

CLXXV.—*Researches on Residual Affinity and Co-ordination. Part XXIX. Cupric Salts Stabilised by Ethylenediamine.*

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ALTHOUGH cupric salts of the more strongly electronegative anions are stable exothermic compounds, this condition of stability depends largely on the nature of the acidic ions, and as their electronegative character diminishes, the normal cupric salts exhibit an increasing tendency to decompose either by hydrolytic change or by a spontaneous decrease of valency from bivalent to univalent copper.

The former mode of decomposition is exhibited by cupric carbonate, the latter by cupric iodide ($\text{CuI}_2 = \text{CuI} + \text{I} + 11,560 \text{ cal.}$).

In earlier experiments on this subject (J., 1926, 2018, 2027) it was shown that cupric iodide can be stabilised by combination with ethylenediamine, and accordingly we have employed this new reagent $[\text{Cu}, 2 \text{ en}, 2\text{H}_2\text{O}]_2\text{I}_2$ in a further study of cupric salts of the weaker acids.

Amminated Cupric Carbonates.—The normal salt, CuCO_3 , has not hitherto been obtained, since both laboratory methods and geological processes lead to the formation of basic carbonates. A double carbonate of normal type, $\text{K}_2[\text{Cu}(\text{CO}_3)_2]$, was obtained in anhydrous and hydrated forms by Reynolds (J., 1898, **73**, 262), but this substance is readily decomposed by water. A compound having the composition $\text{CuO}, 3\text{CO}_2, 4\text{NH}_3$ is described by Maumené (*Compt. rend.*, 1882, **95**, 225), and the diamminocupric carbonate, $\text{CuCO}_3, 2\text{NH}_3$, by Favre (*Ann. Chim. Phys.*, 1844, **10**, 116). With the reagents cooled to -18° , Ephraim isolated pentamminocupric carbonate, $\text{CuCO}_3, 5\text{NH}_3$, which at 37° dissociated into the diammine (*Ber.*, 1919, **52**, 940).

By interaction between silver carbonate and aqueous bisethylenediamminocupric iodide we have now obtained *bisacquobisethylene-diamminocupric carbonate*, $[\text{Cu}, 2 \text{ en}]\text{CO}_3, 2\text{H}_2\text{O}$, as a well-defined salt, readily soluble in water or alcohol to solutions which can be boiled without decomposition of the product.

Amminated Cupric Nitrites.—Cupric nitrite has not been obtained in a stable form, for when it is prepared in aqueous media, complex changes occur and nitric oxide is evolved at the ordinary temperature. A basic salt, $\text{Cu}(\text{NO}_2)_2, 3\text{Cu}(\text{OH})_2$, has been isolated (van der Meulen, *Ber.*, 1879, **12**, 758) and double nitrites such as $\text{K}_3[\text{Cu}(\text{NO}_2)_5]$ and $\text{Tl}_3[\text{Cu}(\text{NO}_2)_5]$ have been described (Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204; Cuttica and Paciello, *Gazzetta*, 1922, **52**, i, 141). An amminated compound formerly described by Pélilot (*Compt. rend.*, 1861, **53**, 209) as hydrated diamminocupric nitrite has since been proved by Bassett and Durrant to be anhydrous tetramminocupric nitrite,* $[\text{Cu}, 4\text{NH}_3](\text{NO}_2)_2$, which at 97° dissociates into the anhydrous diammine $\text{Cu}(\text{NH}_3)_2(\text{NO}_2)_2$ (J., 1922, **121**, 2636).

Interaction between silver nitrite and diaquobisethylenediamminocupric iodide leads to *bisethylenediamminocupric nitrite*, an an-

* In Hoffmann's "Lexikon" and Gmelin-Kraut's "Handbuch der anorganischen Chemie," [VII], V, i, pp. 1569, 1123, 1576, 1578, references are given to the preparation by Pudschies of tetramminocupric nitrite, sulphite, and thiosulphate, but we have not been able to obtain the original publication (*Dissert.*, Strassburg, 1904).

hydrous, well-defined salt stable up to 120° and in boiling aqueous or alcoholic solutions.

