

XXI.—*Researches on Residual Affinity and Co-ordination. Part XXX. Complex Ethylene-thiocarbamido-salts of Univalent and Bivalent Metals.*

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THAT associating units containing unoxidised sulphur conduce to the stability of complex salts of univalent copper and gold was illustrated by the behaviour of dimethyldithioethylene towards cupric and auric chlorides when unstable additive products were formed which passed readily into stable complex cuprous and aurous derivatives (Morgan and Ledbury, J., 1922, **121**, 2833).

Thiocarbamide (symbolised by tu in the following discussion) exerts a similar action on cupric salts, the products being, however, complicated by the circumstance that the base contains three associating foci, namely, two amino-radicals and a thiocarbonyl group. Owing to this dual character of thiocarbamide, its interaction with cupric nitrate leads, not only to the mononuclear cuprous salt, $[\text{Cu}, 2\text{tu}]\text{NO}_3, \text{H}_2\text{O}$, but also to more complex polynuclear derivatives, $[\text{Cu}_2, 5\text{tu}](\text{NO}_3)_2, 1$ or $2\text{H}_2\text{O}$, $[\text{Cu}_3, 7\text{tu}](\text{NO}_3)_3$ and $[\text{Cu}_5, 11\text{tu}](\text{NO}_3)_5, 8\text{H}_2\text{O}$, in which substances the amino-groups of thiocarbamide probably serve as bridging units between the metallic atoms of the complex kations (Rathke, *Ber.*, 1884, **17**, 297; Rosen-

heim and Loewenstamm, *Z. anorg. Chem.*, 1903, **34**, 62; Kohlschütter, *Ber.*, 1903, **36**, 1151; *Annalen*, 1906, **349**, 232).

We have now found that such complications are minimised by employing ethylenethiocarbamide, $\begin{matrix} \text{CH}_2 \cdot \text{NH} \\ | \\ \text{CH}_2 \cdot \text{NH} \end{matrix} > \text{C} : \text{S}$ (I; symbolised as etu), a cyclic compound in which the co-ordinating properties of the amino-groups of thiocarbamide are inhibited by involving the two nitrogen atoms in a stable five-membered ring.

1. *Ethylenethiocarbamido-cuprous Salts*.—By operating with ethylenethiocarbamide and cupric nitrate in hot aqueous solutions reduction to the cuprous condition occurs with elimination of sulphur; the colourless solution on concentration then furnishes *tetrakisethylenethiocarbamido-cuprous nitrate*, $[\text{Cu}, 4\text{etu}]\text{NO}_3$, a remarkably stable salt neutral to litmus in aqueous solution. With a smaller proportion of ethylenethiocarbamide, a hydrated binuclear complex salt is formed, which loses three-fourths of its combined water at 110° , this change being reversed on exposing the partly dehydrated salt to the atmosphere: $[\text{Cu}_2, 5\text{etu}, \text{H}_2\text{O}](\text{NO}_3)_2, 3\text{H}_2\text{O} \rightleftharpoons [\text{Cu}_2, 5\text{etu}, \text{H}_2\text{O}](\text{NO}_3)_2$. The combining proportion of ethylenethiocarbamide to copper is affected by the chemical nature of the anion as shown by the compositions of the sulphate, acetate and halide salts.

When treated with aqueous alkalis, the foregoing cuprous salts give rise, not to cuprous oxide, but to a white, hydrous complex oxide which on drying has the composition $[\text{Cu}, \text{etu}]_2\text{O}$.

2. *Ethylenethiocarbamido-argentous Salts*.—Ethylenethiocarbamide combines with silver salts to form co-ordination compounds comparable with the preceding cuprous series. Two nitrates have been identified, *tetrakisethylenethiocarbamido-argentous nitrate*, $[\text{Ag}, 4\text{etu}]\text{NO}_3$, and a binuclear *dinitrate*, $[\text{Ag}_2, 3\text{etu}](\text{NO}_3)_2$. Silver chloride dissolves readily in aqueous ethylenethiocarbamide and the solution yields *trisethylenethiocarbamido-argentous chloride*, $[\text{Ag}, 3\text{etu}]\text{Cl}$. The insoluble complex *oxide*, $[\text{Ag}, \text{etu}]_2\text{O}$, is precipitated in a hydrous form by the action of alkalis on the preceding salts. It is noteworthy that these thiocarbamido-argentous salts are not photosensitive on exposure to ordinary daylight.

3. *Ethylenethiocarbamido-aurous Salts*.—With ethylenethiocarbamide, an aqueous solution of auric chloride yields at first an orange caseous precipitate which on boiling speedily dissolves with loss of colour; the concentrated solution yields *bisethylenethiocarbamido-aurous chloride*, $[\text{Au}, 2\text{etu}]\text{Cl}, \text{H}_2\text{O}$. Addition of nitric acid to the colourless solution gives rise to a complex *nitrate*, $[\text{Au}, 2\text{etu}]\text{NO}_3$, which differs from the thiocarbamido-derivative, $[\text{Au}, 2\text{tu}]\text{NO}_3, \text{H}_2\text{O}$, in being anhydrous (compare Reynolds, J., 1869, **22**, 1). The com-

plèx hydrated bromide, $[\text{Au}, 2\text{etu}]\text{Br}, \text{H}_2\text{O}$, is readily soluble, whereas the *iodide*, $[\text{Au}, \text{etu}]\text{I}$, dissolves only sparingly and the white, insoluble, amorphous *oxide*, $[\text{Au}, \text{etu}]_2\text{O}$, corresponds with the complex oxides of the copper and silver series (pp. 149, 151).

