494. *Ion Association in Aqueous Solutions of Metal Dicarboxylates.*

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The ion association which occurs between cations and dicarboxylate anions in aqueous solution has been studied by potentiometric, conductometric, and spectrophotometric methods. Dissociation constants are reported for the products of such association, and the significance of these results is discussed.

Aqueous solutions in which metal cations and dicarboxylate anions are present often show marked specific interaction effects which can satisfactorily be accounted for in terms of mass-action dissociation constants. In some cases the resultant complexes behave as abnormally weak electrolytes, a typical example being copper malonate, which has been shown by Ives and Riley (*J.*, 1931, 1998) to be a considerably weaker electrolyte than acetic acid. The present investigation provides further information as to the effects of structural factors and on the nature of the linkages involved between cations and dicarboxylate anions. Solutions containing cations M [where M = $Ba^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $La^{\cdot\cdot\cdot}$, or $Co(NH_3)_6^{\cdot\cdot\cdot}$] and anions A, from dicarboxylic acids of the series $[CH_2]_x(CO_2H)_2$ have been studied by potentiometric, conductometric, and spectrophotometric methods; less detailed measurements for other dicarboxylic acids are also reported.

Potentiometric Measurements.—In dicarboxylic acid buffer solutions ionic concentrations are governed by the equilibria $H_2A \rightleftharpoons H^{\cdot} + HA'$, $HA' \rightleftharpoons H^{\cdot} + A''$. On addition of a bivalent metal chloride, these equilibria are displaced and a change in the hydrogen-ion concentration occurs, primarily because of the reaction $M^{\cdot\cdot} + HA' \rightleftharpoons MA + H^{\cdot}$. Such pH changes are often large, and the effect has been used by a number of workers (*e.g.*, Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314; Stock and Davies, *J.*, 1949, **1371**) for the determination of the concentrations of the various ionic species present, and thence for the calculation of dissociation constants. This method has been used in the present work, the procedure adopted being to determine the pH's of solutions of concentration (*a*) 0·005M-NaHA, 0·005M-MCl_2 (or MCl_3) and (*b*) 0·005M-NaHA, 0·015M-MCl_2 (or MCl_3) by means of the glass electrode. pH has been taken as defined by $\mathrm{pH} = -\log f_1[\mathrm{H}^{\bullet}]$, where f_1 is the mean activity coefficient for univalent ions. The calculation method was essentially that of Stock and Davies (*loc. cit.*), the concentration of undissolved metal dicarboxylate being obtained as follows. The ionic species present are: $\mathrm{H}^{\bullet}$, $\mathrm{Na}^{\bullet}$, Cl′, $\mathrm{M}^{\bullet\bullet}$, MA, A″, HA′, H_2A, and OH′ (metal chlorides and sodium dicarboxylates are known to be highly dissociated. On general grounds it appears unlikely that other ionic species such as $\mathrm{MHMal}^{\bullet}$ are present in appreciable concentrations). Then the concentrations of $\mathrm{Na}^{\bullet}$ and Cl′ are known, that of OH′ is negligible in acid solution, and the remaining concentrations can be calculated from (i) the measured $pf[\mathrm{H}^{\bullet}]$ value, (ii) the electroneutrality equation, (iii) the known total concentration of bivalent metal, and (iv) and (v) the pK_1 and pK_2 values for the dicarboxylic acid. For tervalent cations $\mathrm{M}^{\bullet\bullet\bullet}$, the concentration of intermediate ion $\mathrm{MA}^{\bullet}$ is found in a similar way. Ionic strengths I can then be calculated from $I = \frac{1}{2}\Sigma \mathrm{m}_i z_i^2$, where m_i is the molar concentration of ions of type i and valency z_i.

Typical results are given for illustration purposes in Table I.

TABLE I.

Ion association in malonate solutions.

