CCXXIX.—*Metallic Hydroxy-acid Complexes. Part IV. Complexes formed by Copper with the Monobasic Monohydroxy-acids.*

By Ian William Wark.

The author has suggested (J., 1923, **123**, 1816) that the stability of the metallic derivatives of a hydroxy-acid may be expected to increase with the acidity of the hydroxylic hydrogen. Thus, although the derivatives of lactic acid (*loc. cit.*) and of glycollic acid (Pickering, J., 1911, **99**, 1347) are easily hydrolysed, it was anticipated that the increased acidity of the hydroxyl group in mandelic and salicylic acids would lead to the formation of more stable complexes. These conclusions have now been verified experimentally.

It has previously been shown that the composition of sodium cuprilactate is most probably $Na_2[(\cdot O\cdot CHMe\cdot CO_2\cdot)_2Cu]$. In order to ascertain whether this compound is representative of a general series formed by the simpler hydroxy-acids, some work with the complexes formed by glycollic, mandelic, and salicylic * acids has been undertaken, and has established the fact that sodium cuprilactate is a definitely representative compound.

After a satisfactory general method of attack had been devised, it seemed desirable to ascertain whether the dihydroxy-phenols and the amino-acids would yield to a similar treatment. Accordingly, the copper derivatives of pyrocatechol and glycine were treated in alcoholic solution with sodium methoxide. Although blue complexes were formed in each case, no stable derivative could be isolated; and the complexes readily decomposed with the precipitation of cuprous or cupric oxide. Cupric phenylglycine is practically insoluble in a solution of sodium methoxide.

The constitution of the complexes will be discussed in a subsequent communication.

EXPERIMENTAL.

A. *Preparations in Aqueous Solution.*

Cuprimandelates.—Cupric *i*-mandelate (Winkler, *Annalen*, 1836, **18**, 320), which is anhydrous when dried at 100°, was obtained as a pale blue, sparingly soluble monohydrate by mixing solutions of sodium mandelate and cupric chloride [Found: Cu, 16·3; H_2O, 5·2. $Cu(C_8H_7O_3)_2,H_2O$ requires Cu, 16·6; H_2O, 4·7%].

Action of alkali on cupric mandelate. Since cupric mandelate is not wetted by water, it was necessary to wet it with alcohol in order to effect solution in alkali. Two equivs. of caustic soda ($N/2$) dissolve 1 mol. of the mandelate, presumably according to the equation $2NaOH + Cu(C_8H_7O_3)_2 = 2H_2O + Na_2[Cu(C_8H_6O_3)_2]$. This solution deposits cupric hydroxide on standing. It may be stabilised by the addition of excess of sodium mandelate [compare cupric lactate (*loc. cit.*, where the reasons for this stabilising effect have been discussed)].

After the addition of slightly less than two equivs. of caustic soda, the solution becomes alkaline to phenolphthalein, but provided that

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* The aromatic β-hydroxy-acids of the salicylic acid type resemble the aliphatic α-hydroxy-acids with respect to complex formation (Weith, *Ber.*, 1876, **9**, 342; Pickering, J., 1912, **101**, 174; Beilstein, 3rd Edn., II, 1492; Piria, *Ann. Chem. Pharm.*, 1855, **17**, 262). Piria states that cupric salicylate readily gives moderately stable derivatives, $K_2[Cu(C_7H_4O_3)_2],4H_2O$ and $Ba[Cu(C_7H_4O_3)_2],4H_2O$, resembling the above cuprilactate, but he gives no experimental detail or analytical figures in support of this contention. Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 577) has found that, in the presence of sulphate ions, the concentration of the copper ions in a solution containing the complex cuprisalicylate is of a low order of magnitude.

a sufficient excess of the sodium mandelate is present, further addition of caustic soda does not precipitate cupric hydroxide, even in boiling solution. Such an alkaline solution, however, readily oxidises glucose.

Salts of Cuprimandelic Acid.—I. *Sodium cuprimandelate,* $Na_2[Cu(C_8H_6O_3)_2]$.
The chemistry of this compound is discussed in Section B.

II. *Sodium hydrogen cuprimandelate,* $NaH[Cu(C_8H_6O_3)_2]$. A concentrated solution of 1 mol. of cupric mandelate in 2 mols. of caustic soda, which has been stabilised by the addition of sodium mandelate, deposits slowly on standing a copious crop of fine, pale blue crystals. These are but slightly soluble in water. Analysis showed them to contain sodium and copper in the proportion 1 : 1, whereas the synthetic proportion was 2 : 1 {Found: Na, 5·2; Cu, 13·4; H_2O, 15·6. $NaH[Cu(C_8H_6O_3)_2],4H_2O$ requires Na, 5·0; Cu, 13·8; H_2O, 15·7%}. Evidently as the compound separates some alkali is liberated; if the solution is exposed to the air, carbon dioxide is absorbed and crystals of sodium carbonate begin to form. This compound is regarded as an acid salt, for 1 mol. of caustic soda dissolves it according to the equation $NaH[Cu(C_8H_6O_3)_2] + NaOH = Na_2[Cu(C_8H_6O_3)_2] + H_2O$, but again, on evaporation, the pale blue acid salt crystallises out. Cuprimandelic acid must be considered a fairly weak acid if carbonic acid is able to extract some of the alkali from its normal salt in this way, even when allowance is made for the fact that the acid salt is rather sparingly soluble.

