

LXXXV.—*Potassium Cupricarbonates.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

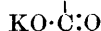
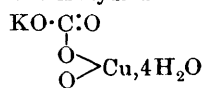
If potassium formed cupricarbonates analogous to all those cupri-compounds which have been isolated, or suggested as existing, in other cases, eight different compounds of copper carbonate with potassium carbonate would exist: these eight compounds have all been isolated, as well as one additional compound. Two are dehydration products of others; one is a gelatinous substance; the other six are crystalline: all have well-marked physical, and, in some cases, chemical properties, differentiating them from each other. In only two cases is the evidence as to composition at all doubtful.

The potassio-cupric carbonate with $4\text{H}_2\text{O}$ (No. 1 below) was first obtained by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75); it forms hard, fairly large, light blue crystals, resembling many other double copper salts. As it is decomposed by water, it cannot exist as such in the liquid yielding it, and this, it has been suggested (*Trans.*, 1910, **97**, 1838, 1842), contains the β -cupricarbonate, No. 3, the copper in it being present as part of the electronegative ion, although in a very labile condition, for it reacts practically at once with a ferrocyanide. The addition of excess of alkali carbonate to the solution ultimately produces a compound which reacts only very slowly with ferrocyanide, the proportions of carbonate necessary for this change indicating the formation of the compound No. 5 (*loc. cit.*, p. 1830), which would be an α -cupri-compound (that

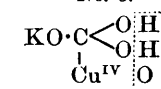
Potassio-cupric Carbonate. β -Cupricarbonate.

No. 1. Tetrahydrate.

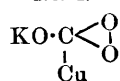
No. 2. Anhydrous.

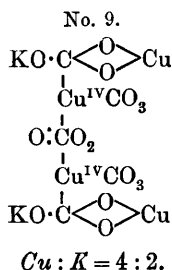
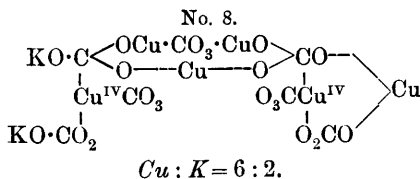
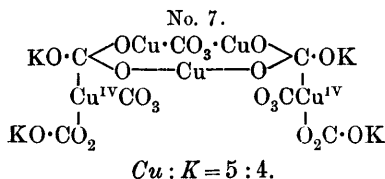
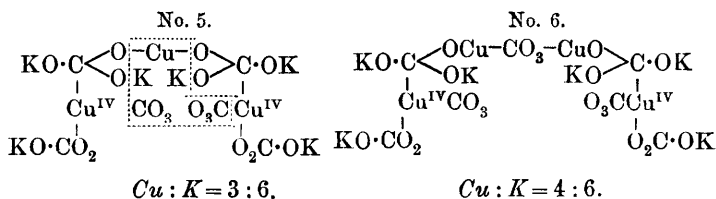
 $\text{Cu} : \text{K} = 1 : 2.$

No. 3.

 $\text{Cu} : \text{K} = 1 : 2.$

No. 4.

 $\text{Cu} : \text{K} = 1 : 2.$

α-Cupricarbonates.

is, containing the group $(\text{Cu}^{\text{IV}}\text{CO}_3)''$, of which the analogue in the case of citric acid has been isolated—a compound consisting of two potassio-cupric citrate nuclei united by the elements of $\text{CuK}_2(\text{CO}_3)_2$ (*loc. cit.*, p. 1844). A similar substance has been obtained in the case of the tartrate, except that the double carbonate, in combining with potassium cupritartrate, loses half of its potassium, the compound obtained being analogous to No. 6 (this vol., p. 174). In all the cupri-compounds obtained up to the present, the potassium in the OK groups may, by the action of water or alkali, be easily displaced by copper: such a displacement in this case would give No. 7, then No. 8, and, ultimately, a substance polymeric with normal copper carbonate. In the case of citric acid, a β -cupri-compound derived from three citric acid nuclei was obtained,

$(C_6H_5O_7)_3K_5Cu_2 \cdot 2Cu^{IV}O$ (*loc. cit.*, p. 1848), the analogue of which, in the α -cupricarbonates, would be No. 9. No. 4 will be referred to below.