4. *Ethylenethiocarbamido Salts of Bivalent Metals*.—Attempts to combine zinc nitrate with ethylenethiocarbamide in aqueous or alcoholic solution were fruitless, although combination occurred with cadmium and mercury salts. The complex *cadmium nitrate*, $[\text{Cd}, 4\text{etu}](\text{NO}_3)_2$ is readily soluble in water to a neutral solution.

Trisethylenethiocarbamido-mercuric nitrate, $[\text{Hg}, 3\text{etu}](\text{NO}_3)_2$, which is neutral to litmus in aqueous solution, may be prepared by interaction of ethylenethiocarbamide with either mercurous or mercuric nitrate, its formation in the former case being accompanied by elimination of mercury. The sparingly soluble complex chloride, $3\text{HgCl}_2, 2\text{etu}$, had already been described by Hofmann (*Ber.*, 1873, 6, 598).

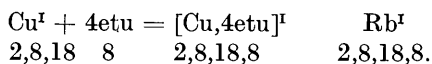
Lead salts do not lend themselves readily to combinations with ethylenethiocarbamide, but the complex dichloride, $\text{PbCl}_2, \text{etu}$, has been obtained as a sparingly soluble product.

Palladous chloride and the thio-base combine to form the orange *tetrakisethylenethiocarbamido-palladous chloride*, $[\text{Pd}, 4\text{etu}]\text{Cl}_2$, a slightly modified procedure leading to the dark brown complex *nitrate*, $[\text{Pd}, 4\text{etu}](\text{NO}_3)_2$. Both salts are very sparingly soluble in cold water.

Electronic Structure of Ethylenethiocarbamido Metallic Nitrates.

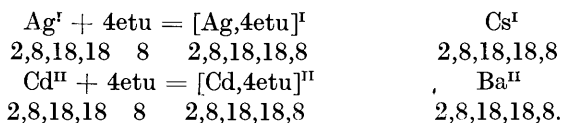
Owing to its cyclic structure, ethylenethiocarbamide probably functions as a single associating unit in the salts under discussion and accordingly each molecule of base contributes to the co-ordination complex two electrons derived from its sulphur atom.

In the compounds examined, the limiting type is reached by a fourfold co-ordination between metal and thio-base as shown by the following series of nitrates: $[\text{Cu}, 4\text{etu}]\text{NO}_3$, $[\text{Ag}, 4\text{etu}]\text{NO}_3$, $[\text{Cd}, 4\text{etu}](\text{NO}_3)_2$, $[\text{Pd}, 4\text{etu}](\text{NO}_3)_2$. The cuprous ion is 8 electrons short of the number required for the rubidium ion, but by becoming co-ordinated with 4 molecular proportions of cyclic thio-base it acquires these additional electrons.



Similar relationships may be traced in the complex nitrates derived from silver and cadmium ions, the silver and cadmium com-

plexes being electronically equivalent to caesium and barium ions, respectively.

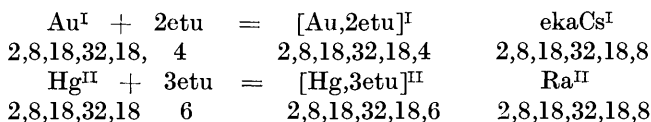


Experimental support for these analogies is afforded by the observation that these soluble complex nitrates behave like nitrates of the metals of the alkalis and alkaline earths in giving rise to neutral solutions. Moreover, a further similarity is discerned on determining the electrical conductivities of these aqueous solutions. The following table gives the molecular conductivities (in reciprocal ohms) of solutions containing one g.-mol. of complex nitrate in v litres of water at 25° :

v	32	64	128	256	512	1024
[Cu,4etu]NO ₃	87	92.5	96	98.3	103	121
[Ag,4etu]NO ₃	81.4	89.2	94.1	97.8	97.2	—
[Cd,4etu](NO ₃) ₂	187.2	203.5	220.4	231.3	237.6	238
[Au,2etu]NO ₃	96.7	104.4	108.2	110.4	109.7	111.2
[Hg,3etu](NO ₃) ₂	142.7	161.0	170.2	178.0	181	181.5

These values for electrical conductivity show that in aqueous solutions the co-ordination complexes [Metal,4etu]^{I or II} play the part of compound alkali radicals.

