CLXX.—*Studies in Complex Salts. Part II. The Preparation, Properties and Stability of Some Bis-dicarboxylato Copper Salts.*

By Harry Lister Riley.

It has been suggested (J., 1928, 2985) that an important factor governing the formation of a co-ordinate linkage between two ions is the distribution of the electric charges in the donor ion. If it were possible to compare the stabilities of a series of complex ions of the type $[AX_1]$, $[AX_2]$, $[AX_3]$, etc., in which A represents the same acceptor ion and X_1, X_2, X_3, etc., represent different donor ions, valuable information would be obtained as to the electron distribution in this series of ions. A survey of complex-salt chemistry indicated that such a comparison would present many difficulties, chiefly in the choice of a suitable series of complex ions, definitely recognised as such, the stabilities of which could be measured; for those acceptor ions which form the largest numbers of complex ions are those which easily pass from one state of valency to another and therefore render any measurements of ion concentration by an electrode potential or conductivity method uncertain. It appeared possible, however, that a series of such measurements might be possible in the case of copper complex salts. The complex-salt chemistry of copper was subjected to extended investigation by Pickering (J., 1911—1915) with reference to its compounds with hydroxy-substituted carboxylic and dicarboxylic acids, but no attempt was made to correlate the compounds obtained with the co-ordination theory. It was therefore decided to investigate the nature of the compounds obtained when copper reacts in aqueous solution with certain dicarboxylic acids in order to determine whether or no a suitable series of similar complex copper salts could be obtained. The carboxylic acids chosen for this study were carbonic, oxalic, malonic, succinic, and phthalic.

The nature of the double compound formed between copper carbonate and sodium carbonate has been studied by Reynolds (J., 1898, **73**, 262), Gröger (*Ber.*, 1901, **34**, 429), Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 171), Pickering (J., 1909, **95**, 1418; 1911, **99**, 800), Applebey and Lane (J., 1918, **113**, 610), Aldridge and Applebey (J., 1922, **121**, 242), and de Carli and Agostini (*Atti R. Accad. Lincei*, 1928, **7**, 921). The weight of evidence appears to be in favour of the formation of the compound $Na_2CO_3,CuCO_3,3H_2O$ and de Carli and Agostini have recently shown (*loc. cit.*) that one molecule of water is lost at 80° and the other two molecules at 120°. It would therefore seem correct on the co-ordination theory to formulate this compound as

$$Na_2[Cu(CO_3)_2(H_2O)_2],H_2O$$

or as $Na_2[Cu(CO_3)_2(H_2O)_3]$, in which one of the carbonato-groups occupies only one position in the co-ordinated complex. The double oxalate of lithium and copper was first prepared by Troost (*Ann. Chim. Phys.*, 1857, **51**, 143), who described it as a compound which forms sky-blue needles and has the formula

$$Li_2C_2O_4,CuC_2O_4,2H_2O.$$

No further study of the double oxalates appears to have been made. It has now been shown that the double *sodium copper* salt also crystallises in sky-blue needles which are readily soluble in water. The two molecules of water are not lost when the salt is kept in a vacuum. It is therefore probably best formulated as $Na_2[Cu(C_2O_4)_2(H_2O)_2]$. Malonic acid forms a similar *compound*, $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$, which is a pale blue, sparingly soluble powder, and phthalic acid also forms a *compound* of the same type, $Na_2[Cu(C_8H_4O_4)_2(H_2O)_2]$, which is easily decomposed by water and is of a deep blue colour. Although none of these compounds has yet been resolved, it seems highly probable that the two molecules of water are co-ordinated with the copper, as they are not removed by desiccation in a vacuum and, what is perhaps more important, they occur in each of these four compounds. The copper ion is therefore apparently displaying a co-ordination number of six.

This view is supported by the work of Wahl (*Soc. Sci. Fennicae*, Comm. Phys. Math., 1927, **4**, 1), who has resolved a compound very similar in type to the above, *viz.*, diethylenediaminediaquocupric tartrate.