Concentration (millimols./l.)	$pf_1[\mathrm{H}^{\bullet}]$	H_2Mal	Mal″	$\mathrm{La}^{\bullet\bullet\bullet}$	$\mathrm{LaMal}^{\bullet}$	HMal′	I	$K \times 10^5$
0·005M-$LaCl_3$ + 0·005M-NaHMal	3·36	0·823	0·0256	4·01	0·992	3·17	31·176	1·4
0·015M-$LaCl_3$ + 0·005M-NaHMal	3·16	1·15	0·0195	13·9	1·09	2·8	92·890	1·2

Dissociation constants have been calculated from the equations $K = [\mathrm{M}^{\bullet\bullet}][\mathrm{A}'']f_{\pm}^2/[\mathrm{MA}]$ for bivalent cations and $K = [\mathrm{M}^{\bullet\bullet\bullet}][\mathrm{A}''] \,.\, f_{\mathrm{M}^{\bullet\bullet\bullet}} f_{\mathrm{A}''}/[\mathrm{MA}^{\bullet}]f_{\mathrm{MA}^{\bullet}}$ for tervalent cations, and are summarised in Table II. The ionic strengths of the solutions used in the present work were too great for the limiting form of the Debye–Hückel equation to be applied, and the empirical extension due to Davies (*J.*, 1938, 2093) has therefore been used for calculation of the activity coefficients.

TABLE II.

Dissociation constants ($K \times 10^4$) *of metal dicarboxylates.*

	CuX	$\mathrm{LaX}^{\bullet}$	$\mathrm{Co(NH_3)_6X}^{\bullet}$		CuX	$\mathrm{LaX}^{\bullet}$	$\mathrm{Co(NH_3)_6X}^{\bullet}$
Malonate	0·0144	0·13	2·9	Phthalate	0·86	0·18	1·8
Succinate	4·7	1·1	11·5	Maleate	1·25	0·28	0·61
Glutarate	6·9	1·5	6·7	Fumarate	31	9·8	43
Adipate	4·2	0·8	4·5				

In the above treatment no account has been taken of further association to give complex ions of the type $\mathrm{M_2A}^{\bullet\bullet}$ and $\mathrm{MA_2}''$. This assumption, which has also been made by previous workers [*e.g.*, Stock and Davies (*loc. cit.*)], appears to be justified at the low concentrations studied.

Conductivity Measurements.—Copper malonate. Salts with abnormally low dissociation constants often show a marked tendency to auto-complex formation, examples being ferrous oxalate and nickel oxalate solutions, for which the conductivities provide evidence of complex formation even in very dilute solution. As copper malonate also appears to be an abnormally weak salt, the use of a potentiometric method neglecting auto-complex formation might not be justifiable here. For this reason, the dissociation constant for copper malonate has also been determined directly from conductivity measurements on dilute aqueous solutions. The results are tabulated in Table III.

TABLE III.

Conductivities of copper malonate solutions at 25° (*c* is given in g.-equivs./l.).

10^4c	Λ	$10^6K'$	10^4c	Λ	$10^6K'$	10^4c	Λ	$10^6K'$	10^4c	Λ	$10^6K'$
Run 1. $K_{H_2O} = 2·92 \times 10^{-7}$.						Run 2. $K_{H_2O} = 5·16 \times 10^{-7}$.					
3·5562	11·57	$1·80_5$	12·835	7·03	2·25	2·4573	13·46	1·73	9·3800	7·78	$2·04_5$
6·0796	9·28	1·93	15·972	6·54	2·41	4·3379	10·54	1·80	13·327	6·86	2·22
9·4586	7·84	$2·09_5$	18·594	6·25	2·54	6·9210	8·74	1·93	18·041	6·22	2·51

At 25°, combination of the value $\Lambda_0(\mathrm{Cu}^{\bullet\bullet}) = 53·6$ given by Owen and Gurry (*J. Amer. Chem. Soc.*, 1938, **60**, 3074) for the copper ion with Jeffrey and Vogel's (*J.*, 1935, 21) value of 64·7 for the malonate ion leads to $\Lambda_0 = 118{\cdot}3$ for the conductivity at infinite dilution. The limiting Onsager and Debye–Hückel equations then become

$$\Lambda = 118{\cdot}3 - 228{\cdot}6I^{\frac{1}{2}} \text{ and } -\log f_{\pm}^{2} = 4{\cdot}074I^{\frac{1}{2}}$$

