ethylenediamine copper (II) ions yields, on cooling, black tetrammine copper (II) bromo-iodo-cuprate (I)  $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{IBr}]_2$  (I) and purple bis-ethylenediamine copper (II) bromo-iodo-cuprate (I)  $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{IBr}]_2$  (II) respectively.

Water, particularly on heating, decomposes these compounds, forming a deep blue and



purple solution of tetrammine and bis-ethylenediamine copper (II) bromide respectively and a white precipitate of copper (I) iodide. Addition of acid decomposes the tetrammine ion as well according to the reaction



providing a means of determining the copper (II) ion in the presence of copper (I) since the addition of iodide ions liberates iodine equivalent to the copper (II).

Treatment of compound II with boiling concentrated potassium iodide solution causes it to dissolve and, on cooling, brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (Harris, *loc. cit.*) are deposited.



Compounds I and II cannot be a physical mixture of the corresponding dibromo- and diiodo-complexes since the diiodo-complexes liberate free iodine (Harris, *loc. cit.*) on treatment with acid and these compounds do not. However, the structures of compounds I and II in the solid state need not necessarily contain discrete  $[\text{CuI}]\text{Br}]^-$  ions. They could contain both  $[\text{CuBr}_2]^-$  and  $[\text{CuI}_2]^-$  ions.

The reaction of the bromo-iodo-cuprate (I) solution with a limited amount of ammonium hydroxide yielded, on cooling, an amminated copper (I) iodide derivative,  $(\text{CuI})_2 \cdot \text{NH}_3$  (III), as white plates. On reacting a solution containing the diiodo-cuprate (I) ion in a similar manner with ammonium hydroxide an entirely different compound,  $\text{CuI} \cdot \text{NH}_3$  (IV), was obtained as yellow prisms. This reaction supports the postulation of the bromo-iodo-cuprate (I) ion in solution indicating that such a solution is not merely a mixture of  $[\text{CuI}_2]^-$  and  $[\text{CuBr}_2]^-$  ions since if this was the case it should yield the same copper (I) iodide derivative with ammonia as a solution containing only  $[\text{CuI}_2]^-$  ions.

Ethylenediamine fails to react with the bromo-iodo-cuprate (I) solution to yield a copper (I) iodide derivative. On shaking the mixture in the presence of air, oxidation takes place and purple prisms of compound II are deposited. The diiodo-cuprate (I) solution reacts immediately with ethylenediamine to deposit a cream microcrystalline compound,  $(\text{CuI})_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2$  (V). The filtrate deposited brown prisms of a compound which was most likely bis-ethylenediamine copper (II) diiodo-cuprate (I) resulting from oxidation of copper (I).

The structure of compound III is unknown. Silberrad (1905) reported the preparation of a green compound  $\text{Cu}_2\text{I}_2 \cdot \text{NH}_3 \cdot 4\text{H}_2\text{O}$ . Since the preparation was performed in the presence of air in a strongly ammoniacal solution and the water was determined by difference it is quite possible that this compound was an oxidised copper (I) derivative in keeping with its colour.

Compound IV can be formulated as either the monomer  $[\text{H}_3\text{N} \rightarrow \text{CuI}]^\circ$ , the dimer  $[\text{Cu}^{\text{I}}(\text{NH}_3)_2][\text{Cu}^{\text{I}}\text{I}_2]$ , or the tetramer  $[\text{H}_3\text{N} \rightarrow \text{CuI}]_4^\circ$ . The last structure is similar to the triethyl arsine derivative  $[\text{Et}_3\text{As} \rightarrow \text{CuI}]_4^\circ$ , whose structure was established by Mann, Purdie and Wells (1936) to consist of a central tetrahedron of copper atoms surrounded by tetrahedral groups of iodine atoms and triethyl arsine molecules. This structure would seem the most likely.