The literature contains few references to the double alkali copper succinates. Reynolds (J., 1898, **73**, 701) describes a compound of the formula $CuK_4(C_4H_4O_4)_3,2H_2O$ and Pickering (J., 1911, **99**, 800) reports $K_2Cu(C_4H_4O_4)_2$. The succinato- and the carbonato-compounds are, however, extremely unstable, existing in aqueous solution only in presence of a very large excess of alkali succinate and carbonate respectively, and it was therefore decided to confine the quantitative measurements of stability to the oxalato-, malonato-, and phthalato-compounds. It seems, however, fairly certain that the carbonato- and succinato-compounds are of the same type, though considerably less stable than the others. In order to form some idea of the relative stabilities of the carbonato- and succinato-compounds the following experiment was performed. Some freshly etched copper was immersed for several weeks in a concentrated solution of sodium carbonate in an open flask. The intensity of the blue colour produced was compared with that formed in a solution of sodium succinate of similar strength, also containing a piece of copper. In the carbonate solution quite a deep blue colour was produced, whereas in the succinate solution only a very pale blue colour was formed; thus showing that the carbonato-ion has a greater tendency than the succinato-ion to co-ordinate with the copper.

Preparation of Disodium Diaquodioxalatocupriate.—26·8 G. of pure sodium oxalate were dissolved in 800 c.c. of water and to the hot solution was added a concentrated solution of copper sulphate until a very faint turbidity was produced. This was cleared by the addition of a little more sodium oxalate solution and the resulting deep blue solution was filtered and allowed to crystallise. The *dioxalato*-compound separated in long, sky-blue needles, which were collected and washed with cold water until free from sulphate and then with alcohol and with ether. After drying in the air, the compound was analysed. The oxalate was estimated by direct titration with standard permanganate in hot acid solution. The copper was weighed as cuprous sulphide, and the sodium as sodium sulphate after separation of the copper with hydrogen sulphide (Found : C_2O_4, 54·51; Cu, 19·89; Na, 14·32. $Na_2[Cu(C_2O_4)_2(H_2O)_2]$ requires C_2O_4, 54·73; Cu, 19·77; Na, 14·30%). No loss in weight occurred over concentrated sulphuric acid in a vacuum. The compound is fairly readily soluble in cold water, giving a deep blue solution; this is only slightly decomposed by prolonged boiling, but a precipitate of copper oxalate is produced at once on the addition of dilute hydrochloric acid. Calcium chloride gives a precipitate of calcium oxalate when added to the cold solution.

Preparation of Disodium Diaquodimalonatocupriate.—To 33·2 g. of sodium malonate, dissolved in 150 c.c. of water, were added 25 g. of copper sulphate, dissolved in 100 c.c. of water. The deep blue solution produced was filtered quickly; on standing, it deposited the *dimalonato*-compound as a pale blue powder. This was collected, washed with cold water until free from sulphate and then with alcohol and with ether. After drying on a porous plate, the compound was analysed, copper and sodium being estimated as before and carbon and hydrogen by combustion (Found: Cu, 18·16; Na, 13·12; C, 20·63; H, 2·36. $Na_2[Cu(C_3H_2O_4)_2(H_2O)_2]$ requires Cu, 18·19; Na, 13·16; C, 20·60; H, 2·29%). No loss in weight occurred on drying in a vacuum. The malonato-compound is paler in colour than the oxalato and somewhat less soluble in water.

Preparation of Disodium Diphthalatodiaquocupriate.—To a solution of 33·2 g. of phthalic acid in the equivalent quantity of aqueous sodium hydroxide were added 200 c.c. of 0·2*M*-copper sulphate (10 g. of $CuSO_4,5H_2O$). The large excess of phthalate was used in order to diminish hydrolysis. From the deep blue, filtered solution, nothing separated over-night, but on vigorous stirring the *diphthalato*-compound was precipitated in blue flakes, deeper in colour than the oxalato-compound. The diphthalato-compound apparently possesses the property of forming highly supersaturated solutions. The separated solid was dried by thorough pressing between filter-papers; it could not be washed, even with a cold 50% alcohol–water mixture, such treatment causing hydrolysis. The dried compound was free from sulphate (Found: Na, 9·81; Cu, 13·46; C, 40·59; H, 2·62. $Na_2[Cu(C_8H_4O_4)_2(H_2O)_2]$ requires Na, 9·71; Cu, 13·42; C, 40·54; H, 2·53%). Practically theoretical yields were obtained in each case.