With the exception of the dehydration products, Nos. 2 and 4, these compounds all result directly from the action of copper acetate on potassium carbonate, and, in addition, there are six other products, namely, copper oxide, a basic carbonate, trihydrated potassium carbonate, malachite, potassium acetate, and one unidentified compound, making thirteen products in all, without counting any copper acetate remaining unattacked. The copper oxide and basic carbonate are formed only under exceptional conditions; so, also, is malachite, which can easily be recognised owing to its appearance as small, bright green, hexagonal crystals, adhering strongly to the containing vessel: potassium acetate crystallises only when the liquid is very concentrated, its separation causing the whole liquid to become converted into an opaque, light blue solid.

The action of potassium carbonate solution on solid copper acetate was studied by Reynolds (*Trans.*, 1898, **73**, 262), who found that the resulting liquid deposited, under various conditions which he did not succeed in defining, the double carbonate in the form of (a) large, light blue * crystals of the tetrahydrate, (b) microscopic, blue, silky needles of a monohydrate, and (c) minute, transparent, hexagonal plates of a remarkably strong, deep blue colour, these being anhydrous. Mr. Reynolds has been good enough to present the author with preparations of (a) and (c), and likewise to place his laboratory note-book at his disposal.

It will be shown below that Reynolds was misled as to the composition of the supposed monohydrate, the salt isolated being No. 6, p. 801, which is the main product of the reaction in many cases: and it appeared evident to the author that neither this, nor the deep blue, anhydrous compound, could be mere dehydration products of the tetrahydrate. The tetrahydrate, it is true, does form the anhydrous compound when heated; but it is a change which takes place suddenly at 55° , under circumstances which preclude its being attributable to the mere abstraction of water; for example, when heated in a capillary tube: moreover, the tetrahydrate can be dehydrated in other ways, and then yields a light blue substance.

Similarly, the supposed monohydrate does not give the dark

* Reynolds describes them as greenish-blue: they are quite blue when pure, but look greenish by contrast when still in the mother liquor. Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 174) describe them as "blue, hexagonal crystals," and they, consequently, assume them to consist of a different compound from that obtained by Reynolds: this was evidently not the case, as Wood and Jones' description would apply very closely to the salt prepared by Reynolds.

blue substance on heating, and undergoes no change until it decomposes at about 200° . It has every appearance of being a cupri-compound, as it shows the closest resemblance in the character of its crystallisation to the cupricitrates, etc., whilst the exceptionally dark blue colour of the anhydrous compound indicates that it, also, is probably not an ordinary copper salt.

In order to obtain evidence as to the reaction giving rise to these substances, copper acetate was ground up with various proportions of dissolved potassium carbonate, filtered, and the product examined. The molecular proportions used, where practicable, were:

$$\frac{1.}{24} \quad \frac{2.}{12} \quad \frac{3.}{8} \quad \frac{4.}{6} \quad \frac{5.}{4} \quad \frac{6.}{3} \quad \text{K to each Cu,}$$

a normal reaction requiring 4K:Cu. The carbonate solution had specific gravities of 1.55, 1.45 and 1.35 in different series, and with each strength, experiments were made at 10° , 40° and 60° , keeping the mixtures at these higher temperatures for two to three hours before cooling.

The general results, in the light of information subsequently obtained, may be summarised roughly as follows:

Sp. Gr. 1.55. At 10° . With proportion 1, copper oxide separates throughout twenty-four hours; then No. 6. With proportion 5, No. 3 separates at once, and then potassium acetate. Intermediate proportions give mixed products.

At 40° and 60° . Copper oxide separates with the proportions 1 and 2. With higher proportions the results are similar to those at 10° , but the crystallisation is more rapid.