This electronic analogy between the ethylenethiocarbamido-complexes and the metallic ions of the alkalis and alkaline earths is not, however, fulfilled so completely in the cases of the complex aurous and mercuric nitrates, the electrical conductivities of which are inserted in the foregoing table for the purposes of comparison. The ethylenethiocarbamido-aurous complex is still 4 electrons short of the number required for the hypothetical eka-caesium and the mercuric complex is 2 electrons short of the number required for the radium ion as shown below :



Nevertheless, the two complex aurous and mercuric nitrates dissolve in water to neutral solutions which have high electrical conductivities.

The palladous ion is 10 electrons short of the number required for the caesium ion and in both complex salts (nitrate and chloride) the metal is associated with 4 molecular proportions of ethylene-

thiocarbamide, so that the complex is still 2 electrons short of the limiting number. The complex chloride and nitrate are, however, of very sparing solubility, this fact suggesting a considerable degree of association, which persists in the presence of water. But in spite of low solubility, the electrical conductivity of the nitrate has been determined with a dilution of 1 g.-mol. in 1024 litres and found to be 156.6 reciprocal ohms at 25°. This result indicates that the dissolved nitrate is an electrolyte having the structural formula $[\text{Pd},4\text{etu}](\text{NO}_3)_2$. Moreover, cold saturated solutions of the nitrate and chloride, although very dilute, give ionic reactions with "nitron" acetate and silver nitrate respectively.

EXPERIMENTAL.

Ethylenethiocarbamide, melting at 194°, was prepared according to Hofmann's method (*Ber.*, 1872, 5, 240).

1. *Ethylenethiocarbamido-cuprous Salts.*

Tetrakisethylenethiocarbamido-cuprous Nitrate, $[\text{Cu},4\text{etu}]\text{NO}_3$.—On mixing warm aqueous solutions of 5.0 g. of ethylenethiocarbamide and 2.5 g. of cupric nitrate, a green colour was developed which rapidly faded; and the colourless liquid became opaque owing to the separation of sulphur. The filtrate on concentration and cooling deposited long, colourless, prismatic crystals, which were purified by recrystallisation from warm water (Found: C, 27.0; H, 4.8; N, 23.3; S, 24.3; Cu, 11.9. $\text{C}_{12}\text{H}_{24}\text{O}_3\text{N}_9\text{S}_4\text{Cu}$ requires C, 27.0; H, 4.5; N, 23.6; S, 24.0; Cu, 11.9%). This complex nitrate, which melted to a colourless liquid at 140–141°, was readily soluble in water to neutral and stable solutions, but insoluble in the common organic media. An aqueous solution gave a brown, colloidal suspension with hydrogen sulphide or yellow ammonium sulphide, cuprous sulphide being precipitated on warming. Caustic soda and sodium carbonate in the cold produced flocculent precipitates changing to a white, granular oxide on boiling. Ammonium hydroxide caused the separation of a white solid in concentrated but not in dilute solutions of the complex nitrate; a blue colour was slowly developed in both cases. Hydrochloric acid gave an immediate precipitate, soluble on warming and crystallising on cooling to a felted mass of white needles. Dilute nitric acid slowly produced a white crystalline deposit. Disodium hydrogen phosphate had no action in the cold, but on warming a white precipitate was formed which redissolved on cooling. Both potassium ferrocyanide and ferricyanide gave amorphous deposits, the former, a white solid decomposed on boiling and the latter, a reddish-brown solid unaffected by warming. Sodium cyanide and potassium iodide

precipitated white solids, the former soluble in excess of reagent but not on boiling, whereas the latter dissolved on heating but was unaffected by excess of iodide. These chemical reactions and the insolubility in organic media are properties also characteristic of the following cuprous salts.

Monoaquopentaethylenethiocarbamido-dicuprous Nitrate Trihydrate, $[\text{Cu}_2, 5\text{etu}, \text{H}_2\text{O}](\text{NO}_3)_2, 3\text{H}_2\text{O}$.—On adding aqueous cupric nitrate (2.5 g.) to a warm solution of ethylenethiocarbamide (3.0 g.), a colourless liquid was obtained with deposition of sulphur. After evaporation and cooling, large, white, six-sided, prismatic crystals separated which were recrystallised and air-dried (Found: C, 21.7, 21.6; H, 4.8, 4.5; N, 20.2; S, 18.8; Cu, 15.1. $\text{C}_{15}\text{H}_{38}\text{O}_{10}\text{N}_{12}\text{S}_5\text{Cu}_2$ requires C, 21.6; H, 4.6; N, 20.2; S, 19.2; Cu, 15.25%).

This complex nitrate melted to a colourless liquid at 145–146°. Its freshly prepared aqueous solution was colourless and neutral to litmus, but soon oxidised when exposed to air. When this hydrated salt was left over sulphuric acid, it lost three molecules of its combined water, leaving a white residue of *monoaquopentaethylenethiocarbamido-dicuprous nitrate*, $[\text{Cu}_2, 5\text{etu}, \text{H}_2\text{O}](\text{NO}_3)_2$ (Found: C, 22.6; H, 4.3; N, 22.1; S, 19.8; Cu, 16.3. $\text{C}_{15}\text{H}_{32}\text{O}_7\text{N}_{12}\text{S}_5\text{Cu}_2$ requires C, 23.1; H, 4.1; N, 21.6; S, 20.6; Cu, 16.3%. Found: loss of water, 6.2. Calc. for $3\text{H}_2\text{O}$, 6.3%). This dehydrated salt was exceedingly hygroscopic and was also easily oxidised, becoming green on keeping.