Evidence was also gained of the existence of a similar complex cupric hyponitrite, although the compound was not isolated in a state of purity. A more decisive result was, however, obtained with cupric hypophosphite.

Bisethylenediamminocupric hypophosphite, $[\text{Cu}, 2 \text{ en}](\text{H}_2\text{PO}_2)_2$, is stable up to 115° and in aqueous or alcoholic solution. The reducing action of the hypophosphite ion on bivalent copper is far less noticeable than with cupric hypophosphite, which furnishes copper hydride.

Amminated Cupric Sulphites.—The normal salt, CuSO_3 , has not been isolated with certainty, and the causes of its instability are similar to those inducing the decomposition of cupric nitrite. Reduction of the cupric ion by the sulphite radical leads to the formation of cuprous compounds and the precipitation of sparingly soluble, red cupric cuprosulphite, $\text{Cu}(\text{CuSO}_3)_2 \cdot 2\text{H}_2\text{O}$.

The stability of cupric sulphite is enhanced by ammination, for the tetrammine, $[\text{Cu}, 4\text{NH}_3]\text{SO}_3 \cdot 2\text{H}_2\text{O}$, is recorded by Pudschies (*loc. cit.*).

We have now obtained two ethylenediamine derivatives of normal cupric sulphite: *Monoaquoethylenediamminocupric sulphite*, $[\text{Cu}, \text{en}, \text{H}_2\text{O}]\text{SO}_3$, by the action of aqueous ethylenediamine on cupric cuprosulphite, and *bisethylenediamminocupric sulphite*, $[\text{Cu}, 2 \text{ en}]\text{SO}_3$, by adding copper to a suspension of silver sulphite in ethylenediamine. The latter method is of general application in the preparation of amminated cupric salts.

The chemical properties of the foregoing complex cupric sulphites indicate clearly that the more fully co-ordinated compound, $[\text{Cu}, 2 \text{ en}]\text{SO}_3$, is much the more stable of the two.

Amminated Cupric Thiosulphates.—A reducing action of the cupric ion occurs in interactions between soluble cupric salts and alkali thiosulphates, so that normal cupric thiosulphate has not hitherto been isolated. Amminated derivatives have, however, been recorded. Pudschies (*loc. cit.*) cites the tetrammine, $[\text{Cu}, 4\text{NH}_3]\text{S}_2\text{O}_3$, and a more complex binuclear salt, $[\text{Cu}_2, 3 \text{ en}, 2\text{H}_2\text{O}](\text{S}_2\text{O}_3)_2$, is described by Benrath (*Z. anorg. Chem.*, 1917, **99**, 5).

Bisethylenediamminocupric thiosulphate, $[\text{Cu}, 2 \text{ en}]\text{S}_2\text{O}_3$, which is stable up to 130°, is prepared by double decomposition between barium thiosulphate and bisethylenediamminocupric sulphate.

Amminated Cupric Polythionates.—Cupric dithionate crystallising with 4 or 5 molecules of water has long been known (Heeren, *Pogg. Annalen*, 1826, **7**, 181; Grailich and Murmann, *Ber. Wien. Akad.*, 1857, **27**, 171); it decomposes readily to a basic salt,

$[\text{Cu}_3\text{Cu}(\text{OH})_2]\text{S}_2\text{O}_6$, of the atacamite type (compare the basic nitrite, p. 1260).

Two amminated derivatives of cupric dithionate are described: the tetrammine, $[\text{Cu}_4\text{NH}_3]\text{S}_2\text{O}_6$ (Heeren, *loc. cit.*; Schweitzer, *J. pr. Chem.*, 1856, **67**, 430; Horn, *Amer. Chem. J.*, 1908, **39**, 212), and the monoammine, obtained by the last-mentioned investigator from the tetrammine and liquid ammonia.

Bisethylenediamminocupric dithionate, $[\text{Cu}_2\text{en}]\text{S}_2\text{O}_6$, is a well-defined, sparingly soluble salt remaining undecomposed up to 280° . When trithionates and cupric salts interact in warm aqueous solution, copper sulphide is precipitated. Ammonia derivatives of cupric trithionate are not recorded, but stabilisation of this salt has now been obtained by the isolation of *bisethylenediamminocupric trithionate*, $[\text{Cu}_2\text{en}]\text{S}_3\text{O}_6$, stable up to 170° .