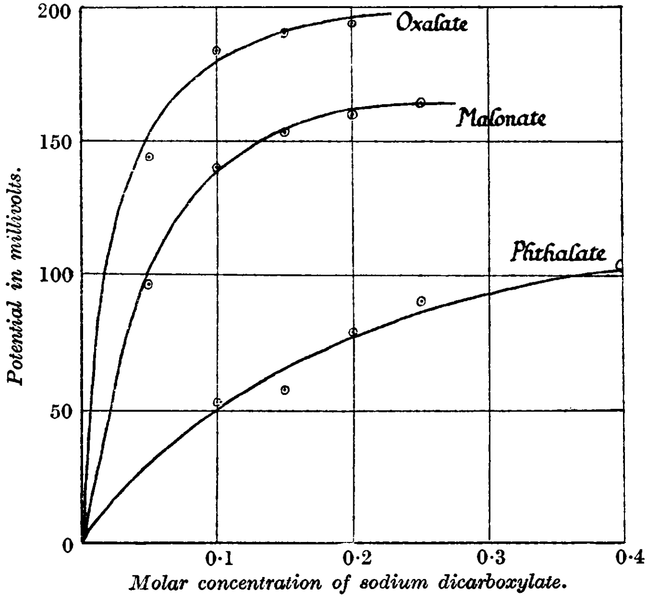
The constants of instability of these three compounds (*i.e.*, $[Cu^{++}][X^-]^2/[CuX_2^{--}]$, where X = the carboxylato-ion) were measured by an electrode potential method, the following concentration cell being used: Cu|0·01*M*-$CuSO_4$|Sat. KNO_3|0·01*M*-$CuSO_4$ + 0·03*M*-Na_2X|Cu, where Na_2X represents the sodium salt of the dicarboxylic acid under consideration. Preliminary investigation showed that 0·03*M*-solutions of the dicarboxylic acid were most suitable for these measurements for two reasons; *viz.*, the excess of free dicarboxylate being reduced to a minimum (the phthalato-compound just giving a clear solution under these conditions), the solvent action of the dicarboxylate on the copper electrode, in presence of traces of oxygen, will also be reduced to a minimum; and secondly, the uncombined dicarboxylate may, in the calculation of the instability constant, be assumed, without any appreciable error being introduced, to be completely dissociated. The following assumptions were made in calculating the constants of instability: (1) $[Cu^{++}]$ is given by the expression $E = RT/nF \cdot \log C_2/C_1$; (2) the concentration of the undissociated complex ion present can be calculated from "total copper present minus $[Cu^{++}]$"; (3) the concentration of the free dicarboxylato-ion is equal to the total dicarboxylate present (0·03*M*) less that united to the undissociated copper.

The potential measurements were made by means of a metre bridge potentiometer, a capillary electrometer, and a standard Weston cell. The half-elements were small wide-mouthed glass bottles, of about 40 c.c. capacity, each carrying a rubber bung through which passed a piece of stout copper wire (S.W.G. 14) and the usual glass tubes. Four such half-elements were constructed and the copper electrodes, after being etched in dilute nitric acid, were washed, connected together, and plated (current density, 0·5 amp. per 100 sq. cm.) in a bath of the following composition: $CuSO_4,5H_2O$, 30 g.; H_2SO_4, 10 g.; alcohol, 50 g.; water, 200 g. The plating was continued for 48 hours, the circuit was then broken, and the electrodes, still connected together, were left in the plating solution for a further period of 3 days. They were then removed, rapidly rinsed with cold, air-free, distilled water, dried, and introduced at once into their respective half-element cells.

The solutions used in the half-elements were made up from a standard solution of copper sulphate (0·1*M*) and standard solutions of the sodium salts of the respective dicarboxylic acids (0·12*M*). In the standard sodium oxalate solution, "reagent" sodium oxalate, previously dried at 110°, was used. For the malonate and phthalate solutions the pure recrystallised acids were neutralised by the exactly equivalent quantities of carbonate-free, standard caustic soda, and the solutions made up to a definite volume. Before the copper sulphate solution was mixed with the solution of the sodium dicarboxylate, both solutions were boiled, to remove dissolved air, rapidly cooled, and made up to a definite volume with air-free, distilled water. The half-elements were completely filled with their respective solutions and tightly stoppered. By these means the amount of dissolved oxygen in the various solutions was reduced to a minimum.

Some preliminary measurements indicating the variation of the potential of the concentration cells with the concentration of the sodium dicarboxylate are shown in Fig. 1. These results were obtained with 0·02*M*-copper sulphate. Fig. 2 shows the variation of potential with time in cells containing 0·01*M*-copper sulphate and 0·03*M*-sodium dicarboxylate. The potentials were measured against the same 0·01*M*-copper sulphate half-element. The potentials fell rapidly at first and then became steady after a few hours. The effect of admitting oxygen (at point A) is shown in the oxalate curve, a slow but steady fall resulting. This effect is not so marked with the malonate and the phthalate. The values obtained are reproducible to within 1 or 2 millivolts. All the measurements were carried out at room temperature.