Trisethylenethiocarbamido-cuprous Sulphate, $[\text{Cu}, 3\text{etu}]_2\text{SO}_4$.—An aqueous solution of cupric sulphate (2.5 g.) and ethylenethiocarbamide (5.0 g.) was heated until colourless; the sparingly soluble sulphate separated in almost quantitative yield on cooling, and was recrystallised from hot water containing ethylenethiocarbamide. Colourless, three-sided prisms separated which were washed with water and dried over sulphuric acid (Found: C, 25.9; H, 4.5; N, 20.5; S, 27.5; Cu, 15.2. $\text{C}_{18}\text{H}_{36}\text{O}_4\text{N}_{12}\text{S}_7\text{Cu}_2$ requires C, 25.8; H, 4.3; N, 20.1; S, 26.8; Cu, 15.2%). This complex sulphate was quite stable in air, but when heated it blackened at 240° and melted with decomposition at 251°. Barium chloride gave an immediate precipitate with aqueous solutions of the complex sulphate, showing that this salt was ionised in aqueous media.

Trisethylenethiocarbamido-cuprous Acetate, $[\text{Cu}, 3\text{etu}]\text{C}_2\text{H}_3\text{O}_2$, separated, when a warm decolorised solution of its generators was cooled, in colourless, elongated plates and was recrystallised from water containing ethylenethiocarbamide (Found: N, 19.5; S, 22.3; Cu, 14.9, 15.0. $\text{C}_{11}\text{H}_{21}\text{O}_2\text{N}_6\text{S}_3\text{Cu}$ requires N, 19.6; S, 22.4; Cu, 14.8%). This complex acetate was stable in air, but on heating it decomposed with blackening at 250–255°. It was fairly soluble

in warm water, the solution being neutral to litmus and stable on boiling.

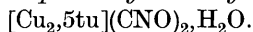
Bisethylenethiocarbamido-cuprous Chloride $[\text{Cu}_2\text{etu}]\text{Cl}$.—Freshly prepared cuprous chloride (1.0 g.) was dissolved in a hot aqueous solution of ethylenethiocarbamide (3.0 g.), and the filtrate evaporated to 70 c.c.; transparent, rhombic crystals were then deposited (Found: C, 23.5; H, 4.2; N, 18.3; S, 21.5; Cl, 11.3; Cu, 20.6. $\text{C}_6\text{H}_{12}\text{N}_4\text{ClS}_2\text{Cu}$ requires C, 23.7; H, 4.0; N, 18.5; S, 21.15; Cl, 11.7; Cu, 21.0%). The complex chloride melted to a colourless liquid at 166—167°. Although soluble in aqueous ethylenethiocarbamide, this salt decomposed in pure water; the crystals became opaque and a large part of the complex chloride remained undissolved, even on boiling.

The complex *bromide*, $[\text{Cu}_2\text{etu}]\text{Br}$, crystallised in small clumps of transparent, glistening rhombohedra (m. p. 162—163°), which were recrystallised from aqueous ethylenethiocarbamide (Found: C, 20.4; H, 3.9; N, 16.6; S, 17.85; Br, 22.8; Cu, 18.55. $\text{C}_6\text{H}_{12}\text{N}_4\text{BrS}_2\text{Cu}$ requires C, 20.7; H, 3.5; N, 16.5; S, 18.4; Br, 23.0; Cu, 18.3%).

The complex *iodide*, $[\text{Cu}_2\text{etu}]\text{I}$, after recrystallisation from aqueous ethylenethiocarbamide, was obtained as a white, crystalline powder, m. p. 160—161° (Found: C, 18.6; H, 3.4; N, 14.0; S, 15.8; I, 31.8; Cu, 15.75. $\text{C}_6\text{H}_{12}\text{N}_4\text{IS}_2\text{Cu}$ requires C, 18.2; H, 3.1; N, 14.2; S, 16.2; I, 32.15; Cu, 16.1%).

Ethylenethiocarbamido-cuprous Oxide, $[\text{Cu}_2\text{etu}]\text{O}$.—The flocculent white precipitate produced on adding excess of aqueous sodium hydroxide to a cold solution of tetrakisethylenethiocarbamido-cuprous nitrate was rendered granular by heating the turbid mixture to boiling. The segregated deposit was washed with hot water until free from alkali salts and dried over sulphuric acid (Found: C, 21.5, 21.2; H, 3.6, 3.5; N, 16.9; S, 18.2; Cu, 37.0. $\text{C}_6\text{H}_{12}\text{ON}_4\text{S}_2\text{Cu}_2$ requires C, 20.7; H, 3.5; N, 16.5; S, 18.5; Cu, 36.6%). This complex oxide, which darkened at 180° and decomposed without melting at 200°, was a white powder very slowly becoming tinged with blue on exposure to air. It dissolved in warm dilute hydrochloric and sulphuric acids to solutions which deposited crystalline complex cuprous salts on cooling. Dilute nitric acid and sodium cyanide both had a solvent action, but the oxide was insoluble in ammonia although slowly oxidised in contact with this reagent.

