394. *The So-called Diaquobisethylenediaminocupric Ion. A Re-investigation of its Simple Salts and Alleged Optical Isomerism.*

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THE co-ordination valency of cupric ion is generally four but occasionally six. In the latter category stands the diaquobisethylenediaminocupric ion, $[\mathrm{Cu\ en_2(H_2O)_2}]^{++}$, salts of which were first prepared by Werner and his co-workers (*Z. anorg. Chem.*, 1899, **21**, 201). In 1927, Wahl (*Soc. Sci. Fenn. Comm. Phys.-Math.*, **4**, 14) claimed to have prepared a lævorotatory iodide and thus to have established the existence of an octahedral symmetry within the molecular ion; it might therefore appear that the constitution of the ion had been finally settled, but for reasons which have been explained elsewhere (Johnson, *Trans. Faraday Soc.*, 1932, **28**, 845), we consider it important to confirm all cases of alleged optical isomerism, and consequently a reinvestigation was undertaken.

Our results can be summarised as follows. All attempts at resolution were unsuccessful, and the analyses show there are no grounds for presuming that the ion is present in the crystalline salts. Whether it is formed in aqueous solution cannot be ascertained; its existence was previously inferred from incorrect or misleading analytical data and from the work of Wahl, which we have been unable to verify. The present research is confined to six simple salts, *viz.*, the chloride, bromide, iodide, nitrate, sulphate, and tartrate. Previous investigators have conferred the general formula $[\mathrm{Cu\ en_2(H_2O)_2}]^{++}$ uniformly upon the first five (the tartrate was not analysed), but it is important to note that except in the case of the iodide no direct determination of water had been made. Our analyses prove the water content of the salts to be exceedingly variable. The nitrate, $[\mathrm{Cu\ en_2}](\mathrm{NO_3})_2$, is anhydrous; the chloride and bromide are monohydrates, the iodide contains 1 or $2\mathrm{H_2O}$, the sulphate 2 or $4\mathrm{H_2O}$, depending on the method of preparation, and the tartrate $2\frac{1}{2}$—$3\mathrm{H_2O}$.

In every case the water is quickly and completely lost over phosphoric oxide in a vacuum, whilst the crystalline sulphates and the iodide dihydrate effloresce in air.

A possible interpretation of these facts is that the constitution of the ion in the crystals is $[Cu\ en_2]^{++}$ and the co-ordination valency four, not six. Morgan and Burstall (J., 1927, 1259) apparently reached this conclusion with regard to ten other salts but did not question the results of earlier investigations. If the ion does not contain water, optical isomerism cannot arise.

The ratio en : Cu = 2 : 1 in the complex ion is well established, and is implied in the general method of preparation of the salts. Acids immediately break up the complex; even cold acetic acid destroys the purple colour. Grossmann and Schück (*Z. anorg. Chem.*, 1906, **50**, 1) state that ethylenediamine in copper compounds may be accurately determined by titration with sulphuric acid, methyl-orange or litmus being used as indicator. Our experience has been much less satisfactory: several indicators were tried but none gave sharp end-points, and results with the two specified differed by several units %, the former yielding consistently higher values. Apart from helping to distinguish between mono-, di-, and tri-ethylenediamine cupric salts, the titration method is valueless.

EXPERIMENTAL.

Sulphate.—Werner and his co-workers (*loc. cit.*) prepared this salt by addition of the requisite amount of ethylenediamine hydrate to an aqueous solution of copper sulphate, and precipitated it with alcohol. Their analytical data for carbon and nitrogen suggest the constitution $[Cu\ en_2,2H_2O]SO_4$, *but the value for sulphate,* 34·95%, *is that pertaining to the anhydrous substance although quoted as supporting the above formula.*