A number of alternative structures are possible for compound V also. It may be formulated as the complex copper (I) cuprate (I),  $[\text{Cu}^{\text{I}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)][\text{Cu}^{\text{I}}\text{I}_2]$ . This, however, seems unlikely, since apart from a lack of symmetry the  $[\text{Cu}^{\text{I}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)]^+$  ion would involve considerable strain in the carbon-nitrogen bonds if it was to possess the linear configuration which is associated with two covalent copper (I) complexes (Wells, 1945). This view is supported by the fact that no compounds containing the ethylenediamine copper (I) ion are known. Compound V can be satisfactorily formulated with a tetrahedral structure similar to the arsine derivative mentioned previously save that the intramolecular bridging that would be required of ethylenediamine for the existence of discrete tetrahedral molecules in the structure is unlikely from a consideration of bond lengths and angles. An infinite three-dimensional structure, however, would be possible with intermolecular bridging of the tetrahedral units by means of the ethylenediamine.

Compounds corresponding to III and IV have previously been postulated by Biltz and Stollenwerk (1921). They investigated tensimetrically the formation of ammoniates with copper (I) halides and in the case of the iodide obtained evidence for the existence of the ammoniates  $\text{CuI} \cdot n\text{NH}_3$  where  $n=0.5, 1, 2$  and 3.



During the course of this work an attempt was made to form the diammine (ethylenediamine) copper (II) ion,  $[\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_4(\text{NH}_2)_2)]^{++}$ , in solution and isolate it as its diiodo-cuprate (I) derivative. This was not realised and on reacting one mole of a copper (II) salt with one mole of ethylenediamine and a limited excess of ammonium hydroxide followed by metathesis with a potassium iodo-cuprate (I) solution an earth green mixture of tetrammine and bis-ethylenediamine copper (II) diiodo-cuprates (I) was obtained. The tetrammine compound in the mixture was decomposed to copper (I) iodide by heating the mixture at  $100^\circ\text{C}$ . to constant weight. From the loss in weight was calculated the percentage of tetrammine compound present. The residue was treated with concentrated potassium iodide solution to remove copper (I) iodide and the bis-ethylenediamine compound that remained was filtered off and identified.

Compounds I–V inclusive reduce silver nitrate solution to the metal instantly in the cold due to the copper (I) present in their molecules and also give a simultaneous precipitate of silver halide. They are insoluble in the usual organic solvents and unstable to water.

Copper (I) iodide also dissolves to a small extent in boiling concentrated ammonium and alkali chloride solutions presumably forming the chloro-iodo-cuprate (I) ion. Attempts to isolate this ion as its bis-ethylenediamine copper (II) derivative were unsuccessful due to the large amounts of ammonium or alkali chloride that crystallised out on cooling the reaction mixture.

#### EXPERIMENTAL.

##### (I) *Tetrammine Copper (II) Bromo-iodo-cuprate (I).*

To diammine copper (II) acetate (1.6 g., 0.0074 g. mole (Horn, 1908)) dissolved in a solution of ammonium hydroxide (1.3 ml. of 15 N) in water (25 ml.) was added acetic acid (0.3 ml. of 17 N). After the addition of ammonium bromide (5.0 g.) the solution was heated to  $80\text{--}85^\circ\text{C}$ . A boiling solution of copper (I) iodide (2.8 g., 0.015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added in a thin stream with constant stirring and the stirring continued while the solution was cooled to  $25^\circ\text{C}$ . After immediate filtration the black microcrystals were washed with 90% alcohol, followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. Yield 2.4 g. (42%).

Found: Cu (total), 28.2;  $\text{Cu}^{++}$ , 9.31;  $\text{NH}_3$ , 10.1%. 0.497 and 0.502 g. complex gave 0.623 and 0.631 g. of  $\text{AgBr} + \text{AgI}$ .

$[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{IBr}]_2$  requires Cu (total), 28.36;  $\text{Cu}^{++}$ , 9.45;  $\text{NH}_3$ , 10.13%. 0.497 and 0.502 g. complex give 0.625 and 0.631 g. of  $\text{AgBr} + \text{AgI}$ .

The compound is readily oxidised in the presence of moist air, assuming a greenish colour. Water decomposes it instantly in the cold, according to the reaction given previously. It is unaffected by alcohol, acetone and the usual organic solvents. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver with simultaneous precipitation of silver halides.