Cupric tetrathionate has been prepared by adding copper carbonate to Wackenroder's solution (Curtis and Hinkel, *J. pr. Chem.*, 1888, **37**, 148), but the only amminated derivative on record is the tetrapyridine compound $[\text{Cu}_4\text{Py}]\text{S}_4\text{O}_6$ (Calzolari, *Atti R. Accad. Lincei*, 1915, **24**, i, 921).

Bisethylenediamminocupric tetrathionate, $[\text{Cu}_2\text{en}]\text{S}_4\text{O}_6$, is a well-defined salt stable up to 160° .

The foregoing complex cupric polythionates which have the same general formula $[\text{Cu}_2\text{en}]\text{S}_x\text{O}_6$ exhibit a well-marked gradation of physical and chemical properties. As the sulphur accumulates in the molecule, the colour of the salt deepens, its solubility in water increases, and its decomposition temperature decreases.

Owing to the destructive action of ethylenediamine on alkali pentathionates from Wackenroder's solution, the complex cupric pentathionate of this series was not isolated. Other attempts made to complete the series of ethylenediamminocupric salts of sulphur oxy-acids were unsuccessful as regards hydrosulphurous acid, $\text{H}_2\text{S}_2\text{O}_4$, and formaldehydesulphoxylic acid, $\text{CH}(\text{OH})\text{HSO}_2$, but the corresponding salt of persulphuric acid was isolated.

Amminated Cupric Persulphates.—Cupric persulphate has not been isolated, but its tetrammino- and tetrapyridine-derivatives, $[\text{Cu}_4\text{base}]\text{S}_2\text{O}_8$, have been prepared (Barbieri and Calzolari, *Z. anorg. Chem.*, 1911, **71**, 347).

Bisethylenediamminocupric persulphate, $[\text{Cu}_2\text{en}]\text{S}_2\text{O}_8$, is a sparingly soluble salt comparable in its explosive properties with ethylenediamminocupric perchlorate (J., 1926, 2026).

Bisethylenediamminocupric selenocyanate, $[\text{Cu}_2\text{en}](\text{CNSe})_2$, furnishes a noteworthy example of the stabilising effect of ethylenediamine on a very decomposable cupric salt. Interaction of soluble selenocyanates and cupric salts leads to the precipitation of copper

selenide, both cupric and cuprous selenocyanates being unstable under these conditions. When, however, ethylenediamine is present, the separation of copper selenide is inhibited, and the complex salt, $\text{Cu}(\text{CNSe})_{2,2} \text{en}$, is obtained in stable, well-defined, anhydrous crystals.

Co-ordination Numbers of Bivalent Copper.

Of the eleven complex cupric salts described in this communication, ten contain two molecular proportions of ethylenediamine to one atomic proportion of copper, and of these ten salts, nine are anhydrous and include no other addenda than the diamine. Of the two anomalous salts, the sulphite $[\text{Cu}, \text{en}, \text{H}_2\text{O}]\text{SO}_3$ may be regarded as co-ordinatively unsaturated, whereas the dihydrated carbonate, $\text{CuCO}_3, 2 \text{en}, 2\text{H}_2\text{O}$, is of ambiguous character, with a co-ordination number for copper ranging from 4 to 6, according to the allocation of the two molecules of water between kation and anion.

In the other nine cases of anhydrous salts having the general formulæ $[\text{Cu}, 2 \text{en}]\text{X}'$ and $[\text{Cu}, 2 \text{en}]\text{X}''$ (X' and X'' being monobasic and dibasic anions), the experimental evidence points to a co-ordination value of 4 for bivalent copper as being the predominant type most conducive to molecular stability.

