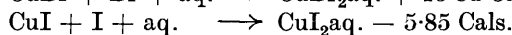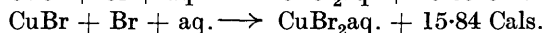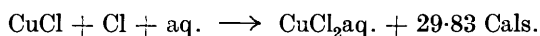CCLXXI.—*Researches on Residual Affinity and Co-ordination. Part XXVIII. Thermal Measurements on Derivatives of Cupric Iodide.*

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and WILLIAM FINNEMORE HARRISON.

IT is well known that cupric iodide is extremely unstable and attempts to prepare it in aqueous solution usually result in the formation of cuprous iodide and free iodine.

On the other hand, cupric bromide and cupric chloride are comparatively stable and the affinity between the cuprous halide and free halogen in solution is represented relatively by the heats of reaction given by Thomsen ("Thermochemische Untersuchungen," iii, p. 319) in which the reaction between cuprous iodide and iodine is decidedly endothermic :

$$CuCl + Cl + aq. \longrightarrow CuCl_2aq. + 29 \cdot 83 \text{ Cals.}$$
$$CuBr + Br + aq. \longrightarrow CuBr_2aq. + 15 \cdot 84 \text{ Cals.}$$
$$CuI + I + aq. \longrightarrow CuI_2aq. - 5 \cdot 85 \text{ Cals.}$$

It is, therefore, of interest to compare these values with the heats

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of chelation of ethanolbisethylenediamminocupric iodide which is also in aqueous solution.

$$CuI + I + 2en \text{ aq.} + C_2H_6O = [Cu,2en,C_2H_6O]I_2\text{aq.} + 22\cdot12 \text{ Cals.}$$
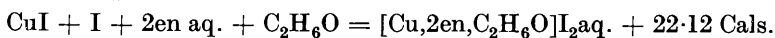
The formation of the co-ordination compound of cupric iodide from its generators, cuprous iodide, free iodine, alcohol, and aqueous ethylenediamine, proceeds with a positive heat evolution ($+ 22\cdot12$ Cals.) which is intermediate between that required for the formation of the simple cupric chloride ($+ 29\cdot83$ Cals.) and cupric bromide ($+ 15\cdot84$ Cals.) from the corresponding halogens and cuprous halides respectively.

The formation of the monoalcoholate is accompanied by practically the same quantity of heat as that observed in the formation of the corresponding hydrates in which the elements of alcohol are replaced by those of water.

The close agreement in the heats of formation of the monoalcoholate ($+ 55\cdot28$ Cals.), monohydrate ($+ 53\cdot78$ Cals.) and of the dihydrate ($+ 55\cdot55$ Cals.) is noteworthy and in the case of the hydrated salts is in accordance with the fact that the dihydrate can be readily transformed into the monohydrate by gentle desiccation.

EXPERIMENTAL.

The preparation described below was carried out before the isolation of the hydrated forms of bisethylenediamminocupric iodide recorded in the preceding paper.

Ethanolbisethylenediamminocupric Iodide, $[Cu,2en,C_2H_6O]I_2$.—On passing air through a suspension of freshly precipitated cuprous iodide in water at 60° containing the calculated amount of ethylenediamine, an intense bluish-violet solution was produced, the iodide dissolving while a brown precipitate containing cuprous hydroxide and copper was deposited. Addition of iodine facilitated the solution of the cuprous iodide. After the greater part of the substance had dissolved, the filtered solution was concentrated to a small volume, cooled in ice and salt, and treated with alcohol; dark bluish-purple, glistening plates then separated. This product, recrystallised by the addition of alcohol to its saturated aqueous solution, was dried in a vacuum desiccator (Found : C, 14·5, 14·5; H, 5·2, 5·1; N, 12·0; Cu, 13·25; I, 52·8; $C_2H_8N_2$, 25·2. $C_6H_{22}ON_4I_2Cu$ requires C, 14·9; H, 4·55; N, 11·6; Cu, 13·15; I, 52·5; $C_2H_8N_2$, 24·8%).