Sp. Gr. 1.45. At 10° . With proportion 1, copper oxide separates throughout three days: no crystallisation. With proportions 2, No. 6 separates, and with proportions 3 and 4, some of No. 1 first, and then some of No. 6. With proportions 3 to 5 there are also increasing amounts of No. 9 formed at once before filtration, and a certain amount of it continues to form in the liquid. With the crystals of No. 1 there are often present dark blue crystals of No. 5.

At 40° and 60° the action is similar, but more oxide is formed with the lower proportions, and, with the higher ones, after cooling, the crystals of the tetrahydrate (No. 1) are interspersed with larger and bluer crystals, which could be picked out, and proved to be the compound $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ coloured with copper.

Sp. Gr. 1.35. At 10° . With proportions 1 and 2, a little basic salt separates, but no crystals: with higher proportions, increasing amounts of No. 1.

At 40° and 60° . Copper oxide separates with the first two

proportions. With the higher proportions, Nos. 7 and 8 separate while the liquid is hot, and, if the heating is prolonged, malachite forms. On cooling, some of No. 1 often separates.

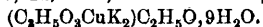
All these substances are decomposed by water, and it is difficult to free them from the mother liquor. Reynolds displaced this by pouring on to them, while on the filter, a mixture of glycerol and alcohol, 1:2 (which does not mix with a saturated solution of potassium carbonate), and then alcohol: this may be fairly satisfactory in the case of large or pulverulent crystals, but in other cases it is not so: experiments with the compound No. 6, with silica, and other substances, showed that the amount of potassium carbonate retained when present as a 1.55 solution might raise the potassium found on analysis by 20 to 30 per cent. and of its proper amount. An error of this magnitude would explain how it was that Reynolds obtained the ratio $\text{Cu}:\text{K}=1:2$ for the substance described by him as the monohydrate, in the place of 1:1.5, as it should have been. He has recently been good enough to reinvestigate the matter, and has been able to confirm the present results, obtaining the ratio 1:1.49.*

If, however, the proportion of glycerol to alcohol is increased to 2:1, the mother liquor dissolves in it, and can be completely removed. As such a mixture is in many cases unfilterable, the method adopted was to incorporate the substance with this mixture, and spread it out in a very thin layer on tiles: when apparently dry, it was mixed with glycerol and alcohol, 1:2, and spread again on tiles: then mixed with glycerol and alcohol, 1:4, put on a filter, and washed with alcohol, being finally dried on a tile or in a vacuum. With two exceptions, none of the substances dealt with were affected by this treatment, although they are all attacked by prolonged treatment with glycerol when moisture is present, some copper passing into solution, and a deliquescent cupriglycerol being formed.†

The various products were also examined by washing them with a little potassium carbonate solution sp. gr. 1.35, the weakest which

* Wood and Jones obtained the same value, 1:2 (details not given), as that originally obtained by Reynolds, when the crystals were filtered off without washing from a mother liquor containing 80 per cent. of potassium carbonate—a sufficient proof that the crystals themselves must have contained less than 2K to each Cu (*loc. cit.*, p. 176).

† Bullnheimer (*Ber.*, 1898, 31, 1453) obtained a compound



Mr. Reynolds informs the author that he has found washing with glycerol and alcohol, 1:2, to be successful if followed by the use of glycerol, alcohol and water in equal proportions, and then with alcohol,

it is safe to use, and then drying them by working them about on a tile. The carbonate left adhering to them after such treatment is fairly constant with the same substance, but varies with its physical condition: with the potassio-cupric carbonate No. 1, it amounted to 0.9 per cent. of the weight of dried salt; with the finely divided compound No. 6, it was 8 per cent. Such rough analyses afforded a useful check on the results obtained after treatment with glycerol, indicating whether such treatment had altered the substance or not.

The various compounds described below are, except where otherwise stated, fairly stable in air, but after several days' exposure they absorb enough water to become partly converted into a light blue basic salt, probably $5\text{CuO}, 2\text{CO}_2$ (Trans., 1909, 95, 1412): with excess of water, they all yield this compound, which, on drying, becomes partially converted into malachite. They are all practically dehydrated at 100° , only losing, however, the last traces of water (with a slight loss of carbon dioxide, also) at a higher temperature, but suffer no visible decomposition below 170° to 200° .