##### (II) *Bis-ethylenediamine Copper (II) Bromo-iodo-cuprate (I).*

To a solution of bis-ethylene diamine copper (II) bromide monohydrate (2.5 g., 0.0069 g. mole (Johnson and Bryant, 1934)) dissolved in water (30 ml.) was added ammonium bromide (5.0 g.), and the solution was heated to  $85^\circ\text{C}$ . A boiling solution of copper (I) iodide (2.6 g., 0.015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added with constant stirring and the stirring continued while the solution was cooled to  $25^\circ\text{C}$ . After filtration the compound was washed with methyl alcohol followed by dry ether. Yield 4.6 g. (92%).

Found: Cu (total), 26.4;  $\text{Cu}^{++}$ , 8.73%. 0.496 g. complex gave 0.474 g.  $\text{AgBr} + \text{AgI}$ .

$[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{IBr}]_2$  requires Cu (total), 26.3;  $\text{Cu}^{++}$ , 8.77%. 0.496 g. complex gives 0.479 g.  $\text{AgBr} + \text{AgI}$ .



The compound crystallises as purple prisms stable in air. Water decomposes the compound more slowly than the corresponding tetrammine but completely on boiling in accordance with the equation given previously. It reduces silver nitrate solution instantly in the cold to silver with simultaneous precipitation of silver halides. Dilute acetic and sulphuric acid decomposes the compound, according to the equation given previously to copper (I) iodide. (Found: Cu, 66.0; calculated: Cu, 66.6%.) The compound dissolves in boiling 50% potassium iodide solution, from which brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (*loc. cit.*) is deposited on cooling. (Found: Cu (total), 23.4; calculated: Cu (total), 23.3%.) The compound is unaffected by alcohol, acetone and the usual organic solvents.

(III) *Monammine Bis-(Copper (I) Iodide).*

To copper (I) iodide (2.0 g.) dissolved in a boiling solution of potassium bromide (35 g.) in water (50 ml.) and cooled to 85° C. was added ammonium hydroxide (0.70 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with 90% alcohol followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. The ether was removed under vacuum and the compound sealed from the atmosphere. Yield 0.8 g. (38%).

Found: Cu, 31.4; NH<sub>3</sub>, 4.4; I, 63.8%. (Cu<sup>I</sup>I)<sub>2</sub>.NH<sub>3</sub> requires Cu, 31.9; NH<sub>3</sub>, 4.3; I, 63.8%.

The compound crystallises as lustrous pearly plates and is readily oxidised in the atmosphere assuming a green colour. It is decomposed immediately in the cold by water, with the appearance of the blue tetrammine copper (II) colour due to oxidation. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver, with simultaneous precipitation of silver iodide. On heating at 100° C. to constant weight the compound (0.202 g.) loses its ammonia, and copper (I) iodide (0.192 g.) (calc. 0.193 g.) remains. It is insoluble in organic solvents.

(IV) *Monammine Copper (I) Iodide.*

To copper (I) iodide (7.5 g.) dissolved in a boiling solution of potassium iodide (45 g.) in water (30 ml.) and cooled to 75° C. was added ammonium hydroxide (2.5 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. The ether was removed and the compound sealed from the atmosphere. Yield 5.0 g. (61%).

Found: Cu, 30.3; NH<sub>3</sub>, 8.2; I, 61.3%.

Cu<sup>I</sup>I.NH<sub>3</sub> requires Cu, 30.6; NH<sub>3</sub>, 8.2; I, 61.2%.

The compound is decomposed by water similarly to the previous compound and gives the same reaction with silver nitrate. It crystallises as yellow prisms, readily oxidised by the atmosphere, when it assumes a green colour.

(V) *Ethylenediamine Bis-(Copper(I) Iodide).*

To copper (I) iodide (2.9 g., 0.015 g. mole) dissolved in a boiling solution of potassium iodide (22 g.) in water (15 ml.) and cooled to 55° C. was added a solution of ethylenediamine (0.40 ml. of anhydrous, 0.006 g. mole) and potassium iodide (5.0 g.) in water (5 ml.) at 55° C. with stirring. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. Yield 2.6 g. (98%).

Found: Cu, 28.7; I, 57.6%.