Pentathiocarbamido-dicuprous Cyanate Hydrate,



—When excess of a concentrated aqueous solution of potassium cyanate was added to aqueous cupric sulphate saturated with sulphur dioxide, a white crystalline double salt was deposited approximat-

ing in composition to the formula $\text{Cu}_2\text{K}(\text{CNO})_3$. This compound when triturated with a cold concentrated solution of thiocarbamide, dissolved to a solution from which colourless tufts of acicular crystals separated (Found : C, 13.7; H, 3.5; N, 27.4; S, 26.85; Cu, 20.8. $\text{C}_7\text{H}_{22}\text{O}_3\text{N}_{12}\text{S}_5\text{Cu}_2$ requires C, 13.8; H, 3.6; N, 27.6; S, 26.3; Cu, 20.85%). The complex cyanate, which decomposed at 135° , was soluble in water but insoluble in organic solvents. Its aqueous solution slowly decomposed in the cold and very rapidly on warming, giving cuprous sulphide. Cold aqueous caustic soda solution produced an immediate black precipitate.

2. Ethylenethiocarbamido-argentous Salts.

Tetrakisethylenethiocarbamido-argentous Nitrate, $[\text{Ag}_4\text{tetu}]\text{NO}_3$.—A warm aqueous solution of 1.7 g. of silver nitrate and 4.0 g. of ethylenethiocarbamide deposited, on cooling, radiating clusters of colourless acicular prisms, which were recrystallised from a small amount of water (Found : C, 24.6, 24.75; H, 4.6, 5.1; N, 22.2; S, 22.1; Ag, 18.6. $\text{C}_{12}\text{H}_{24}\text{O}_3\text{N}_9\text{S}_4\text{Ag}$ requires C, 24.9; H, 4.2; N, 21.8; S, 22.2; Ag, 18.7%). This complex nitrate, which melted to a colourless liquid at 96 – 97° , was readily soluble in water and slightly soluble in alcohol, but insoluble in other organic media. With potassium iodide, the nitrate gave a white precipitate, decomposed on boiling and leaving a residue of silver iodide. These chemical reactions are also characteristic of the series of silver salts, except that the following compounds are insoluble in alcohol and other organic media.

Trisethylenethiocarbamido-diargentous Nitrate, $[\text{Ag}_2\text{3etu}](\text{NO}_3)_2$.—When an aqueous solution of silver nitrate (1.7 g.) was added to a solution of ethylenethiocarbamide (2.0 g.) in 400 c.c. of water, an amorphous, white precipitate was deposited which readily redissolved on heating. On slow cooling, the liquid became filled with a mass of felted, colourless, silky needles which, being only sparingly soluble, required a large volume of hot water for recrystallisation (Found : C, 17.15, 17.2; H, 3.35, 3.1; N, 17.8; S, 15.2; Ag, 33.1. $\text{C}_9\text{H}_{18}\text{O}_6\text{N}_8\text{S}_3\text{Ag}_2$ requires C, 16.7; H, 2.8; N, 17.3; S, 14.9; Ag, 33.4%). The salt blackened at 200° and decomposed with explosive violence at 224° .

Trisethylenethiocarbamido-diargentous persulphate, $[\text{Ag}_2\text{3etu}]\text{S}_2\text{O}_8$, was obtained as a colourless crystalline precipitate when a cold concentrated solution of potassium persulphate was added to a cold aqueous solution of tetrakisethylenethiocarbamido-argentous nitrate (Found : C, 14.6; H, 2.8; N, 11.9; S, 23.0; Ag, 29.9. $\text{C}_9\text{H}_{18}\text{O}_8\text{N}_6\text{S}_5\text{Ag}_2$ requires C, 15.1; H, 2.55; N, 11.8; S, 22.4; Ag, 30.2%). The complex persulphate was quite stable in air; it

darkened at 160° and melted with decomposition at 205°. The sparingly soluble complex salt was slowly decomposed by warm water. It liberated iodine from acidified potassium iodide.

Trisethylenethiocarbamido-argentous Chloride, [Ag,3etu]Cl.—A freshly prepared sample of silver chloride (1.4 g.) was dissolved in an aqueous solution of ethylenethiocarbamide (3.0 g.). The hot solution, when filtered, evaporated and cooled, deposited a mass of small white needles. This readily soluble complex chloride was recrystallised from hot water (Found: C, 24.4; H, 4.2; N, 19.0; S, 21.8; Cl, 7.7; Ag, 23.5. $C_9H_{18}N_6ClS_3Ag$ requires C, 24.0; H, 4.0; N, 18.7; S, 21.4; Cl, 7.9; Ag, 24.0%). This complex silver salt was very stable and quite unaffected by light. It melted to a colourless liquid at 167–168°.