No. 1.—Potassio-cupric Carbonate with $4\text{H}_2\text{O}$.—Best prepared by tritulating 30 grams of copper acetate with 125 c.c. of potassium carbonate solution sp. gr. 1.45, filtering, and leaving to crystallise. The proportions and strength of carbonate solution may be varied considerably. Any fine, bluish-green deposit of No. 9, which may separate at the same time, can be removed by lixiviation with the mother liquor. Analyses of it confirmed Reynolds' results. It melts at 55° , and forms the deep blue compound, No. 5.

No. 5.—This, however, cannot be prepared quite pure in the above way, as the water cannot be eliminated before it has reacted to form traces of basic salt. The author obtained only a few crystals of it (mixed with other compounds) by the direct action of copper acetate on potassium carbonate, and he is indebted for his knowledge of it to a fine specimen of 30 grams supplied to him by Mr. Reynolds.

The tetrahydrate apparently changes into this compound, even at a lower temperature, for a specimen of the former, which had been kept for twelve years, contained particles of it.

No. 2.—What is apparently the anhydrous potassio-cupric carbonate may be prepared by sprinkling the hydrated salt into a dish of boiling alcohol. It melts, and forms the deep blue compound No. 5: but on grinding it up with the boiling alcohol, it becomes lighter in colour, and, on drying, forms a light blue powder, unaltered at higher temperatures.

No. 6.—Obtained by tritulating 10 to 20 grams of copper acetate with 100 c.c. of potassium carbonate solution sp. gr. 1.55, and

filtering so long as any cupric oxide separates. From the stronger solutions it is deposited in what appear to be large crystals, but these consist of sheafs of fine hairs, like bundles of spun glass tied tightly in the middle. From weaker solutions, the crystals are deposited throughout the liquid, giving it a silky sheen, and appearing to fill the whole liquid, but, on filtering under pressure, they are found to occupy only a very small space, forming a thin film on the filter paper, which is easily detached, and itself looks like a piece of blue paper; it can be cut, folded, or torn, the long, silky crystals being knitted together like the cellulose fibres of paper.

After treatment with glycerol and alcohol, and drying at 100° , it gave on analysis: *

	Found.	Calc.
Copper	$27.45 = 4.00$	$27.98 = 4$
Potassium	$25.22 = 5.98$	$25.81 = 6$

Nos. 7 and 8, as well as the decomposition product (malachite) of what would be the last member of this series, are all formed under nearly similar conditions. When 40 to 60 grams of copper acetate are dissolved in 170 c.c. of potassium carbonate solution sp. gr. 1.35 at temperatures from 60° to 100° , and the product kept at these temperatures for ten to fifteen minutes, a considerable crystallisation occurs, sometimes blue, and sometimes green, more often an evident mixture of the two. The blue crystals are very small, and correspond in composition with No. 7.

	Found.	Calc.
Copper	$34.76 = 5.00$	$34.77 = 5$
Potassium	$17.89 = 4.07$	$17.51 = 4$

The green crystals are more pulverulent: they were only obtained once without any evident mixtures of No. 7, and then gave:

	Found.	Calc.
Copper	$42.43 = 6.00$	$43.36 = 6$
Potassium	$10.92 = 2.5$	$8.89 = 2$

indicating that they probably consisted of No. 8, with some of No. 7 mixed with them. They contained no malachite, the crystals of which can be easily recognised under a microscope. Malachite forms only on the prolonged heating of these solutions, appearing as a deposit adhering strongly to the glass.