The contradiction is easily reconciled with the nature of the compound, for it is efflorescent and loses practically all its water in the course of a few days. When ethyl alcohol is cautiously added to an aqueous solution, bluish-purple crystals are precipitated (Found: H_2O, 22·3; Cu, 17·8; SO_4, 27·0. $[Cu\ en_2]SO_4,4\frac{1}{2}H_2O$ requires H_2O, 22·5; Cu, 17·6; SO_4, 26·6%), whereas a large excess produces a pale blue powder (Found: H_2O, 10·0; Cu, 20·6; SO_4, 30·9. Calc. for $[Cu\ en_2]SO_4,2H_2O$: H_2O, 11·4; Cu, 20·2; SO_4, 30·4%) which can also be obtained by washing the crystals with absolute alcohol. The latter seem to contain $4\frac{1}{2}H_2O$, but this is difficult to verify. They may also be prepared by slow crystallisation from water, although the high solubility makes it impossible to grow large crystals. Like the dihydrate, they effloresce in air, gradually losing all water (Found: $H_2O < 0·5$; Cu, 22·6; SO_4, 34·5. $[Cu\ en_2]SO_4$ requires Cu, 22·7; SO_4, 34·4%).

Chloride.—Crystallisation from water, or precipitation from aqueous solution by methyl or ethyl alcohol at temperatures between 15° and 0°, produces an identical product, the *monohydrate.* It is very soluble in water, stable in air, but quickly loses $1H_2O$ in a vacuum over phosphoric oxide (Found: H_2O, 6·2; Cu, 23·3; Cl, 25·9. $[Cu\ en_2]Cl_2,H_2O$ requires H_2O, 6·6; Cu, 23·3; Cl, 26·0%).

Nitrate.—Grossmann and Schück (*loc. cit.*) prepared the nitrate and bromide. Both were reported to be dihydrates although water was not determined. Examination of this salt convinced us that the recorded analytical data were erroneous, for the nitrate was *anhydrous,* no matter how prepared, whether crystallised from water or precipitated by alcohol from aqueous solution. Large monoclinic crystals can be grown, which remain lustrous in a vacuum over phosphoric oxide and suffer no loss of weight {Found: Cu, 20·7; NO_3, 40·2. $[Cu\ en_2](NO_3)_2$ requires Cu, 20·7; NO_3, 40·3%}.

Bromide.—Being less soluble than the chloride, this is easily obtained in large monoclinic crystals; like the chloride, these are the *monohydrate* (Found: H_2O, 5·0; Cu, 17·6; Br, 44·0. $[Cu\ en_2]Br_2,H_2O$ requires H_2O, 5·0; Cu, 17·6; Br, 44·2%).

Iodide.—Wahl's paper (*loc. cit.*) contained no analytical data; these were reserved for future publication, but we cannot trace such a record. By Morgan and Burstall's procedure (J., 1926, 2018), magnificent purple crystals (triclinic) were prepared; although the analyses confirm the formula $[Cu\ en_2]I_2,2H_2O$ (Found: H_2O, 8·0; Cu, 13·3; I, 52·7. Calc.: H_2O, 7·6; Cu, 13·4; I, 53·6%) our experience differs from that of these authors in certain respects; for instance, they say that only $1H_2O$ is lost on desiccation in a vacuum, and infer that the second is tightly bound, whereas we put a different interpretation on this result. The freshly prepared crystals are almost certainly the dihydrate (actually our analytical data indicate slightly more water), *but in air they rapidly effloresce, lose their lustre, and form the monohydrate*

(Found: H_2O, 3·7; Cu, 14·0; I, 55·4. Calc. for [Cu en_2]I_2,H_2O: H_2O, 3·95; Cu, 14·0; I, 55·7%). Indeed, so loosely is this water held that the mere act of gently crushing the crystals is sufficient to remove it. The process can be followed by making a rapid series of volumetric determinations for copper. The normal form of the iodide is therefore the monohydrate analogous to the chloride and bromide, and readily dehydrated by phosphoric oxide in a vacuum. We think it likely that Morgan and Burstall found only $1H_2O$ in the iodide on desiccation because the other had already disappeared. The iodide is somewhat unstable in air. After a few weeks, analysis reveals a high copper content, and when the salt is placed in water, cuprous iodide remains undissolved. A sample prepared from the sulphate and barium iodide and crystallised from hot water showed this property in marked degree. A large crystal of the dihydrate left in air lost $\frac{1}{2}H_2O$ within 5 days, and another $\frac{1}{2}H_2O$ after 3 weeks. As the monohydrate, it continued slowly to lose weight owing to superficial decomposition.