The ionic strength is given by $I = 2\alpha c$, where c is the concentration in g.-equivs./l. Values for α, the degree of dissociation, have been calculated, and dissociation constants, K', have then been calculated for each point from the equation

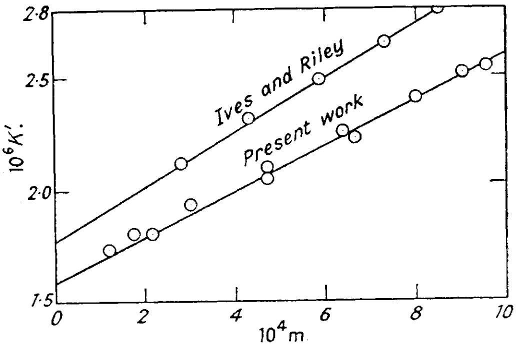
$$\log K' = -\ 4{\cdot}074I^{\frac{1}{2}} + \log\ [\alpha^2 c/2(1 - \alpha)]$$

Values of K' are given in Table III, and have been plotted against c in Fig. 1; a steady increase in K' with increase in concentration occurs, presumably because of further association to give complex ions Cu_2Mal^{++} and $CuMal_2''$. A short linear extrapolation to zero concentration gives $K = 1{\cdot}59 \times 10^{-6}$ for the true dissociation constant of copper malonate.

Ives and Riley (*loc. cit.*) obtained the value $K = 2{\cdot}5 \times 10^{-6}$ from conductivity measurements; these workers, however, used the value $\Lambda_0 = 113{\cdot}8$ as a basis for calculation. Recalculation of this result, Λ_0 being taken as 118·3, gave results which have been plotted in Fig. 1, and lead to the value $K = 1{\cdot}77 \times 10^{-6}$ on extrapolation to zero concentration. The potentiometric method gives $K = 1{\cdot}4_4 \times 10^{-6}$, and although the agreement with the conductivity method may be to some extent caused by a compensation of errors, it would appear that the primary dissociation constants derived from this method are not greatly in error, and may safely be used for the purpose of making a general survey of the extent of dissociation of metal dicarboxylates.

FIG. 1.

The dissociation of copper malonate solutions.



Hexamminocobaltic oxalate. The dissociation of this salt has been studied by conductivity measurements on very dilute aqueous solutions, since the solubility (0·383 millimol./l.) is too low for convenient application of the potentiometric method. The results are set out in Table IV.

TABLE IV.

Conductivities of hexamminocobaltic oxalate solutions at 25° (*c* in g.-equivs./l.).

(*c* in g.-equivs./l.)

10^4c	4·5960	5·3031	5·9578	9·1920	10·213	13·788	9·722
Λ	134·0	132·3	128·9	123·3	120·4	114·7	121·2
$K \times 10^4$	4·58	4·97	4·73	4·92	5·44	5·64	5·38

The conductivity at infinite dilution has been taken to be 173·3, from the values $\Lambda_0[Co(NH_3)_6^{\cdot\cdot\cdot}] = 99{\cdot}2$ (Jenkins and Monk, *J.*, 1951, 68) and $\Lambda_0(C_2O_4'') = 74{\cdot}1$ (Darken, *J. Amer. Chem. Soc.*, 1940, **62**, 846). Marked deviations from the limiting Onsager equation occur even in very dilute solution, as is to be expected with a salt of this valency type. The extent of such association has been estimated by the method described by Jenkins and Monk (*ibid.*, 1950, **72**, 2695) for the similar 3—2-valency type electrolyte lanthanum sulphate. In the present case, deviations from the limiting Onsager equation have been ascribed to formation of the intermediate ion $[Co(NH_3)_6][C_2O_4]^{\cdot}$, the mobility for this ion being taken as $\frac{1}{3} \times 99{\cdot}2 = 33$. Values derived for the dissociation constant of this ion are given in Table IV. The drift in K values does not appear to be due to auto-complex formation, since solubility measurements (James, unpublished work) give no indication of such tendencies, but is probably the result of the approximations necessarily made in the calculation. Extrapolation to zero concentration gives the value $4{\cdot}0 \times 10^{-4}$ for K.

