193. *The Chelation of Diamines with Cupric Salts.*

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Cupric chloride reacts with ethylenediamine to give three substances, to which the formulæ Cu $\mathrm{enCl_2}$, Cu $\mathrm{en_2Cl_2}$, and Cu $\mathrm{en_3Cl_2}$ have been given (see, *e.g.*, Dubsky and Dostál, *Pub. Fac. Sci. Univ. Masaryk*, 1932, No. 160, 3). Cupric sulphate behaves similarly (Grossmann and Schück, *Z. anorg. Chem.*, 1906, **50**, 16). The salts of the third type are relatively unstable, readily changing into those of the second type by the loss of a molecule of diamine. With a view to study the stereochemistry of copper, we re-examined the action of cupric chloride with ethylenediamine and extended the work to the case of *iso*butylenediamine (ib). The point of chief interest which arose was that the supposed Cu $\mathrm{enCl_2}$ is in reality a dimeric substance, *bisethylenediaminocupric cuprichloride*, $[\mathrm{Cu\,en_2}]\mathrm{CuCl_4}$, and that the iso*butylenediamino*-analogue also has this structure. They are greenish-blue, like hydrated cupric chloride, contrasting with the purple Cu $\mathrm{en_2Cl_2}$ and Cu $\mathrm{ib_2Cl_2}$; in aqueous solution their ions are in equilibrium with those of Cu $\mathrm{en_2Cl_2}$ (or of Cu $\mathrm{ib_2Cl_2}$) and of cupric chloride, as can be inferred from the fact that the cuprichlorides separate satisfactorily from saturated aqueous solutions only when an excess of cupric chloride is added.

It has frequently been suggested that the saturated solutions of simple copper salts contain anions such as $\mathrm{CuCl_4}''$. In particular, Kohlschütter (*Ber.*, 1904, **37**, 1161) demonstrated experimentally that this anion was discharged at the anode during the electrolysis of solutions containing cupric chloride, and he also postulated the presence of the kation $\mathrm{Cu(H_2O)_4}^{\cdot\cdot}$. Our observations are in agreement with this suggestion in so far as the formal analogy between the structures $[\mathrm{Cu\,en_2}]\mathrm{CuCl_4}$ and $[\mathrm{Cu(H_2O)_4}]\mathrm{CuCl_4}$ may be regarded as relevant. This consideration led us to examine the case of copper sulphate and we found here also that the substance formulated by Grossmann and Schück (*loc. cit.*) as Cu $\mathrm{enSO_4,3H_2O}$ was really the dimeric *cuprisulphate hexahydrate*, $[\mathrm{Cu\,en_2}][\mathrm{Cu(SO_4)_2,6H_2O}]$. Since the kation is the same as that in the cuprichloride, it is presumably anhydrous, and since the copper of the anion is electronically saturated, the six water molecules must be associated with the sulphate radicals. If, therefore, copper sulphate pentahydrate can be regarded as a cuprisulphate, it must have the formula $[\mathrm{Cu(H_2O)_4}][\mathrm{Cu(SO_4)_2,6H_2O}]$, in which again six water molecules are associated with the sulphate radicals. The analogy is remarkable when taken in conjunction with that of the chlorides. On the contrary, Beevers and Lipson, as the result of an *X*-ray study (*Proc. Roy. Soc.*, 1934, *A*, **146**, 570), have deduced that in $\mathrm{CuSO_4,5H_2O}$ each copper atom is surrounded by four water molecules, the fifth being united to two other water molecules and to two sulphate oxygen atoms.

The dimeric character of the foregoing co-ordinated salts was proved by the following reactions (shown for the compounds of en only, but carried out also with those of ib):

$$\begin{tikzcd}
\text{(1)}\ {[\mathrm{Cu\,en_2}]\mathrm{CuCl_4}} \arrow[r, "\mathrm{K_2PtCl_4}"] & {[\mathrm{Cu\,en_2}]\mathrm{PtCl_4} + \mathrm{K_2CuCl_4}} \arrow[dr, "{[\mathrm{Pt\,am_4}]\mathrm{Cl_2}}"] & \\
& & {[\mathrm{Cu\,en_2}]\mathrm{Cl_2} + [\mathrm{Pt\,am_4}]\mathrm{PtCl_4}} \\
\text{(2)}\ {[\mathrm{Cu\,en_2}]\mathrm{Cl_2}} \arrow[uu, "\mathrm{CuCl_2}"'] \arrow[r, "\mathrm{K_2PtCl_4}"] & {[\mathrm{Cu\,en_2}]\mathrm{PtCl_4} + 2\mathrm{KCl}} &
\end{tikzcd}$$

Thus the two compounds which Dubsky and Dostál formulated as Cu $\mathrm{enCl_2}$ and Cu $\mathrm{en_2Cl_2}$ give, on treatment with potassium chloroplatinite, the same plato-salt, half the copper being eliminated in the case of the first substance.

With dilute hydrochloric acid, even in the cold, $[\mathrm{Cu\,en_2}]\mathrm{CuCl_4}$ gives the yellow salt $[\mathrm{en\,H_2}]\mathrm{CuCl_4}$, described by Grossmann (*Z. anorg. Chem.*, 1906, **50**, 1); this reaction was reversed by aqueous sodium hydroxide. It was not found possible to isolate an intermediate stage in which the chelate loops are opened but not detached from copper, as was effected in the case of the platinum analogue (Drew and Tress, J., **1933**, **1335**). Copper is bound much less firmly to the chelating diamines than is platinum (cobalt is intermediate); we were unable to isolate geometric isomerides of Cu $\mathrm{ib_2Cl_2}$ or to resolve it as the *α-bromocamphor-π-sulphonate.*

EXPERIMENTAL.