No. 9 is the compound which separates first whenever copper acetate in sufficient proportion is ground up with potassium carbonate solution of a specific gravity of about 1.45—1.35. The best way to obtain it is to grind 40—60 grams of the acetate with 100 c.c. of

* The mean results from many samples are alone quoted in this and other cases.

the carbonate, pour off the bulk of the liquid, and grind up the undissolved residue afresh: this soon dissolves to form a light blue paste, consisting of a mass of very small crystals, which, after treatment with glycerol and alcohol, and drying at 100° , give:

	Found.	Calc.
Copper	39.55 = 4.00	40.20 = 4
Potassium	12.40 = 2.02	12.36 = 2

No. 3. Potassium β -Cupricarbonate.—To prepare this, 30 grams of copper acetate are triturated with 50 c.c. of potassium carbonate solution sp. gr. 1.55, and filtered under pressure as rapidly as possible. In the filtrate, a gelatinous deposit begins to form, and, as soon as the liquid is thick with it, an equal volume of potassium carbonate solution sp. gr. 1.35 must be added, or it solidifies to an opaque, amorphous mass, interspersed with crystals of potassium acetate. The jelly cannot be actually washed with carbonate solution sp. gr. 1.35 without slight decomposition; also, on treatment with glycerol, unlike all the previously described compounds, it is decomposed, forming a dark violet-blue, sticky mass: its composition, therefore, cannot be exactly determined. After being worked on a tile until apparently dry, and heating at 100° , two samples gave:

	Found.	Corrected.	Calc.
Copper	$\left\{ \begin{array}{l} 20.17 \\ 21.71 \end{array} \right.$	$\left\{ \begin{array}{l} 21.9 \\ 23.6 \end{array} \right\} = 1.00$	22.72 = 1
Potassium	$\left\{ \begin{array}{l} 29.80 \\ 30.35 \end{array} \right.$	$\left\{ \begin{array}{l} 27.5 \\ 28.1 \end{array} \right\} = 1.98$	27.95 = 2

The correction applied is based on the assumption that 8 per cent. of potassium carbonate is retained by the salt after being dried in this way (see p. 805). The close concordance between these corrected values and those calculated for the β -cupricarbonate must not be pressed, but, independently of the analyses, it is evident that this substance belongs to a different class from the α -compounds already described.

It appears to be one of the initial products of the action of potassium carbonate and copper acetate, the tetrahydrate and No. 5 being derived from it: thus, if about 60 grams of acetate are dissolved in about 125 c.c. of the carbonate sp. gr. 1.45, and filtered, the filtrate entirely gelatinises after ten minutes, and the dark blue jelly, when collected, or allowed to remain for some time, becomes entirely converted into a mass of light blue tetrahydrate crystals, interspersed with some of the dark blue compound, No. 5, although this latter, in its turn, generally changes into the tetrahydrate also. The metamorphosis of the jelly can be followed under the microscope, and it is brought about instantly by pouring it on to a tile. Interspersed in the jelly there are microscopic,

although relatively large and well formed, elongated, lozenge-shaped crystals of some unidentified compound: these also change into the tetrahydrate.

The metamorphosis of the jelly into the tetrahydrate can be reversed: if the latter is dissolved in strong, cold potassium carbonate solution sp. gr. 1.55, or, preferably, in a still stronger, slightly warmed solution, the deep blue liquid soon gelatinises, and, if strong enough, gradually becomes opaque and almost solid, as in the preparation of No. 3 from the acetate. Such a reaction would by itself be sufficient to show that No. 3 and the tetrahydrate cannot consist of the same substance in different states of hydration. When the liquid is somewhat weaker, the jelly changes, on standing, into a mass of crystals of No. 6.

No. 4.—When tetrahydrated potassio-cupric carbonate (No. 1), in a finely powdered condition, is sprinkled over a sheet of paper and placed on a plate heated to 50°, it darkens, becomes lavender-blue, and loses its water without melting. It does not further change in colour by subsequent heating up to 170°. It is attacked in the same way as the β -cupricarbonate, No. 3, by glycerol, this differentiating it both from No. 2 and the deep blue compound, No. 5, with which it is metameric, suggesting that it is a β -cupricarbonate deprived of the elements of water, that is, No. 4, p. 800. This compound is also obtained by dehydrating the tetrahydrate over sulphuric acid in a vacuum, although it takes some two months to deprive it of all its water.

Unlike the α -cupricarbonates, it is very hygroscopic, forming, on exposure to air, first, a dark blue, sticky mass, which dries up and becomes apparently converted into the tetrahydrate, the latter subsequently forming a basic carbonate, as already described.