From the wide range of derivatives examined, it is obvious that the stability of this fourfold co-ordination is not appreciably influenced either by the chemical nature or by the valency of the anion. The recurrence of the co-ordination complex with two implicated ethylenediamine molecules suggests the influence of forces making for symmetrical orientation of the two chelate groups. The discovery by Mills and Gotts of optical activity among copper compounds having a co-ordination number of 4 (J., 1926, 3124) affords direct proof of tetrahedral arrangement of the four associating units round the central copper atom. It is accordingly highly probable that in the bisethylenediamminocupric salts described below, a tetrahedral arrangement of the two chelate diamine groups is also present.

Regarded from the electronic point of view, the co-ordination complex $[\text{Cu}, 2 \text{en}]''$ is still unsaturated, since the bivalent cupric ion with electronic structure 2,224,22445 (Main Smith, *J. Soc. Chem. Ind.*, 1924, 43, 323) shares eight additional electrons with the two ethylenediamines, thereby giving to the co-ordinated atom the electronic structure 2,224,22445,224, which differs from the arrangement 2,224,22446,224 for krypton, the next inert gas, in a shortage of one electron in the ninth sub-group. Any addendum supplying one additional electron would complete the inert-gas structure with a co-ordination number of 5.

As, however, many 6-co-ordinated cupric complexes are also known, it is evident either that an electronic structure with three electrons in excess of krypton is possible, or, alternatively, that certain of the six associating units are contributing only one electron each, instead of the two which are generally regarded as operative in a non-polar linking.

It seems evident from a general survey of co-ordinated copper compounds that the forces making for symmetrical arrangement (co-ordination numbers 4 and 6) prevail over forces tending to reproduce the electronic structure of an inert gas. The co-ordination number 4 offers, in the case of the cupric ion, the optimum condition as regards symmetrical arrangement of associating units, coupled with a very close approximation to the saturated electronic structure of krypton.

EXPERIMENTAL.

Bisquobisethylenediamminocupric Carbonate, $[\text{Cu}, 2 \text{ en}]\text{CO}_3 \cdot 2\text{H}_2\text{O}$.—A concentrated aqueous solution of hydrated bisethylenediamminocupric iodide, $[\text{Cu}, 2 \text{ en}, 2\text{H}_2\text{O}]\text{I}_2$, was triturated with a slight excess of freshly prepared silver carbonate. The purple filtrate was treated with alcohol-ether; the complex carbonate was then precipitated. Recrystallised from water after the addition of alcohol and ether, this salt separated as a very hygroscopic, purple, crystalline powder, m. p. 135° (decomp.), readily soluble in water or alcohol (Found in material dried over sulphuric acid: C, 21.2; H, 7.3; N, 19.8; Cu, 23.1. $\text{C}_5\text{H}_{20}\text{O}_5\text{N}_4\text{Cu}$ requires C, 21.45; H, 7.2; N, 20.0; Cu, 22.7%).

Aqueous or alcoholic solutions of this complex normal carbonate could be boiled without decomposition and were stable in the presence of caustic alkali, but were decomposed by dilute acids. Silver nitrate produced in them an immediate precipitation of silver carbonate even in the cold, thus indicating the ionised condition of the dissolved complex salt.

Bisethylenediamminocupric nitrite, $[\text{Cu}, 2 \text{ en}](\text{NO}_2)_2$, was prepared by triturating together bisquobisethylenediamminocupric iodide and freshly prepared silver nitrite (in slight excess); the filtrate from silver iodide was concentrated to a small bulk and left over sulphuric acid. The complex *nitrite* crystallised slowly from the syrupy solution in dark purple needles, which were purified by recrystallisation from water or alcohol, and also by reprecipitation from aqueous solution with ether and alcohol. After drying over sulphuric acid in a vacuum desiccator, the complex salt was anhydrous (Found: C, 17.9; H, 5.95; N, 29.9; Cu, 23.2; NO_2 , 33.3. $\text{C}_4\text{H}_{16}\text{O}_4\text{N}_6\text{Cu}$ requires C, 17.4; H, 5.85; N, 30.5; Cu, 23.05; NO_2 , 33.4%).

This complex nitrite, which melted with rapid decomposition at 128° , was extremely soluble in water, but less soluble in alcohol. In aqueous or alcoholic solution the salt was not decomposed even on boiling; caustic alkalis had no effect, but dilute acid caused immediate evolution of nitrous fumes. Silver nitrate produced a quantitative separation of silver nitrite in alcoholic solution, showing that the dissolved complex nitrite was ionised in this medium.