III. *Silver cuprimandelate.* A neutral solution of sodium cuprimandelate, prepared by treating an excess of cupric mandelate * with caustic soda solution, is rapidly filtered into a solution of the calculated quantity of silver nitrate; a pale blue precipitate of *silver cuprimandelate* is formed immediately: $Na_2[Cu(C_8H_6O_3)_2] + 2AgNO_3 = 2NaNO_3 + Ag_2[Cu(C_8H_6O_3)_2]$. The salt is quite stable on boiling, but darkens after exposure to light for several months {Found: Ag, 36·8; Cu, 11·4. $Ag_2[Cu(C_8H_6O_3)_2]$ requires Ag, 37·3; Cu, 11·0%}. (The author is indebted to Mr. W. J. Lawrence for this analysis and that of the following mercurous salt.)

IV. *Mercurous cuprimandelate* may be prepared in a like manner to the silver salt, which it resembles in appearance {Found: Hg, 47·4; Cu, 7·2. $Hg_2[Cu(C_8H_6O_3)_2],5H_2O$ requires Hg, 46·9; Cu, 7·4%}. On prolonged heating, the mercury volatilises with the water of crystallisation, leaving pure cupric mandelate.

V. *Ferric cuprimandelate* also may be prepared by double decomposition. If excess of ferric chloride be present, a yellow or red solution is formed. With calculated quantities of the reagents, a

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* It is advisable to use only small quantities of the cupric mandelate and to work rapidly, for the solution of sodium cuprimandelate is somewhat unstable.

yellowish-brown, crystalline precipitate forms on boiling {Found : Fe, 7·5; Cu, 12·7; H_2O, 16·8. $Fe_2[Cu(C_8H_6O_3)_2]_3,14H_2O$ requires Fe, 7·7; Cu, 13·1; H_2O, 17·3%}.

VI. *Cupric cuprimandelate* was prepared as a pale blue, crystalline powder by double decomposition {Found : Cu, 29·3.

$Cu[Cu(C_8H_6O_3)_2]$

requires Cu, 29·6%}. There was no loss in weight on heating to 130°.

B. *Preparations in Non-aqueous Solvents.*

The main difficulties encountered in the present work arise from the ease with which the complexes are hydrolysed. Hence it was decided to use cupric salicylate, which is soluble in alcohol, acetone, and even chloroform, and exclude all traces of water. Later, it was found possible to deal in a similar manner with the mandelate, glycollate, and lactate, although they themselves are practically insoluble in these solvents.

I. *Sodium Cuprisalicylate.*—As a starting point, normal cupric salicylate is readily obtained by the method outlined by Pickering (*loc. cit.*). Piria (*loc. cit.*) has reported that this compound easily breaks down into free salicylic acid and the basic salicylate. Indeed, on prolonged heating at 110°, some of the acid volatilises, leaving dark brown patches of the basic salt, which should be regarded as the cupric salt of cuprisalicylic acid, $Cu[Cu(C_7H_4O_3)_2]$. Normal cupric salicylate crystallises both from alcohol and from acetone with solvent of crystallisation. Solutions in both solvents readily deposit dull green crystals of the basic salt. To a solution of cupric salicylate in ethyl alcohol was added an alcoholic solution of sodium ethoxide, such that the proportion was approximately 2Na : Cu. A pale green crystalline precipitate formed immediately and was collected, washed, and dried over concentrated sulphuric acid in a vacuum desiccator. It is soluble in water but rapidly undergoes hydrolysis to cupric hydroxide {Found : Cu, 16·3; Na, 12·3. $Na_2[Cu(C_7H_4O_3)_2]$ requires Cu, 16·6; Na, 12·1%}.

II. *Sodium Cuprimandelate.*—It was pointed out in Section A that disodium cuprimandelate cannot be isolated readily from its aqueous solution. It can, however, be obtained by dissolution of 1 mol. of anhydrous cupric mandelate in an alcoholic solution of 2 mols. of sodium ethoxide :

$$2NaOEt + Cu(C_8H_7O_3)_2 = Na_2[Cu(C_8H_6O_3)_2] + 2EtOH.$$

This solution was rapidly filtered while hot, and on standing overnight pale blue crystals separated {Found : Na, 9·2; Cu, 12·7. $Na_2[Cu(C_8H_6O_3)_2],2C_2H_5{\cdot}OH$ requires Na, 9·2; Cu, 12·7%}. The loss in weight on drying at 90° was 17·8% (Calc. for $2C_2H_5{\cdot}OH$, 18·3%); at 100° the compound gradually decomposed giving the odour of benzaldehyde.