Bisethylenethiocarbamido-argentous bromide, [Ag,2etu]Br, was prepared in a similar manner to the foregoing chloride, but it was found necessary to add ethylenethiocarbamide in order to obtain complete solution during recrystallisation (Found: C, 18.7; H, 3.5; N, 14.0; S, 16.0; Br, 20.3; Ag, 27.4. $C_6H_{12}N_4BrS_2Ag$ requires C, 18.4; H, 3.1; N, 14.3; S, 16.4; Br, 20.4; Ag, 27.5%). The complex bromide, obtained in short, prismatic crystals, melted at 152° and was only sparingly soluble in water even on boiling. It resembled the corresponding cuprous bromide complex in the loss of its crystalline appearance in these circumstances (p. 149).

Ethylenethiocarbamido-argentous Iodide, [Ag,etu]I.—Owing to the insolubility of silver iodide in aqueous ethylenethiocarbamide, a modified method had to be used for the isolation of a complex silver iodide derivative. Potassium iodide was added in slight excess to an aqueous solution of tetraethylenethiocarbamido-argentous nitrate. The microcrystalline precipitate was filtered off, washed with a little cold water, and dried over sulphuric acid (Found: N, 7.3; S, 8.8; I, 38.8; Ag, 33.7. $C_3H_6N_2ISAg$ requires N, 8.3; S, 9.5; I, 37.7; Ag, 32.0%). The poor analytical results obtained for this complex iodide were due to dissociation during washing. This sparingly soluble salt melted at 162° to a yellow liquid.

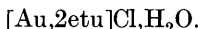
Ethylenethiocarbamido-argentous Oxide, [Ag,etu]₂O.—Pure aqueous sodium hydroxide was added in slight excess to a boiling solution of tetrakisethylenethiocarbamido-argentous nitrate. The white granular precipitate was washed free of alkali salts with hot water and dried in a vacuum over sulphuric acid (Found: C, 16.7; H, 2.9; N, 12.6; S, 14.5; Ag, 50.1. $C_6H_{12}ON_4S_2Ag_2$ requires C, 16.5; H, 2.8; N, 12.85; S, 14.7; Ag, 49.5%). This complex oxide slowly decomposed on keeping, its surface becoming brown and finally black; it darkened at 120° and decomposed at 170°. It dissolved readily in warm dilute hydrochloric and sulphuric acids, the solutions

giving crystalline salts on cooling. Dilute nitric acid and sodium cyanide also exercised a solvent action in hot solutions.

3. *Ethylenethiocarbamido-aurous Salts.*

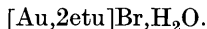
Bisethylenethiocarbamido-aurous Nitrate, $[\text{Au}, 2\text{etu}]\text{NO}_3$.—An aqueous solution of auric chloride, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (2.0 g.) was added to one of ethylenethiocarbamide (2.0 g.). The orange precipitate at first formed, immediately redissolved on warming and the solution became colourless. Dilute nitric acid was then added in slight excess and white feathery crystals separated on cooling (Found: C, 15.85; H, 2.75; N, 14.9; S, 14.2; Au, 42.3. $\text{C}_6\text{H}_{12}\text{O}_3\text{N}_5\text{S}_2\text{Au}$ requires C, 15.5; H, 2.6; N, 15.1; S, 13.8; Au, 42.55%). The complex nitrate melted with decomposition at 173° . It was soluble in water and in warm alcohol, giving stable and neutral solutions in both solvents, but insoluble in ether, acetone, benzene, and chloroform. Caustic soda, sodium carbonate, and ammonium hydroxide all gave white precipitates with a solution of this complex nitrate. Sodium cyanide and potassium iodide produced white solids, the former soluble in excess of reagent, whereas the latter decomposed on boiling. Hydrogen sulphide formed a yellow, colloidal suspension of aurous sulphide, precipitated by heat. Potassium ferrocyanide gave a white salt which changed on heating to yellow, green, and finally blue. The complex nitrate was not reduced to colloidal gold by formaldehyde.

Bisdiethylenethiocarbamido-aurous Chloride Hydrate,



—On warming an aqueous solution containing equal parts of auric chloride, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, and ethylenethiocarbamide, the liquid became decolorised and turbid. The concentrated filtrate deposited pearly plates, which were recrystallised from water and dried over sulphuric acid (Found: C, 16.1; H, 3.5; N, 12.7; S, 14.55; Cl, 7.6; Au, 42.9, 43.0. $\text{C}_6\text{H}_{14}\text{ON}_4\text{ClS}_2\text{Au}$ requires C, 15.8; H, 3.1; N, 12.3; S, 14.1; Cl, 7.8; Au, 43.3%). This complex chloride became yellow at 210° and melted with decomposition at 242° . When the salt was maintained at 110° , water was eliminated, leaving a residue of anhydrous *bisethylenethiocarbamido-aurous chloride*, $[\text{Au}, 2\text{etu}]\text{Cl}$ (Found: loss, 4.1. Calc. for $1\text{H}_2\text{O}$, 4.0%). The chloride was easily soluble in water and alcohol but insoluble in other organic media.

