

## 52 *The Dissociation Constants in Water of Some Bivalent Metal Alkanedicarboxylates.*

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A colorimetric method is described for determining the dissociation constants of some bivalent metal alkanedicarboxylates in aqueous solution. The method has been applied to the salts of copper (cupric), nickel, cobalt, manganese, cadmium, magnesium, calcium, and barium with malonic, succinic, glutaric, adipic, and  $\alpha$ -methyl-,  $\beta$ -methyl-, and  $\beta\beta$ -dimethyl-glutaric acids. The effects of the nature of the ligands on the dissociation constants are discussed.

THE existence of ion association in aqueous solutions of bi-bivalent metal salts has long been recognised,<sup>1,2</sup> and though electrometric or conductimetric methods are those most generally used for its study it has previously been shown<sup>3</sup> that a colorimetric method has a number of advantages. In this earlier work colour comparisons were made by means of a simple visual comparator, and the pH values of the solutions could be determined to an accuracy of 0.01 pH unit. In the present paper the range of salts examined has been extended by making measurements on a number of salts of seven alkanedicarboxylic acids, and the comparison technique refined by making use of a Unicam S.P. 600 spectrophotometer in place of the visual comparator, whereby the accuracy has been increased to an estimated uncertainty of  $\pm 0.002_5$  pH unit. In particular the effect on the stability of the complex of substitution in the methylene chain, and of chain length, has been investigated.

*Ion Association in Alkanedicarboxylate Solutions.*—The solutions were prepared by the addition of a stock solution of the bivalent metal chloride to a dicarboxylic acid solution approximately half-neutralised with sodium hydroxide. A standard volume of indicator solution was added, and the whole made up to a standard volume with conductivity water. The colours of these solutions were then matched against those of standard buffer solutions containing the same concentration of indicator. These standards were prepared from partly neutralised solutions of monobasic weak acids, the hydrogen-ion concentrations of which could be calculated very accurately from known dissociation constants. It has been shown<sup>3</sup> that equality of colour in two solutions containing sulphonephthalein indicators such as Bromophenol Blue and Bromocresol Green, used in the present work, will indicate identity not of pH but of the quantity  $p f_2 H^+ = -\log_{10} f_2 [H^+]$ , where  $f_2$  signifies the activity coefficient of a bivalent ion, and  $[H^+]$  the concentration of hydrogen ions. The addition of a bivalent cation to a dicarboxylate buffer invariably increases the hydrogen-ion concentration, owing primarily to the reaction  $M^{2+} + HA^- = MA + H^+$ . The concentration of the associated species MA can then be calculated as follows. The solution contains, besides indicator, the following species:  $Na^+$ ,  $Cl^-$ ,  $M^{2+}$ , MA,  $A^{2-}$ ,  $HA^-$ ,  $H_2A$ ,  $H^+$ , and  $OH^-$ . The species  $MCl^+$  and  $NaA^-$  can be discounted as the sodium alkanedicarboxylates and the metal chlorides are known to be highly dissociated at the concentrations used. There is also the possibility of there being some  $MOH^+$  and  $MHA^+$ . Of all these species, the concentrations of  $Na^+$  and of  $Cl^-$  are known, while that of  $MHA^-$ , though unknown, is certainly very unlikely to be large enough to affect the relative concentrations of the other species. Calculations also show that the concentration of  $MOH^+$  is quite negligible, even in the most unfavourable case of copper. There now remain six species whose concentrations must be determined. These can be evaluated by successive approximations from the six simultaneous equations: (i) the experimentally determined  $p f_2 [H^+]$  value, (ii) the equation for electroneutrality, (iii) the known total

<sup>1</sup> Davies, *Trans. Faraday Soc.*, 1927, **23**, 354.

<sup>2</sup> Davies, *Discuss. Faraday Soc.*, 1957, **24**, 83.