Morgan and co-workers (J., 1926, 2018, 2027) discovered another interesting property of the iodide which appears to be unique amongst these compounds. When it is precipitated by methyl or ethyl alcohol from aqueous solution, the crystals contain alcohol, having the composition [Cu en_2,ROH]I_2. We have confirmed this result qualitatively, but the ethyl alcoholate was found to be disolvated (Found: H_2O, 1·5; Cu, 12·2; I, 48·5. [Cu en_2]I_2,2EtOH requires Cu, 12·0; I, 48·0%). The presence of nearly 4% of water in the methyl alcoholate makes it difficult to decide its composition. It is probably a mixture of dialcoholate and monoalcoholate–monohydrate (Found: H_2O, 3·9; Cu, 12·8; I, 50·2. [Cu en_2]I_2,2MeOH requires Cu, 12·7; I, 50·6%. [Cu en_2]I_2,MeOH,H_2O requires H_2O, 3·7; Cu, 13·0; I, 52·1%). The compounds are crystalline, and keep indefinitely in stoppered bottles. No alcohol is lost during desiccation in a vacuum.

These *alcoholates* are important because Wahl, in his alleged isolation of an optically active iodide, precipitated the salt from solution by means of alcohol; therefore the material could not have had the constitution [Cu en_2,$2H_2O$]I_2 which he arbitrarily assigned to it. Further, even if two water molecules are attached to the complex ion in aqueous solution, it is difficult to believe that racemisation would not occur when they are replaced by alcohol. If, by chance, his iodide contained some dihydrate it could hardly have escaped racemisation by efflorescence.

Tartrate.—Wahl prepared but did not analyse the *tartrate*. His method of preparation from barium tartrate and [Cu en_2]SO_4 is unsatisfactory, for the product is invariably contaminated with the latter. A better method is to add a slight excess of ethylenediamine hydrate to copper tartrate suspended in water; the solid quickly dissolves, giving a deep purple solution from which the compound is conveniently precipitated by methyl alcohol. Alternatively, the solution can be evaporated almost to dryness on a water-bath, and the solid which separates pressed upon a porous tile and further purified (Found: H_2O, 13·2; Cu, 16·6; tartrate, 39·4. [Cu en_2]$C_4H_4O_6$,$2·75H_2O$ requires H_2O, 13·0; Cu, 16·7; tartrate, 38·9%). The salt is excessively soluble in water, and the concentrated solution very viscous; consequently we have been unable to grow crystals. The water content varies from one sample to another (12·5—13·5%), but in every case a corresponding variation in the copper analysis was recorded. The hygroscopic nature of the compound is doubtless responsible for these fluctuations. The *anhydrous* salt was also prepared (Found: Cu, 19·2; tartrate, 45·1. [Cu en_2]$C_4H_4O_6$ requires Cu, 19·2; tartrate, 44·6%).

Attempts at Resolution.—Two methods were repeatedly tried, *viz.*, fractional crystallisation of the tartrate from hot water, and fractional extraction with aqueous alcohol, the latter being particularly recommended by Wahl; he seems to imply the use of ethyl rather than methyl alcohol, thereby ignoring the fact that the tartrate invariably forms an oil with aqueous ethyl alcohol. Care was taken to follow his directions as closely as possible, but without success. For instance, 10 g. of the tartrate were extracted four times with aqueous alcohol (75%) and the extracts precipitated by further addition of alcohol; 1% solutions of these, the initial substance, and the final residue (about 0·5 g.) were examined individually in a polarimeter ($l = 1$ dcm.). The solutions passed practically no light of wave-length longer than 4600 Å., so a carbon arc had to be employed, and the liquids served as their own light filters. The arc is by no means an ideal illuminant for polarimetric work, and deep violet light is fatiguing to the eyes; nevertheless, fairly concordant results were obtained. All the solutions were dextrorotatory, *ca.* 0·3°, and the rotations remained unchanged for several days. This significantly small rotation is larger than the majority of those registered by Wahl. A solution of ammonium tartrate containing the same concentration of tartrate was examined with a light filter of [Cu en_2]SO_4 and gave an almost identical rotation. Therefore there can be no reasonable doubt that the rotation of bisethylenediaminocupric tartrate is due solely to the tartrate ion.