Although it is derived from the tetrahydrate under the simplest conditions, and is reconverted into it by hydration, both changes appear to be indirect, and it seems more probable that No. 2, and not this compound, is the anhydrous potassio-cupric carbonate. The difference between this substance and its metamerides, Nos. 2 and 5, was further emphasised by determining their heats of dissolution in dilute hydrochloric acid, the mean results being*:

No. 2.	14462	calories for $(\text{CO}_3)_2\text{CuK}_2$.
No. 4.	12400	„ „
No. 5.	11837	„ „

* Five grams dissolved in 60 c.c. of strong acid diluted to 600 c.c., the specific heat of which was taken as unity, and no allowance made for the heat absorbed by the evolution of carbon dioxide.

General.

The α -cupricarbonates isolated may be represented as consisting of two nuclei of double carbonate with the copper quadrivalent, united by a carbonate group, and the following groups (I, II and III) of such compounds might exist:

α -Cupricarbonates ($R = CO_3$).	β -Cupricarbonates.
I. <i>a.</i> $(R_4K_4Cu_2^{IV})CuK_2(CO_3)_2$	<i>a.</i> $(R_2K_2Cu^{IV})H_2O$
II. $\left\{ \begin{array}{l} e. (R_4K_4Cu_2^{IV})_2Cu_2K_2(CO_3)_3 \\ f. (R_4K_4Cu_2^{IV})Cu_3(CO_3)_3 \\ g. (R_4K_2CuCu_2^{IV})Cu_3(CO_3)_3 \\ h. (R_4Cu_2Cu_2^{IV})Cu_3(CO_3)_3 \end{array} \right.$	<i>b.</i> $(R_2K_2Cu^{IV})KHO$
III. <i>i.</i> $(R_4K_4Cu_2^{IV})Cu_4(CO_3)_4$	<i>c.</i> $(R_2K_2Cu^{IV})CuO$
IV. <i>l.</i> $(R_2K_2Cu^{IV})K_2CO_3$	<i>d.</i> $(R_2CuCu^{IV})CuO$
V. <i>p.</i> $(R_2K_2Cu_2^{IV})Cu_2(CO_3)_2$	

I, *a*, which is the deep blue compound described above, might give rise to three other members by the substitution of copper for potassium, but these have not been isolated: the individuals in the second group, *e*—*h*, have all been isolated, except *h*, of which the decomposition product, malachite, has alone been obtained. The third group of three members (see III, *i*) is conceivable by substituting a second $-CuCO_3Cu-$ group for the two OK groups in the formula No. 6, p. 801.

So far as the formulæ are concerned, a single double carbonate nucleus (that is, two simple carbonate nuclei) might have a carbonate molecule attached, giving rise to another group, of which IV, *l* would be the first member, or three simple carbonate nuclei might be similarly united, giving rise to a fifth group, of which V, *p* would be the third member; this being, apparently, the substance described above as No. 9, p. 801, analogous to one of the β -cupricitrates. More than three carbonate nuclei could not be strung together in this way.

Of the β -cupricarbonates, where oxygen plays the part of CO_3 , the only member probably isolated is *a*, the action of potassium hydrate being required to produce the others, if they exist. But in the case of the citrates, evidence of the existence of all four members has been given, as well as of another, rendered possible by the acid being tribasic. With the cupritartrates, where $R = C_2H_4O_2CuO$, Nos. *a*, *c*, and, probably, *d* have all been isolated, as well as one consisting of a molecule of *a* and *c* united; and *c* has been isolated in the case of the cuprisaccharate and cuprimucate, as well as in other cases not yet published. It does not seem possible to obtain the member $(R_2K_2Cu^{IV})K_2O$ for reasons previously given (Trans., 1910, 97, 1844).