The monoalcoholate, although stable in air, has a faint but appreciable odour of iodoform due to a slight interaction of the iodine and alcohol present in its molecule. On heating, the crystals darkened at 100° and melted with decomposition to a deep blue

liquid at 235°. Extremely soluble in water, the compound dissolved less freely in methyl or ethyl alcohol; it was only slightly soluble in ether and insoluble in benzene, acetone, or chloroform. The aqueous solution was unaffected by sodium hydroxide or potassium iodide, whereas with silver nitrate it gave a copious precipitate of silver iodide.
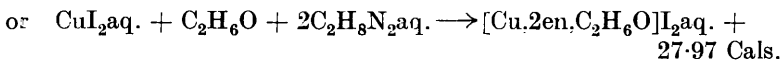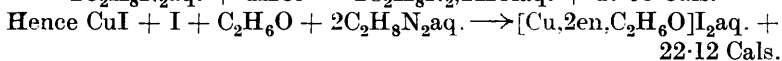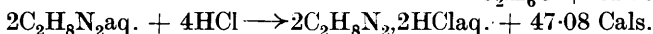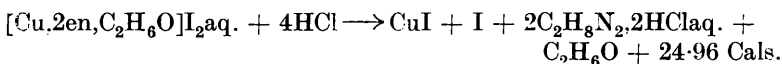
Thermal Measurements.

A thin-walled glass beaker was used for the calorimeter, since the aqueous solution attacked both nickel and silver. The dry, finely divided compounds could not be added directly to the hydrochloric acid solution, since the powder tended to conglomerate into lumps which were not entirely decomposed. Consequently the compound was first dissolved in water and the solution then acted upon by the acid.

Ethanolbisethylenediamminocupric Iodide. $[Cu,2en,C_2H_6O]I_2$.—The heat of dissociation of this compound was determined by adding 200 c.c. of N-hydrochloric acid to 3 g. of the compound dissolved in 200 c.c. of water and observing the temperature change, the additive compound being decomposed with formation of cuprous iodide and free iodine. The heat of dissociation found was $+ 24.96$ Cals., whilst the heat of solution of the compound in water (1 : 70) was $- 12.41$ Cals. Thomsen (*op. cit.*, p. 319) gives the following data :

$$[Cu_2,I_2] = + 32.52 \text{ Cals. and } [Cu,I_2,aq.] = + 10.41 \text{ Cals.}$$
Hence $\qquad CuI + I + aq. \longrightarrow CuI_2aq. - 5.85 \text{ Cals.}$

The heat of neutralisation of ethylenediamine in aqueous solution by two molecules of hydrochloric acid is $+ 23.54$ Cals. (Colson and Darzens, *Compt. rend.*, 1894, **118**, 250). The heat of solution of anhydrous ethylenediamine (1 : 65) is $+ 7.45$ Cals. and the heat of solution of ethylenediamine monohydrate (1 : 65) is $+ 4.68$ Cals. (Berthelot, *Ann. Chim.*, 1900, **20**, 163).

$$[Cu.2en,C_2H_6O]I_2aq. + 4HCl \longrightarrow CuI + I + 2C_2H_8N_2,2HClaq. + C_2H_6O + 24.96 \text{ Cals.}$$

$$2C_2H_8N_2aq. + 4HCl \longrightarrow 2C_2H_8N_2,2HClaq. + 47.08 \text{ Cals.}$$

Hence $CuI + I + C_2H_6O + 2C_2H_8N_2aq. \longrightarrow [Cu,2en,C_2H_6O]I_2aq. + 22.12 \text{ Cals.}$

or $\quad CuI_2aq. + C_2H_6O + 2C_2H_8N_2aq. \longrightarrow [Cu.2en,C_2H_6O]I_2aq. + 27.97 \text{ Cals.}$

Correcting for the heats of solution of ethylenediamine and the additive compound in water, a value of $+ 55.28$ Cals. is obtained for the heat of reaction of cupric iodide and two molecules of ethylenediamine.

Monoaquobisethylenediamminocupric Iodide, [Cu,2en,H$_2$O]I$_2$.—By adopting the foregoing method, the heat of solution in water (1 : 100) was found to be − 9·55 Cals. and the heat of dissociation by 0·5 *N*-hydrochloric acid was + 23·60 Cals. This gives a heat of reaction of + 53·78 Cals.

Diaquobisethylenediamminocupric Iodide, [Cu,2en,2H$_2$O]I$_2$.—The heat of solution in water (1 : 100) was − 11·82 Cals., whilst the heat of dissociation by 0·5 *N*-hydrochloric acid was + 24·10 Cals., which gives a value of + 55·55 Cals. for the heat of reaction of ethylenediamine with cupric iodide in forming the above compound.