The solid extracts were analysed for water and copper and found to have undergone no change in composition.

Electrode-potential Measurements.—Attempts were made to form an estimate of the stability of the molecular ion by measuring the potentials of copper electrodes dipping into aqueous solutions of the salts. The potentials were unsteady even when all obvious precautions were taken, but the important fact was established that appreciable dissociation of the complex occurred in every case. Such dissociation must inevitably result in rapid racemisation whatever may be the constitution of the ion; yet Wahl observed no change in optical activity during 16 hours.

Absorption Spectra.—Morgan and Burstall (*loc. cit.*) remarked the slight differences in colour between various crystalline salts ranging from purple or violet to mauve. On dehydration, the colour becomes distinctly more blue. Aqueous solutions, however, are indistinguishable, having a rich purple-violet hue.

Absorption spectra in the visible region of all six salts have been measured, and found to agree within about 2%, the limit of accuracy of measurement. Thus, additional confirmation is provided of the analytical data. A 10 cm. length of a 0·1% solution of anhydrous sulphate, $[\mathrm{Cu\ en_2}]\mathrm{SO_4}$, and equivalent concentrations of the other salts were examined in a Hilger–Nutting spectrophotometer. The absorption of the sulphate in the ultra-violet was also determined quantitatively with a Hilger sector photometer and medium quartz spectrograph. A hydrogen discharge tube supplied continuous ultra-violet radiation. Solutions containing 0·10, 0·98, and 10·35 g. of anhydrous sulphate in 1000 c.c. were required, in 4 cm. tubes, for various parts of the ultra-violet spectrum. All determinations were made at about 16°. Molecular absorption coefficients, α_M, are presented below; $\alpha_M = (\log_{10} I_0/I)/lc$, l being the length (cm.) of the absorption tube, and c the concentration (mols./l.).

λ, Å.	α_M.	λ, Å.	α_M.	λ, Å.	α_M.	λ, Å.	α_M.	λ, Å.	α_M.
7000	11·0	5800	54·3	5200	54·0	4175	1·4	3075	22
6700	18·2	5600	60·1	5000	39·4	4060	0·4	3010	36
6500	22·9	5500	61·0	4800	24·6	3340	0·3	2940	74
6300	29·9	5450	61·0	4600	13·4	3210	1·4	2815	280
6000	45·6	5400	60·1	4300	2·8	3125	14	2740	690

The main features comprise a broad absorption band in the visible spectrum with a flat maximum at or about 5475 Å.; and a region of almost perfect transparency between 4000 and 3400 Å., followed by increasingly strong continuous absorption below 3000 Å. The substance is not photosensitive and should prove a valuable light-filter.

An interesting experiment was performed with the methyl and ethyl alcoholates of the iodide. First, by choosing suitable concentrations, it was found that their absorption spectra in aqueous solution exactly reproduced the curve obtained for the other salts. This suggests, but does not prove, that the absorbing unit is the same in all cases, and that the alcohol is not attached to the complex ion in solution. Assuming the molecular absorption coefficients were also unaffected by the presence of alcohol, calculation was made of the molecular weights of the alcoholates. For the ethyl alcoholate the result was 521 (Calc. for dialcoholate: 529·5), and for the methyl alcoholate it was 496 (Calc. for monoalcoholate–monohydrate: 487·5. Calc. for dialcoholate: 501·5), in reasonable agreement with the analytical data.

CONCLUSION.

A summary of the main results was given in the introductory paragraphs. Clearly the existence of the ion $[\mathrm{Cu\ en_2(H_2O)_2}]^{++}$ is extremely doubtful. This being so, discussion of its optical activity becomes superfluous. Even if formed in aqueous solution, it is too unstable to permit of resolution. Had correct analytical data been presented by the original investigators, and had they examined the obvious physical properties of the crystalline salts, optical isomerism would not have been sought for amongst these compounds.

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