(Cu<sup>I</sup>I)<sub>2</sub>.C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> requires Cu, 28.8; I, 57.5%.

The compound is insoluble in organic solvents and is stable in air. It crystallises as cream micro-prisms and reduces silver nitrate in the cold to metallic silver with simultaneous precipitation of silver iodide. It is insoluble in cold water but decomposed readily on warming, oxidation to bis-ethylenediamine copper (II) iodide taking place (see Morgan and Burstal, 1926). The filtrate from the above preparation deposited a small amount of brown prisms which were probably bis-ethylenediamine copper (II) diiodo-cuprate (I), resulting from partial oxidation of some of the copper (I).



*Reaction of Ethylenediamine with a Solution of the Bromo-iodo-cuprate (I) Ion.*

To copper (I) iodide (1.0 g.) dissolved in a boiling solution of ammonium bromide (20 g.) in water (20 ml.) and cooled to 60° C. was added a solution of ethylenediamine (0.15 ml. of anhydrous) in water (5 ml.) containing ammonium bromide (5.0 g.) at 55° C. No precipitate appeared on cooling to 30° C. but on shaking for 10–15 minutes purple prisms of compound II were deposited. Yield 0.5 g.

Found: Cu (total), 26.4.

Calculated: 26.3%.

*Attempted Preparation of Diammine (Ethylenediamine) Copper (II) Diiodo-cuprate (I).*

To a solution of anhydrous copper (II) chloride (0.85 g., 0.0063 g. mole) in water (15 ml.) was added ethylenediamine (0.62 ml. of 69%, 0.0071 g. mole) followed by ammonium hydroxide (1.0 ml. of 15N). After the addition of potassium iodide (2.0 g.) the stirred solution was heated to 75° C. and to it was added in a fine stream a boiling solution of copper (I) iodide (2.4 g., 0.013 g. mole) and potassium iodide (15.0 g.) in water (10 ml.). The stirring was continued and the solution cooled to 25° C. After filtration the compound was washed with 90% alcohol followed by ether. Yield 4.4 g.

Found: Cu, 23.8%.

Calculated for a 1:2 mixture of  $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{I}_2]_2$  and  $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{I}_2]_2$ : Cu, 23.8%.

The mixture, which was micro-crystalline, possessed an earthy colour with a green reflex. Brown and dark green crystals could be distinguished under the microscope. The mixture (0.511 g.) was heated to 100° C. to constant weight (0.468 g.). From the loss in weight (0.043 g.) the amount of tetrammine copper (II) diiodo cuprate (I) (0.173 g.) present in the mixture was calculated.

The residue was boiled with 50% potassium iodide solution (10 ml.) and on cooling to 30–40° C. the brown bis-ethylenediamine copper (II) diiodo-cuprate (I) was filtered off and washed with 50% potassium iodide solution (5 ml.) followed by methyl alcohol and ether. Yield 0.29 g.

Found: Cu, 23.3%.

Calculated: 23.3%.

## SUMMARY.

Copper (I) iodide dissolves in concentrated ammonium or alkali bromide solution to form the bromo-iodo-cuprate (I) ion. Double decomposition of solutions containing this ion with solutions of tetrammine and bis-ethylenediamine copper (II) ions yields the corresponding tetrammine and bis-ethylenediamine copper (II) bromo-iodo-cuprates (I) of general formula  $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{IBr}]_2$ . Solutions containing the bromo-iodo-cuprate (I) ion give with ammonium hydroxide a compound of empirical formula  $(\text{CuI})_2\cdot\text{NH}_3$ , whose structure is unknown. With ethylenediamine, however, partial oxidation takes place and bis-ethylenediamine copper (II) bromo-iodo-cuprate (I) is obtained. Similarly solutions of the diiodo cuprate (I) ion yields with ammonia and ethylenediamine compounds of empirical formula  $\text{CuI}\cdot\text{NH}_3$  and  $(\text{CuI})_2\cdot\text{C}_2\text{H}_4(\text{NH}_2)_2$  respectively. Possible structures for these compounds are suggested. Attempts to prepare diamine (ethylenediamine) copper (II) diiodo-cuprate (I) were unsuccessful.

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Chemistry Department,  
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Australia.



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