Attempted Preparation of an Ethylenediamminocupric Hyponitrite.—The replacement method (see p. 1266) employed in the case of the complex sulphite $[\text{Cu}, 2 \text{ en}][\text{SO}_3]$ was tried with silver hyponitrite and metallic copper in the presence of ethylenediamine. Silver was deposited, and the resulting dark purple solution of complex cupric salts was concentrated to the crystallising point; purplish-blue plates were then obtained which had the composition of a complex cupric hyponitrite, $[\text{Cu}, 3 \text{ en}][\text{N}_2\text{O}_2]$, mixed with the carbonate $[\text{Cu}, 2 \text{ en}][\text{CO}_3, 2\text{H}_2\text{O}]$, the latter being produced by absorption of carbon dioxide from the atmosphere. The impure salt dissolved readily in water, and on addition of silver nitrate the solution gave yellow silver hyponitrite.

Bisethylenediamminocupric Hypophosphite, $[\text{Cu}, 2 \text{ en}](\text{H}_2\text{PO}_2)_2$.—An aqueous solution of barium hypophosphite (5.3 g.) was added to one of copper sulphate (5.0 g.) containing ethylenediamine (2.4 g.), and the mixture shaken for some hours. After filtration from barium sulphate, the purplish-blue liquid was concentrated on the water-bath and left over concentrated sulphuric acid. The surface of the liquid soon became covered with a pale mauve, crystalline crust of hypophosphite, which was recrystallised from water and dried over sulphuric acid (Found: C, 15.7; H, 6.9; N, 17.9; P, 19.5; Cu, 20.5. $\text{C}_4\text{H}_{20}\text{O}_4\text{N}_4\text{P}_2\text{Cu}$ requires C, 15.3; H, 6.4; N, 17.85; P, 19.8; Cu, 20.3%).

Although this complex hypophosphite was hygroscopic, it remained unchanged when kept quite dry. On heating, the dry salt decomposed rapidly at 115 – 118° to a dark brown solid. It dissolved readily in alcohol; this solution was slowly decomposed in presence of sodium hydroxide, although the aqueous solution was unaffected. Hydrochloric and sulphuric acids caused decolorisation of the solution, and the latter acid gave a reddish precipitate of metallic copper. Silver nitrate solution gave a white precipitate in the cold, which darkened rapidly, with the separation of black metallic silver; in acid solution a silver mirror was obtained.

Bisethylenediamminocupric persulphate, $[\text{Cu}, 2 \text{ en}]\text{S}_2\text{O}_8$, was deposited in purplish-red, acicular crystals when aqueous potassium persulphate was added to an aqueous solution of copper sulphate

(1 mol.) containing ethylenediamine (2 mols.). The crystals were washed successively with cold water, alcohol, and dry ether and analysed immediately (Found : Cu, 16·8; S₂O₃, 51·0. C₄H₁₆O₈N₄S₂Cu requires Cu, 16·9; S₂O₃, 51·15%).

The complex persulphate was extremely unstable, and when left in air or in the desiccator it decomposed, leaving a blue residue; one preparation exploded when contained in a cooled specimen tube. The salt detonated on percussion and exploded on heating or on warming with concentrated sulphuric acid.

Although only very sparingly soluble in cold water, the persulphate dissolved more readily on warming; the purple solution, which changed to blue without appreciable evolution of gas, yielded with barium salts a copious precipitate of barium sulphate. Silver nitrate gave no reaction in the cold, but, on warming, oxygen was evolved and the purple solution changed to blue. Concentrated hydrochloric acid caused decomposition with evolution of chlorine.