Bisethylenediaminocupric cuprichloride, $\mathrm{[Cu\,en_2]CuCl_4}$, was prepared from an aqueous solution of hydrated cupric chloride (5·3 g.) and ethylenediamine (1·9 g.). It formed light greenish-blue needles, m. p. 233° (Found : C, 12·15; H, 4·2; N, 14·05. $\mathrm{C_4H_{16}N_4Cl_4Cu_2}$ requires C, 12·3; H, 4·1; N, 14·4%); it dissolved readily in water but not in organic solvents. If twice the amount of ethylenediamine was used, bisethylenediaminocupric chloride was formed; it was extracted with cold ethyl alcohol and then crystallised from this solvent several times, forming deep purple needles of the monohydrate, m. p. 218° (Found : N, 20·7; $\mathrm{H_2O}$, 6·55. Calc. for $\mathrm{C_4H_{16}N_4Cl_2Cu,H_2O}$: N, 20·55; $\mathrm{H_2O}$, 6·6%).

The corresponding chloroplatinite, $\mathrm{[Cu\,en_2]PtCl_4}$, was prepared from either of the above salts and aqueous potassium chloroplatinite. It formed lilac-pink crystals nearly insoluble in water (Found : C, 9·35; H, 3·3; N, 10·7. Calc. for $\mathrm{C_4H_{16}N_4Cl_4CuPt}$: C, 9·2; H, 3·1; N, 10·75%). Grünberg (*Z. anorg. Chem.*, 1926, **157**, 173) described this salt as a violet-red substance obtained on heating the salt $\mathrm{[Cu\,en_3]PtCl_4}$ or allowing it to stand.

$\mathrm{[en\,H_2]CuCl_4}$, prepared by adding dilute hydrochloric acid (2 or 4 equivs.) to aqueous $\mathrm{[Cu\,en_2]CuCl_4}$, formed golden-yellow leaflets, m. p. 272° (Found : C, 9·0; H, 3·9; N, 10·9; Cl, 52·0; Cu, 24·0. Calc. : C, 9·0; H, 3·75; N, 10·5; Cl, 53·1; Cu, 23·8%). The same compound was produced from $\mathrm{[Cu\,en_2]Cl_2}$ and hydrochloric acid.

*Bis*iso*butylenediaminocupric cuprichloride*, $\mathrm{[Cu\,ib_2]CuCl_4}$, from cupric chloride and *iso*butylenediamine *or* from $\mathrm{[Cu\,ib_2]Cl_2}$ and aqueous cupric chloride, formed light blue or bluish-green plates, m. p. 232° (decomp.), soluble in water or hot alcohol (Found : C, 21·3, 21·4; H, 5·6, 5·9; N, 12·3; Cu, 28·4. $\mathrm{C_8H_{24}N_4Cl_4Cu_2}$ requires C, 21·55; H, 5·4; N, 12·6; Cu, 28·6%). The corresponding *chloride*, obtained as for the ethylenediamino-analogue, formed dark-purple crystals, very soluble in water and soluble in cold alcohol; the air-dried substance melted at 245° (frothing) and appeared to be a hemihydrate (Found : C, 29·5; H, 8·25; $\mathrm{H_2O}$, 2·7, 2·9. $\mathrm{C_8H_{24}N_4Cl_2Cu,\frac{1}{2}H_2O}$ requires C, 30·0; H, 7·8; $\mathrm{H_2O}$, 2·8%), but a *dihydrate* was also obtained (Found : N, 16·1, 16·3; Cu, 18·3. $\mathrm{C_8H_{24}N_4Cl_2Cu,2H_2O}$ requires N, 16·15, Cu, 18·3%). The *chloroplatinite* formed lilac crystals, m. p. about 228° (decomp.), insoluble in water (Found : C, 16·7; H, 4·5; N, 10·0. $\mathrm{C_8H_{24}N_4Cl_4CuPt}$ requires C, 16·65; H, 4·2; N, 9·7%). The chloropalladite was unstable, decomposing in contact with the aqueous reaction solution into a soluble copper salt and iso*butylenediaminopalladous chloride*, which formed dark yellow, domed prisms, recrystallisable from water (Found : Pd, 40·6. $\mathrm{C_4H_{12}N_2Cl_2Pd}$ requires Pd, 40·2%).

*Bis*iso*butylenediaminocupric α-bromocamphor-π-sulphonate* was obtained from the chloride and ammonium α-bromocamphor-π-sulphonate in aqueous solution, as mauve reactangular plates, m. p. 237°, readily crystallised from water (Found : Cu, 7·3. $\mathrm{C_{28}H_{52}O_8N_4Br_2S_2Cu}$ requires Cu, 7·4%).

Bisethylenediaminocupric cuprisulphate hexahydrate formed light blue crystals, which were drained on porous tile and air-dried (Found : Cu, 23·6; $\mathrm{H_2O}$, 19·55. $\mathrm{C_4H_{16}N_4O_8S_2Cu_2,6H_2O}$ requires Cu, 23·2; $\mathrm{H_2O}$, 19·75%). With potassium chloroplatinite it gave $\mathrm{[Cu\,en_2]PtCl_4}$, half the copper being set free as copper sulphate.

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