Just as the nucleus may contain various radicles, so, apparently, may various radicles play the part of the CO_3 in the connecting

group of the α -cupri-salts. By dissolving metallic acetates in potassium succinate solution, Reynolds (Trans., 1898, **73**, 701) obtained a number of double salts, that in the case of copper being represented by the formula $\text{CuK}_4(\text{C}_4\text{H}_4\text{O}_4)_3$, and being inexplicable on the then existing views, except as a "molecular" compound: but it may now be represented as the analogue of the α -cupricarbonate IV, *l*, above, and it forms blue, microscopic crystals with a slight violet tinge, suggestive of its being a cupri-compound. The present author has obtained the ordinary potassio-cupric salt, $\text{CuK}_2(\text{C}_4\text{H}_4\text{O}_4)_2$, which forms large, hard crystals of a pure blue colour, and which, unlike Reynolds' salt, is not decomposed by water, unless the solution is dilute (0.17 per cent. Cu).

The same method was applied by the author to obtain indications as to which acids probably form cupri-salts under like conditions. In the following cases, deeply coloured, viscous liquids were obtained, from which minute, soft crystals gradually separated, or from which no crystals were obtained, but cupri-compounds were precipitated by alcohol: lactate, malate (two forms of crystals), glycollate (two forms of crystals, one of which gave $(\text{C}_2\text{H}_3\text{O}_3)_7\text{Cu}_4\text{K}$ on analysis), glycerate (giving $(\text{C}_3\text{H}_5\text{O}_4)_4\text{K}(\text{CuO})_4$), tartrate (Cu:K about 3:1), quinate (giving $(\text{C}_7\text{H}_{11}\text{O}_6)_2\text{Cu}_3\text{CuO}$, and also an ordinary basic salt, $(\text{C}_7\text{H}_{11}\text{O}_6)_2\text{Cu}_2\text{CuO}$), and citrate (giving $(\text{C}_6\text{H}_5\text{O}_7)_2\text{K}_2\text{Cu}_2\text{CuO}$, previously obtained in other ways, Trans., 1910, **97**, 1846).

On the other hand, limpid solutions of what appeared to be ordinary cupric salts were obtained with the fumarate, aconitate (including an acid salt, $\text{C}_6\text{H}_3\text{O}_6\text{CuH}$), salicylate, mucate, phthalate (the double salt, $(\text{C}_8\text{H}_4\text{O}_4)_2\text{CuK}_2$, and a basic copper salt with 2 or 3 CuO being obtained), toluate, protocatechuate (the double salt $(\text{C}_5\text{H}_6\text{O}_4)_3\text{Cu}_2\text{K}_2$ being obtained), pyrotartrate, and malate (giving $(\text{C}_3\text{H}_2\text{O}_4)_3\text{Cu}_2\text{K}_2$ *).

With the benzoate, oxalate and cinnamate, no action at all took place.

None of the compounds above mentioned, except the citrate, appear to have been previously obtained.

There does not seem to be any evident connexion between the constitution of the acid and the nature of the reaction in such cases: all the acids forming cupri-compounds contain alcoholic hydroxyl, but the presence of such hydroxyl does not necessarily involve the formation of cupri-compounds.

The last member of each of the five series of α -cupricarbonates would be a polymeride of normal copper carbonate, and, like it, would probably be incapable of a separate existence: but other

* The liquid was viscid in this case, but the crystals were gritty, like those of an ordinary cupric salt,

copper salts are not so unstable, and it is possible that in their case they might exist as ordinary cupric salts, and also as copper cupri-salts.

There is only one instance where members of the series shown above would be polymeric, *b* and *m*, neither of which have been isolated, but *a* (No. 5 on p. 801) is polymeric with anhydrous potassio-cupric carbonate (No. 2, p. 800), and also with the dehydrated β -cupricarbonate (No. 4, p. 800), and it has been shown that these three compounds are well characterised by differences in physical and chemical properties. This is of special interest in view of the fact that the author established twenty-five years ago (Trans., 1886, **49**, 1) that anhydrous potassio-cupric sulphate exists in three distinct modifications, well differentiated by their colour and heats of dissolution, and of this no explanation has been forthcoming until now.

HARPENDEN,
HERTS.