III. *Sodium Cupriglycollate.*—Cupric glycollate, the starting point, has been described by Pickering (J., 1911, **99**, 1347), Fahlburg (*J. pr. Chem.*, 1873, **7**, 339), and Heintz (J., 1861, **14**, 439). Pickering and Kahlenberg (*loc. cit.*) have both investigated the action of aqueous alkalis upon this salt. Pickering came to the conclusion that for the formation of a neutral complex the ratio KOH : Cu was 1·64, and by the addition of alcohol he precipitated from the colloidal solution so formed an emulsion in which K : Cu = 1 : 1. These conclusions, if verified, would stamp the glycollate as being quite exceptional. Pickering also described a strongly alkaline compound in which the proportion was 2K : Cu.

Finely powdered, anhydrous cupric glycollate, although it dissolves in an alcoholic solution of sodium ethoxide, readily gives rise to an insoluble derivative. Consequently, sodium methoxide was substituted : $2NaOMe + Cu(C_2H_3O_3)_2 = Na_2[Cu(C_2H_2O_3)_2] + 2MeOH$. A fine crop of bright blue crystals formed over-night {Found : Na, 13·7 ; Cu, 19·0 ; loss at 110°, 23·2. $Na_2[Cu(C_2H_2O_3)_2],2\frac{1}{2}CH_3{\cdot}OH$ requires Na, 13·6 ; Cu, 18·8 ; $2\frac{1}{2}CH_4O$, 23·7%}. At temperatures higher than 110°, decomposition occurred. An aqueous solution deposited copper hydroxide in a few minutes.

IV. *Sodium Cuprilactate.*—The reactions of this compound in aqueous solution were discussed in an earlier paper (*loc. cit.*). Finely powdered, anhydrous cupric lactate, dissolved in the theoretical quantity of sodium ethoxide, deposits slowly on standing a pale violet, crystalline salt of low density {Found : Na, 12·8 ; Cu, 16·6 ; loss at 110°, 13·1. $Na_2[Cu(C_3H_4O_3)_2],2C_2H_6O$ requires Na, 12·2 ; Cu, 16·8 ; $2C_2H_6O$, 12·2%}. Heating to higher temperatures rapidly decomposed the compound.

C. *Measurements of Hydrogen-Ion Concentration.*

Darmois (*J. Phys. Radium*, 1924, [vi], **5**, 225), using the quinhydrone electrode, has investigated the action of caustic soda on cupric malate (compare J., 1923, **123**, 1831). He followed the effect produced by the gradual addition of alkali to a solution containing cupric malate, confirming the results of the work cited above. It seemed that this method, which owes its application to the fact that the electrode functions whilst there is still insufficient hydrogen present to allow the reaction $Cu^{\cdot\cdot} + H_2 = 2H^{\cdot} + Cu$ to proceed, would be useful in deciding quickly, without the necessity for laborious analyses such as have been outlined in the preceding sections, whether all these cupric salts behaved in a similar manner to the cupric mandelate, the derivatives of which were, at the time, the only series which had been investigated.

The method failed when any alkali metal was present, for the quinhydrone was oxidised and a deposit of cuprous oxide formed.

However, some useful results were obtained before alkali had been added. According to the views advanced by the author, the cupric salts from which the complexes are derived are usually isomeric with the parent acids of the complexes themselves. Thus it was shown that cupric malate, $CuC_4H_4O_5$, is isomeric with cuprimalic acid, $H\cdot CuC_4H_3O_5$, and that in solution both compounds exist side by side. Likewise one might expect isomerism between cupric lactate and cuprilactic acid, cupric salicylate and cuprisalicylic acid, etc. Hence it seemed advisable to estimate roughly the hydrogen-ion concentrations in solutions of the various cupric salts under investigation. The quinhydrone electrode is useful for this purpose, and the results were checked by means of indicators, as shown in the following table.

	Cupric salt employed.	Salicylate.	Glycollate.	Lactate.
p_H	By indicators	4	5	5
	By quinhydrone–quinol electrode	3·5	4·7	4·7

Cupric salicylate is markedly acidic compared with the glycollate or lactate. One might expect, therefore, that cuprisalicylic acid would be a stronger acid than cuprilactic or cupriglycollic acid, and that its salts would be more stable—a prediction abundantly verified by experiment. It is unfortunate that cupric mandelate is not sufficiently soluble to enable a comparison with the other salts to be made.

Summary.

1. It has been shown that several monobasic monohydroxy-acids, *viz.*, lactic, mandelic, glycollic, and salicylic acids, all give rise to similar copper-containing complex acids.
2. The sodium salts of these complex acids have been isolated from alcoholic solutions. Their formulæ are of the type

$$Na_2[(\cdot O\cdot CHR\cdot CO_2\cdot)_2Cu]$$

and they all hydrolyse readily in aqueous solution.

3. The derivatives of cuprimandelic acid, which are more stable in aqueous solutions than most of the other complexes, have been investigated more fully.
4. The hydrogen-ion concentrations in solutions of the cupric salts of lactic, glycollic, and salicylic acids have been estimated.

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