Bisethylenethiocarbamido-aurous Bromide Hydrate,



—The white precipitate produced by adding excess of sodium hydroxide to an aqueous solution of the preceding complex chloride was dissolved in warm, dilute hydrobromic acid containing ethylenethiocarbamide. The cooled solution yielded colourless needles of the

complex bromide, which were recrystallised from warm water and dried over calcium chloride (Found : Au, 39·75. $C_6H_{14}ON_4BrS_2Au$ requires Au, 39·5%). This complex bromide, which was readily soluble in alcohol, melted in its water of crystallisation at 100° , then resolidified and melted again to a colourless liquid at 191° . When left over sulphuric acid, it became dehydrated into *bisethylenethiocarbamido-aurous bromide*, $[Au,2etu]Br$, which reverted to the monohydrate on exposure to the atmosphere (Found : C, 15·3; H, 2·9; N, 11·9; Br, 16·3; Au, 40·5. $C_6H_{12}N_4BrS_2Au$ requires C, 15·0; H, 2·5; N, 11·6; Br, 16·6; Au, 41·0%. Found : loss on drying, 3·3. Required for $1H_2O$, 3·6 %).

Ethylenethiocarbamido-aurous iodide, $[Au,etu]I$, separated as a sparingly soluble, white powder, melting with decomposition at 225° , on addition of potassium iodide to an aqueous solution of the complex chloride (Found : C, 8·7; H, 1·7; N, 6·8; I, 30·1; Au, 46·0. $C_3H_6N_2ISAu$ requires C, 8·45; H, 1·4; N, 6·6; I, 29·8; Au, 46·4%).

Ethylenethiocarbamido-aurous Oxide, $[Au,etu]_2O$.—Pure caustic soda added in slight excess to an aqueous solution of aquobisethylenethiocarbamido-aurous chloride produced a white, flocculent precipitate, which was granulated by boiling and washed thoroughly with hot water until free from alkali salts (Found : C, 11·45; H, 2·1; N, 9·3; S, 10·5; Au, 64·8. $C_6H_{12}ON_4S_2Au_2$ requires C, 11·7; H, 2·0; N, 9·1; S, 10·4; Au, 64·2%). This complex aurous oxide blackened at 200° and became blue on exposure. It differed from the corresponding cuprous and silver oxides in being decomposed by dilute mineral acids. Although unaffected by dilute alkali, it was readily soluble in warm sodium cyanide solution.

Bisthiocarbamido-aurous Nitrate Hydrate, $[Au,2tu]NO_3 \cdot H_2O$.—Dilute nitric acid added to a solution of auric chloride decolorised by thiocarbamide produced an amorphous, white precipitate; this dissolved in warm water and separated again in an amorphous condition, but gradually redissolved and was replaced by lustrous, colourless crystals, which were air-dried (Found : C, 5·4; H, 2·5; N, 16·1; S, 15·4; Au, 45·8. $C_2H_{10}O_4N_5S_2Au$ requires C, 5·6; H, 2·3; N, 16·3; S, 14·9; Au, 45·9%). This complex nitrate, although stable in air, was slowly decomposed by light; it decomposed at 155° . It was readily soluble in alcohol but not in other organic media. The aqueous solution decomposed slightly on boiling. Caustic soda gave a yellow precipitate in the cold but, on warming, this rapidly darkened. When desiccated over sulphuric acid, this complex nitrate lost water, leaving an opaque residue of *bisthiocarbamido-aurous nitrate*, $[Au,2tu]NO_3$ (Found : C, 5·75; H, 2·1; Au, 48·0. $C_2H_8O_3N_5S_2Au$ requires C, 5·8; H, 2·0; Au, 47·9%. Found : loss, 4·5. Calc. for $1H_2O$, 4·2%).

4. *Ethylenethiocarbamido Salts of Bivalent Metals.*

Tetrakisethylenethiocarbamido-cadmium nitrate, $[\text{Cd},4\text{etu}](\text{NO}_3)_2$, separated in large, tabular crystals on concentrating an aqueous solution of cadmium nitrate (3.0 g.) and ethylenethiocarbamide (4.0 g.) and was recrystallised from water until colourless (Found : C, 22.9; H, 4.1; N, 21.5; S, 19.8; Cd, 17.2. $\text{C}_{12}\text{H}_{24}\text{O}_6\text{N}_{10}\text{S}_4\text{Cd}$ requires C, 22.3; H, 3.75; N, 21.7; S, 19.9; Cd, 17.4%). The complex nitrate melted at 178° and was quite stable in air. It was insoluble in organic media and its aqueous solution gave gelatinous precipitates with caustic soda and sodium carbonate, and cadmium sulphide with hydrogen and ammonium sulphides.