Monoaquoethylenediamminocupric Sulphite, [Cu, en, H₂O]SO₃.—The dark red cupric cuprosulphite prepared by warming a 20% solution of cupric sulphate with concentrated aqueous potassium bisulphite was shaken with a cold aqueous solution of ethylenediamine; a deep purple liquid was then obtained with deposition of copper. On addition of a considerable volume of alcohol to the filtered solution, the complex cupric sulphite separated in pale reddish-mauve nodules. The product was purified by solution in water and reprecipitation with alcohol. After drying over sulphuric acid, the salt was monohydrated (Found : C, 11·1; H, 5·0; N, 13·3; SO₃, 35·6; Cu, 28·5. C₂H₁₀O₄N₂SCu requires C, 10·9; H, 4·5; N, 12·6; SO₃, 36·1; Cu, 28·7%).

The aqueous solution of the complex sulphite decomposed on warming to give a brown precipitate containing cuprous oxide; dilute sulphuric acid caused a separation of red metallic copper, whereas hydrochloric acid gave cuprous chloride, both reactions being accompanied by evolution of sulphur dioxide. On exposure to air this sulphite oxidised slowly; at 100° it blackened, and at higher temperatures its colour changed to brown.

Bisethylenediamminocupric Sulphite, [Cu, 2 en]SO₃.—Metallic copper (2·5 g.) was added with constant stirring to a mixture of freshly prepared silver sulphite (11·8 g.), ethylenediamine (4·8 g.), and 50 c.c. of cold water. After being shaken for an hour, the mixture was filtered from metallic silver and the deep purple filtrate was evaporated to the crystallising point over sulphuric acid. Prismatic crystals of the complex sulphite slowly separated and the surface of the liquid became covered with a pale mauve crust of the salt. Recrystallisation from cold water and desiccation

over sulphuric acid gave well-defined, mauve, opaque, tabular and pyramidal crystals with matt surfaces. This anhydrous sulphite decomposed without melting at 190—200° (Found: C, 18.4; H, 6.2; N, 20.9; S, 12.2; Cu, 24.2. $C_4H_{16}O_3N_4SCu$ requires C, 18.2; H, 6.1; N, 21.25; S, 12.15; Cu, 24.1%).

Although hygroscopic, the complex sulphite remained unchanged in a closed vessel; its aqueous solution was not visibly affected by boiling. In cold solutions of the salt, silver nitrate, and barium chloride produced, respectively, copious white precipitates of silver and barium sulphites. With sodium hydroxide the solution remained clear, but its colour changed from purple to blue; the colour was discharged by mineral acids.

Bisethylenediamminocupric Thiosulphate, $[Cu, 2 en]S_2O_3$.—An aqueous solution of cupric sulphate (5.0 g.) containing 2.4 g. of ethylenediamine was triturated with excess of barium thiosulphate (6.0 g.), and the mixture shaken for several hours. The purplish-blue filtrate was then concentrated and cooled; the blue plates of the complex cupric thiosulphate that separated were crystallised from water containing a few drops of ethylenediamine (Found: C, 16.0; H, 5.6; N, 18.75; S, 21.5; Cu, 21.2. $C_4H_{16}O_3N_4S_2Cu$ requires C, 16.2; H, 5.45; N, 18.9; S, 21.7; Cu, 21.5%).

The complex thiosulphate remained unchanged in air, but on heating it decomposed without melting at 150—155°. The stable purplish-blue solution in water became blue on addition of aqueous sodium hydroxide, whereas warm alcoholic soda precipitated cupric oxide. Silver nitrate gave a white precipitate, blackening rapidly even in the cold. Sulphuric and hydrochloric acids discharged the purplish-blue colour of the solution, in the former case with the formation of a brown precipitate.

Bisethylenediamminocupric Dithionate, $[Cu, 2 en]S_2O_6$.—When 4.8 g. of sodium dithionate, 5.0 g. of copper sulphate, and 2.4 g. of ethylenediamine were mixed together in aqueous solution, a purplish-red, crystalline precipitate separated which became anhydrous after drying over sulphuric acid (Found: C, 13.45; H, 4.9; N, 16.0; S, 18.2; Cu, 19.1. $C_4H_{16}O_6N_4S_2Cu$ requires C, 14.0; H, 4.7; N, 16.3; S, 18.65; Cu, 18.5%).