Barium dicarboxylates. As these salts are too extensively dissociated in aqueous solution for the potentiometric method to be applied, recourse has been had to the conductometric method described by Topp and Davies (*J.*, 1940, 87). Conductivity titrations of dicarboxylic acids have been carried out with standard baryta, rigorous precautions being taken to exclude atmospheric carbon dioxide. The conductivities for the barium salts of the acids were obtained from the end-point conductivities of these titrations, corrections for hydrolysis and solvent conductivity being made by Jeffery and Vogel's method (*loc. cit.*). Conductivities at infinite dilution were obtained by combining Shedlovsky and Brown's value (*J. Amer. Chem. Soc.*, 1934, **56**, 1066) of $\Lambda_0(\text{Ba}^{\bullet\bullet}) = 63{\cdot}64$ with Jeffery and Vogel's (*loc. cit.*) values for the dicarboxylate ions. Results are given in Table V, values for the degree of dissociation α and the dissociation constant K having been calculated for each point by Topp and Davies's method (*loc. cit.*).

TABLE V.

The dissociation of barium dicarboxylates (c in g.-equivs./l.).

10^3c.	Λ.	10^3K.	10^3c.	Λ.	10^3K.	10^3c.	Λ.	10^3K.	10^3c.	Λ.	10^3K.
Barium malonate.			Barium succinate.			Barium glutarate.			Barium adipate.		
1·551	110·6	8·5	1·515	107·6	9·0	1·776	102·1	8·1	1·385	101·1	10
1·899	107·7	7·2	1·855	105·7	8·8	2·088	102·4	12	1·995	100·1	15
2·234	105·2	6·5	2·144	102·9	7·2	2·696	97·5	7·5	2·559	97·2	12

Mean values for K :

	Oxalate.	Malonate.	Succinate.	Glutarate.	Adipate.
Barium	0·0047	0·0074	0·0083	0·0092	0·012

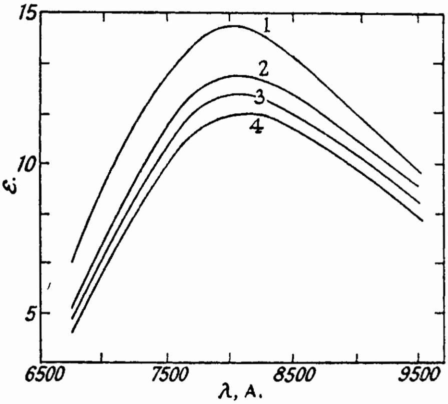
Topp and Davies found $K = 0{\cdot}027$ for barium succinate and $K = 0{\cdot}014$ for barium adipate. The difference between their value and our own would appear to be due to our use of Jeffery and Vogel's values for dicarboxylate ionic mobilities at infinite dilution. Recalculation of Topp and Davies's results on this basis gives $K = 0{\cdot}011$ for barium succinate and $K = 0{\cdot}014$ for barium adipate, in good agreement with our own values.

Spectrophotometric Measurements.—Cupric ion. It has been known for some time that the intensity and wave-length of the cupric-ion absorption peak are markedly displaced in solutions containing anions of organic acids, and use has been made of these effects in the investigation of the formulæ and stability of copper complexes; *e.g.*, spectrophotometric methods have been used by Bobtelsky and Jordan (*J. Amer. Chem. Soc.*, 1945, **67**, 1824) to investigate citrate and tartrate complexes, and by Klotz, Faller, and Urquhart (*J. Phys. Chem.*, 1950, **54**, 18) with copper–protein complexes. It seemed of interest to extend such studies to the cupric salts of dicarboxylic acids, for which no data appear to be available.

In Fig. 2 absorption curves are given for 0·06M-copper sulphate solution and for mixtures with dicarboxylic acids. An appreciable increase in the extent of absorption occurs with malonic acid and, to a lesser extent, with succinic, glutaric, and adipic acids. Similar increases

FIG. 2.