FIG. 1.

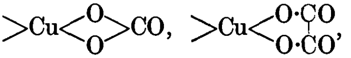


The values obtained for the constants of instability were as follows :—

Compound.	Potential (volt).	$[Cu^{++}]$.	$[X^{--}]$.	$[CuX_2^{--}]$.	$\frac{[Cu^{++}][X^{--}]^2}{[CuX_2^{--}]}$
Oxalato......	0·124	$0{\cdot}33 \times 10^{-6}$	0·0100	0·0100	$0{\cdot}33 \times 10^{-8}$
Malonato ...	0·089	$0{\cdot}54 \times 10^{-5}$	0·0100	0·0100	$0{\cdot}54 \times 10^{-7}$
Phthalato...	0·004	$0{\cdot}46 \times 10^{-2}$	0·0192	0·0054	$0{\cdot}31 \times 10^{-4}$

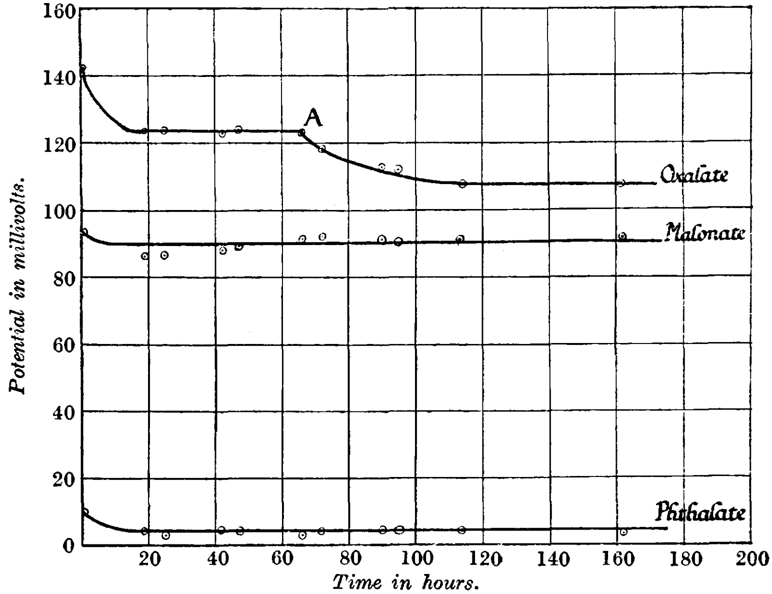
The concentration of the copper ions in 0·01*M*-copper sulphate at 18° is taken to be $0{\cdot}629 \times 10^{-2}$ (see Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475).

The instability constant of the phthalato-compound cannot be considered strictly accurate owing to the comparatively high concentration of the copper ions. These experiments show, however, that the stabilities of the complex ions formed between copper and the various dicarboxylic acids are in the following decreasing order of stability: oxalato, malonato, phthalato, carbonato, and succinato. The chelate rings formed in the various ions would be



$>Cu<\substack{O\\O}>CO$, $>Cu<\substack{O\cdot CO\\ |\\ O\cdot CO}$, etc. The phthalato-compound is unique amongst complex salts in possessing two seven-membered chelate rings.

FIG. 2.



At first sight it appears that the cause of this gradation of stability is the strain in the chelate ring and that the effects observed can be explained by purely steric considerations, the magnitude of the charge on the oxygen atom taking part in the Cu—O bond being a minor consideration. It will be shown, however, in Part III of this series that strain, as a purely steric effect, is totally inadequate to account for the stability of certain substituted malonic acid complex salts and that the chief factor governing stability must be a polar one. It would be premature, however, to theorise as to the polar factors which govern the stability of the complex salts studied in this paper, as the chelate rings concerned contain different numbers of atoms and it is impossible to discriminate between strain and polar factors.

Summary.

Copper forms with certain dicarboxylic acids complex salts of the type $Na_2[Cu(X)_2(H_2O)_2]$ in which the copper is probably displaying a co-ordination number of six.

The preparation of the dioxalato-, the dimalonato-, and the diphthalato-complex salts has been described.

The stabilities of the complexes formed have been shown to be in the following decreasing order : oxalato, malonato, phthalato, carbonato, and succinato.

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