This complex cupric dithionate was quite stable in air at the ordinary temperature, and on heating it decomposed with blackening at 260°. It was only very sparingly soluble in cold water, but dissolved more readily on warming to a stable purple solution. Barium chloride and silver nitrate were without action on the hot or cold solution; with sodium hydroxide the colour was changed to blue, whereas with mineral acids it was discharged.

Bisethylenediamminocupric Trithionate, $[Cu, 2 en]S_3O_6$.—A cold

aqueous solution of sodium trithionate (7.1 g.) was added to a cold solution of cupric acetate (5.9 g.) containing ethylenediamine (3.6 g.). The purple solution was filtered and an excess of alcohol added; the complex *trithionate* then separated in purple, matted needles. After recrystallisation from luke-warm water and desiccation over sulphuric acid, the trithionate was anhydrous (Found: C, 12.7; H, 4.5; N, 15.1; S, 25.9; Cu, 17.1. $C_4H_{16}O_6N_4S_3Cu$ requires C, 12.8; H, 4.3; N, 14.9; S, 25.6; Cu, 16.9%).

This salt was quite stable in the air under normal conditions, but on heating it decomposed without melting at 170—175°. Silver nitrate gave, in the cold, a white precipitate, rapidly becoming yellow and finally black; this decomposition was greatly facilitated by warming. Barium chloride had no action in the cold, but on heating a white precipitate was formed. Sodium hydroxide caused the purple aqueous solution to become blue, whereas dilute acids discharged the intense colour with deposition of copper sulphide.

Bisethylenediamminocupric Tetrathionate, $[Cu,2 en]S_4O_6$.—An aqueous solution of 3.4 g. of cupric chloride, 2.4 g. of ethylenediamine, and 6.0 g. of sodium tetrathionate was cautiously concentrated and cooled; the large, deep purple, rhomboidal prisms that separated were crystallised from water. The original deposition of complex tetrathionate was preferably induced by the addition of alcohol to the original solution, thus obviating evaporation. When dried over calcium chloride, the salt was anhydrous (Found: C, 11.7; H, 4.1; N, 13.8; S, 31.5; Cu, 15.6. $C_4H_{16}O_6N_4S_4Cu$ requires C, 11.8; H, 3.95; N, 13.7; S, 31.4; Cu, 15.6%). The well-defined, prismatic crystals of this complex tetrathionate were permanent in air, but on heating at 160° they decomposed with blackening. The aqueous solution was stable even on boiling; silver nitrate gave a white precipitate which darkened rapidly; barium chloride had no effect, sodium hydroxide changed the colour from purple to blue, and mineral acids discharged it.

The foregoing complex salts of the oxy-acids of sulphur were all insoluble in alcohol and other organic media.

Attempts made to complete this series of polythionates by the preparation of an ethylenediamminocupric pentathionate were unsuccessful, owing to the destructive action of the diamine in removing sulphur from the alkali pentathionates obtained from Wackenroder's solution.

Bisethylenediamminocupric Selenocyanate, $[Cu,2 en](CNSe)_2$.—To an aqueous solution of 5.19 g. of cupric chloride and 3.6 g. of ethylenediamine were added 8.6 g. of potassium selenocyanate, also dissolved in water. The purple solution was concentrated to a small bulk and cooled; bluish-purple, prismatic crystals of the complex

selenocyanate then separated. By recrystallisation from water, large, compact crystals were obtained, which were dried over sulphuric acid (Found: C, 18.3; H, 4.2; N, 21.8; Se, 39.8; Cu, 16.6. $C_6H_{16}N_6Se_2Cu$ requires C, 18.3; H, 4.1; N, 21.3; Se, 40.2; Cu, 16.1%).

This complex cupric selenocyanate was stable in air at the ordinary temperature, but it darkened at 100° and melted at $159-160^\circ$ to a deep blue liquid. The salt was moderately easily soluble in water to a purple solution, which could be boiled without change; it was only slightly soluble in alcohol. With either aqueous or alcoholic solutions, silver nitrate gave a copious white precipitate even in the cold. Mineral acids caused the deposition of elemental selenium. Aqueous or alcoholic soda did not effect any change in the cold, but on warming the alcoholic solution a precipitation of cupric oxide occurred.

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