The effect of dicarboxylic acids on the optical absorption of aqueous copper sulphate solutions.



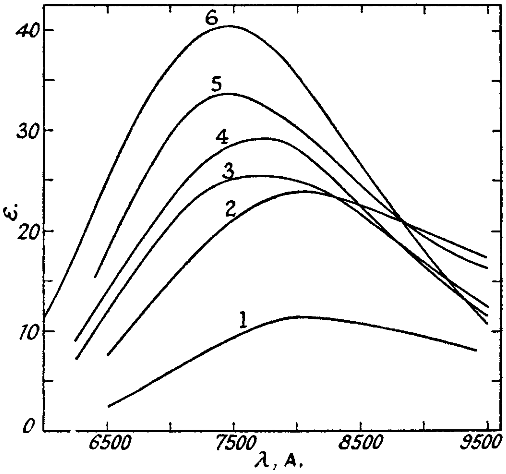
Curve 1. 0·06M-*Copper sulphate*
+0·10M-*malonic acid.*
2. ,, +0·10M-*succinic acid.*
3. ,, +0·10M-*glutaric acid.*
3. ,, +0·10M-*adipic acid.*
4. ,, .

were observed with maleic, fumaric, phthalic, and tartaric acids. In Fig. 3 absorption curves are given for solutions containing equimolecular amounts of copper sulphate and the sodium dicarboxylate; the changes which occur are far more marked than in Fig. 2, as is to be expected if the dicarboxylate group must be ionised for complex formation to occur.

Copper succinate, glutarate, and adipate were too insoluble in neutral solution for the absorptions to be studied.

FIG. 3.

The optical absorption of copper sulphate–sodium dicarboxylate solutions.



Curve 1. 0·02M-*Copper sulphate.*
2. „ +0·02M-*sodium tartrate*, pH 5·42.
3. „ +0·02M-*sodium malonate*, pH 4·09.
4. „ +0·02M-*sodium malate*, pH 4·04.
5. „ +0·02M-*sodium phthalate*, pH 5·70.
6. „ +0·02M-*sodium citrate*, pH 4·00.

FIG. 4.

Optical absorption of solutions containing 0·02M-*copper sulphate and varying amounts of sodium malate.*

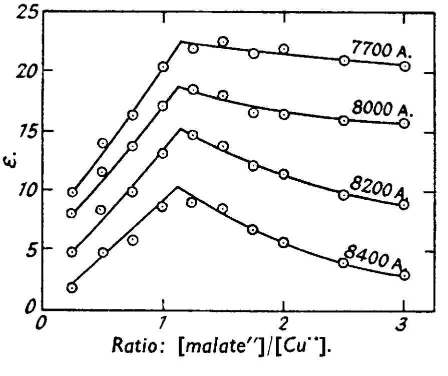
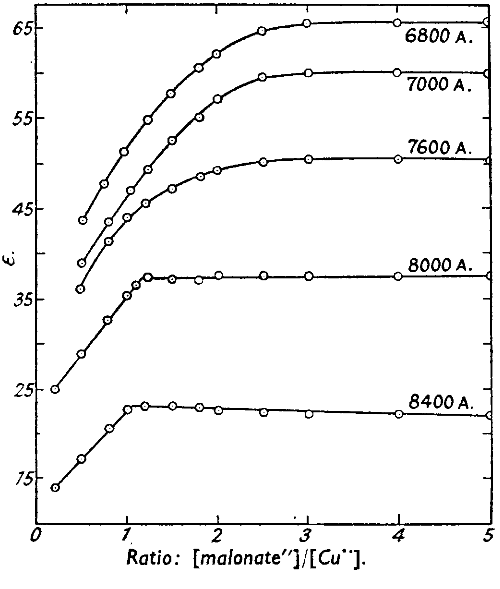


FIG. 5.