Bisethylenethiocarbamido-cadmium chloride, $[\text{Cd},2\text{etu}]\text{Cl}_2$, crystallised from a large volume of water in sparingly soluble, colourless, prismatic needles (Found : C, 18.8; H, 3.55; N, 15.0; S, 16.4; Cl, 17.9; Cd, 28.6. $\text{C}_6\text{H}_{12}\text{N}_4\text{Cl}_2\text{S}_2\text{Cd}$ requires C, 18.6; H, 3.1; N, 14.5; S, 16.5; Cl, 18.3; Cd, 29.0%). This complex chloride, which melted to a yellow liquid at 220° , was neutral to litmus in aqueous solution.

The complex *bromide*, $[\text{Cd},2\text{etu}]\text{Br}_2$, crystallised in flat, colourless plates (Found : C, 15.1; H, 2.5; N, 11.5; S, 13.2; Br, 33.6; Cd, 23.75. $\text{C}_6\text{H}_{12}\text{N}_4\text{Br}_2\text{S}_2\text{Cd}$ requires C, 15.1; H, 2.5; N, 11.8; S, 13.5; Br, 33.5; Cd, 23.55%). This salt, which melted to a yellow liquid at 208° , was more soluble in water than the corresponding chloride.

The complex *iodide*, $[\text{Cd},2\text{etu}]\text{I}_2$, crystallised from aqueous solution in white opaque needles (Found : C, 13.0; H, 2.2; N, 10.0; S, 11.5; I, 44.2; Cd, 19.5. $\text{C}_6\text{H}_{12}\text{N}_4\text{I}_2\text{S}_2\text{Cd}$ requires C, 12.6; H, 2.1; N, 9.8; S, 11.2; I, 44.5; Cd, 19.7%). This salt, the most soluble of the three halides, melted to a colourless liquid at 165° .

Ethylenethiocarbamido-plumbous chloride, $[\text{Pb},\text{etu}]\text{Cl}_2$, a sparingly soluble compound, crystallised in colourless plates when a hot solution of lead chloride in aqueous ethylenethiocarbamide was cooled. It melted to a yellow liquid at 183° (Found : C, 9.6; H, 1.75; N, 7.45; S, 8.7; Cl, 18.5; Pb, 54.6. $\text{C}_3\text{H}_6\text{N}_2\text{Cl}_2\text{SPb}$ requires C, 9.5; H, 1.6; N, 7.4; S, 8.4; Cl, 18.7; Pb, 54.5%).

Trisethylenethiocarbamido-mercuric nitrate, $[\text{Hg},3\text{etu}](\text{NO}_3)_2$, separated in colourless rhombic plates on concentrating an aqueous solution containing two parts of mercuric nitrate and three of ethylenethiocarbamide; it decomposed at 196° (Found : N, 17.55; S, 14.9; Hg, 32.0. $\text{C}_9\text{H}_{18}\text{O}_6\text{N}_8\text{S}_3\text{Hg}$ requires N, 17.8; S, 15.25; Hg, 31.8%). Aqueous caustic soda produced a flocculent white precipitate, but the nitrate was unaffected by dilute mineral acids.

Tetrakisethylenethiocarbamido-palladous Chloride, $[\text{Pd},4\text{etu}]\text{Cl}_2$.— On cooling a boiling aqueous solution of ethylenethiocarbamide to which a third of its weight of palladium chloride had been added,

the complex chloride separated in lustrous orange spangles, which were recrystallised from a large volume of hot water (Found: C, 24.8; H, 4.3; N, 19.75; S, 22.2; Cl, 11.9; Pd, 18.6. $C_{12}H_{24}N_8Cl_2S_4Pd$ requires C, 24.6; H, 4.1; N, 19.1; S, 21.9; Cl, 12.1; Pd, 18.2%). This complex chloride blackened at 210° and melted at 270° . It was insoluble in organic media, but in aqueous solution, caustic and carbonated alkalis gave yellow, amorphous precipitates; potassium iodide developed a deep red coloration, and palladium sulphide was precipitated in warm solutions by hydrogen or ammonium sulphide. A cold saturated solution of the chloride containing less than 0.01% of dissolved substance gave slowly an appreciable precipitate with silver nitrate. In warm concentrated solutions precipitation was rapid and copious.

Tetrakisethylenethiocarbamido-palladous Nitrate, $[Pd,4etu](NO_3)_2$.—Aqueous palladium chloride (1.7 g.) was added to ethylenethiocarbamide (2.0 g.) dissolved in dilute sodium hydroxide solution and the resulting brown precipitate was dissolved in 500 c.c. of water containing 15 c.c. of 2*N*-nitric acid and 4 g. of ethylenethiocarbamide. The complex nitrate separated in almost black nodules on cooling and was recrystallised from a large volume of hot water (Found: N, 22.0; Pd, 16.7. $C_{12}H_{24}O_6N_{10}S_4Pd$ requires N, 21.9; Pd, 16.7%). The nitrate melted with decomposition at 235° ; it was only sparingly soluble in alcohol and insoluble in other organic solvents. With aqueous "nitron" acetate a cold saturated solution of the complex nitrate containing 0.012% of dissolved substance slowly gave a crystalline precipitate of "nitron" nitrate, precipitation being immediate and copious in hot, concentrated solutions.

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