Optical absorption of solutions containing 0·02M-*copper sulphate and varying amounts of sodium malonate.*



The absorptions of solutions containing 0·02 g.-mol./l. of copper sulphate and varying amounts of sodium malate have been studied, and in Fig. 4 optical extinctions have been plotted against the mol. ratio $[\text{malate}'']/[\text{Cu}^{\bullet\bullet}]$ for a series of different wave-lengths in the absorption band. At each wave-length a definite break is obtained at a point corresponding to reaction in the mol. ratio of 1 : 1. Copper lactate was found to behave in the same way, although the lower complex stability causes less sharp breaks in the extinction curves. Bobtelsky and Jordan (*loc. cit.*) report similar results for copper and nickel citrates and for nickel tartrate.

The results of similar measurements on solutions containing copper sulphate and sodium malonate are given in Fig. 5. The results are less satisfactory in this case, as the location of the intercept varies with wave-length, indicating that at least two absorbing species are formed, corresponding probably to CuMal and $CuMal_2''$. With the corresponding copper phthalate system, although marked absorption changes occurred, no definite points of inflection could be detected in the curves, presumably because of the lower stability of the complex.

Hexamminocbaltic ion. In aqueous solution the hexamminocobaltic ion shows absorption maxima at 4714 A. and 3376 A. (Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 5), the first band being generally attributed to electron transitions in the unsaturated transition shell of the central atom and the second band to co-ordination electrons. On adding sodium dicarboxylate solutions to 0·01M-solutions of hexamminocobaltic chloride, we could detect no change in the intensity and location of these bands, indicating that interaction between cation and dicarboylate anion was not marked enough to disturb the optical electrons of the hexamminocobaltic ion. It is probable that any association which may occur is purely electrostatic, to give ion pairs, as is to be expected from the stable electronic configuration of the cation. In this connection it is of interest that with lanthanum ferricyanide solutions no change in the absorption spectrum of the ferricyanide ion could be detected, although extensive ion-pair formation has been shown to occur (James and Davies, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116).

Polarographic Measurements.—The half-wave potential of cupric ion is considerably displaced in presence of citrate ion, and Bobtelsky and Jordan (*loc. cit.*) have utilised this effect for the determination of the dissociation constant of cupric citrate by an amperometric titration method. As it appeared possible that a similar method might be applied to copper malonate, exploratory polarographic measurements were made. No displacement in the half-wave potential for cupric ion could be detected in copper malonate solutions, however, presumably because the complex stability was insufficiently great.

Discussion.—Dissociation constants obtained for metal dicarboxylates in the present work are given in Table VI, together with previous data. With the dicarboxylic acid series $[CH_2]_x(CO_2H)_2$ there is a general tendency for dicarboxylate stability to decrease as x increases. This is particularly noticeable with transition-type metal ions, a 500-fold increase in K occurring on passing from zinc oxalate to glutarate, whereas only a 2-fold increase occurs with the corresponding barium salts. It has been suggested by Jones, Monk, and Davies (*J.*, 1949, 2693) that the magnitude of a dissociation constant is dependent mainly on two factors, the hydration energy of the cation and the energy of interaction of the associating ions. It seems probable that with cations such as magnesium, barium, lanthanum, and hexamminocobalt relatively little chelation occurs, and that the interaction energy is largely of an electrostatic nature. Transition-metal ions have much stronger chelating tendencies, and the stabilities of their dicarboxylates will in consequence be far more markedly dependent on ring size.

TABLE VI.

Dissociation constants ($K \times 10^4$) *of metal dicarboxylates.*

	$Co(NH_3)_6X^{\cdot}$	$LaX^{\cdot}$	MgX	CaX	BaX	ZnX	CuX
Oxalate	4·0	—	(3·7[1], 5·6[2])	(10[3])	(47[3])	(0·13[3], 0·099[4])	(0·007[5])
Malonate ...	2·9	0·13	(14[6], 25[2])	(32[6], 69[2])	74 (196[6], 117[2])	(1·79[7], 2·1[8], 3·3[2])	0·0159 (0·018[8])
Succinate ...	11·5	1·1	(126[2])	(40[9], 126[2])	83 (110°, 186[2])	(33[2])	4·7
Glutarate ...	6·7	1·5	(166[2])	(174[2])	92	(50[2])	6·9
Adipate	4·5	0·8	—	(64[9])	120 (140[9])	—	4·2
Phthalate ...	1·8	0·18	—	—	—	—	0·86
Maleate	0·61	0·28	—	(37[9])	(55[9])	—	1·25
Fumarate ...	43	9·8	—	(100[9])	(260[9])	—	31

[1] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351. [2] Cannan and Kibrick, *loc. cit.* [3] Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609. [4] Vosburgh and Beckman, *loc. cit.* [5] Ives, *J.*, 1933, 1360. [6] Stock and Davies, *loc. cit.* [7] James, *J.*, 1951, 153. [8] Ives and Riley, *loc. cit.* [9] Topp and Davies, *loc. cit.*

Note.—Cannan and Kibrick's constants, which were originally given for an ionic strength of $I = 0·20$, have been recalculated for $I = 0$ by using the conversion factor given by these authors. Topp and Davies's data for succinates and adipates, and those of Ives and Riley for copper malonate have been recalculated as described previously.

Abnormally weak salts usually form auto-complexes readily, as is shown by Vosburgh and Beckman's solubility measurements (*J. Amer. Chem. Soc.*, 1940, **62**, 1028) for zinc and cadmium oxalates and by Ives and Riley's conductivity measurements (*loc. cit.*) for copper malonate. The dicarboxylates of magnesium, calcium, barium, and hexamminocobalt are much stronger salts, and solubility measurements show that no appreciable tendency to auto-complex formation exists (Money and Davies, *J.*, 1934, 400; James, unpublished work).

Maleates and fumarates show differences in K which are to be expected on steric grounds, the variation being especially marked with tervalent ions, which can chelate with maleate but not with fumarate ions, as can be seen from the following dissociation constant ratios for fumarates and maleates :

Cation	$Ca^{\cdot\cdot}$	$Ba^{\cdot\cdot}$	$Co(NH_3)_6^{\cdot\cdot\cdot}$	$La^{\cdot\cdot\cdot}$	$Cu^{\cdot\cdot}$
$K_{\text{fumarate}}/K_{\text{maleate}}$	2·70	4·7	70	35	25

Phthalates appear to occupy a position intermediate in strength between malonates and succinates, and are slightly weaker than maleates.

EXPERIMENTAL.

Hexamminocobaltic chloride and oxalate were prepared and purified by the method of Bjerrum and Reynolds (" Inorganic Syntheses," McGraw-Hill, 1946, Vol. II, Chap. 8), and copper malonate by the method of Ives and Riley (*loc. cit.*). Other materials were Kahlbaum or AnalaR samples, and were used without further purification.

Measurements of pH were made at 25° by the glass-electrode method, Smith and Speakman's " reproducible liquid junction " apparatus (*Trans. Faraday Soc.*, 1948, **44**, 1031) being used in conjunction with a Marconi bench-model pH meter. Standardisation was effected with suitable buffer solutions, as recommended by Hitchcock and Taylor (*J. Amer. Chem. Soc.*, 1937, **59**, 1812). Conductivity measurements on copper malonate and hexamminocobaltic oxalate solutions were carried out with equipment similar to that described previously (Davies, *J.*, 1937, 432; James and Davies, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116). The quartz cell used was of the Hartley and Barrett type, and was calibrated by Davies's method (*Trans. Faraday Soc.*, 1929, **25**, 129). Concentrations of copper malonate stock solutions were determined gravimetrically. Hexamminocobaltic oxalate solutions of known concentration were prepared by dilution of a saturated solution at 25°, the solubility of the salt having been determined by the method of Money and Davies (*loc. cit.*). Conductivities for barium salts of dicarboxylic acids were obtained by using the titration method described by Topp and Davies (*J.*, 1940, 87). Optical absorption measurements were made with a Unicam spectrophotometer and 1-cm. quartz cells. Exploratory polarographic measurements were made by means of manual apparatus of the type described by Kolthoff and Lingane (" Polarography," Interscience Publishers Inc., N.Y., 1946, p. 215).

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