<sup>3</sup> Stock and Davies, *J.*, 1949, 1371.

acid-radical concentration, (iv) the known total concentration of bivalent metal, (v) and (vi) the first and second dissociation constants of the dibasic acids. In this work, in order to minimise errors in computing activity coefficients, the ionic strengths ( $I$ ) of the test solution and of the comparison buffer were made approximately equal by the addition of potassium chloride to the latter.  $I$  was always in the range  $0.035 \pm 0.006$ , so that Davies's activity equation <sup>4</sup> (*viz.*  $\log f_i = -0.5 z_i^2 \{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.2I\}$ ) was used to compute activity coefficients, it having been shown <sup>4</sup> to be applicable up to ionic strengths of 0.05, within the accuracy at which we were aiming.

The composition of each bivalent metal alkanedicarboxylate solution must satisfy the equations:

$$\left. \begin{aligned} K_1 &= [\text{H}^+][\text{HA}^-]f_1^2/[\text{H}_2\text{A}] f_0 \dots\dots\dots (a) \\ K_2 &= [\text{H}^+][\text{A}^{2-}]f_2/[\text{HA}^-] \dots\dots\dots (b) \end{aligned} \right\} \begin{array}{l} \text{First and second} \\ \text{dissociation constants} \\ \text{of the acid} \end{array}$$

(the activity coefficients  $f_1$  of the two univalent ions being taken as equal)

$$\begin{aligned} [\text{H}^+] + [\text{Na}^+] + 2[\text{M}^{2+}] &= [\text{Cl}^-] + [\text{HA}^-] + 2[\text{A}^{2-}] \dots (c) \text{ (electroneutrality)} \\ [\text{A}^{2-}] + [\text{HA}^-] + [\text{H}_2\text{A}] + [\text{MA}] &= \text{total acid-radical concentration} \dots (d) \\ [\text{M}^{2+}] + [\text{MA}] &= \text{total bivalent-metal concentration} \dots\dots\dots (e) \end{aligned}$$

The most convenient method of solving these equations is to estimate  $I$  from the stoichiometric salt composition, and hence to obtain values for  $f_1$  and  $f_2$  by use of Davies's equation. From the composition of the comparison buffer the value of  $f_2[\text{H}^+]$  in the test solution is known, and hence a first approximation for  $[\text{H}^+]$ . Now, by eliminating  $[\text{MA}]$ ,  $[\text{A}^{2-}]$ , and  $[\text{HA}^-]$  between equations (a), (c), (d), and (e) it can easily be shown that

$$[\text{H}_2\text{A}] = \{2(\text{total acid}) - [\text{Na}^+] - [\text{H}^+]\}f_1^2[\text{H}^+]/(K_1 + 2f_1^2[\text{H}^+]),$$

giving a first value for  $[\text{H}_2\text{A}]$ . The concentrations of the species  $\text{HA}^-$ ,  $\text{A}^{2-}$ ,  $\text{MA}$ , and  $\text{M}^{2+}$  are then obtained successively from equations (a), (b), (d), and (e).  $[\text{Na}^+]$  and  $[\text{Cl}^-]$  being known, a second approximation for  $I$  is obtained, and the whole calculation repeated to constancy. Columns 4—14 in Table 1 show the final values for these variables. The dissociation constant of the species  $\text{MA}$  is then calculated from the equation  $K_{\text{MA}} = f_2^2[\text{M}^{2+}][\text{A}^{2-}]/f_0[\text{MA}]$ ,  $f_0$  being taken as unity—a reasonable assumption in solutions of ionic strengths as low as these.

These dissociation constants (expressed as  $\text{p}K_{\text{MA}}$  values) are given in column 15 in Table 1. The first and the second dissociation constant of the acids used were those determined in a previous paper,<sup>5</sup> except for the  $K_2$  of  $\beta\beta$ -dimethylglutaric acid, which is too small to be obtained with the necessary accuracy by our method, and for which a mean of previous values has been used. Columns 2 and 3 in Table 1 show the total stoichiometric concentrations of  $\text{MCl}_2$  and of dicarboxylate radical respectively, these being expressed in g. formula weights per litre, as are all the other concentrations.

#### EXPERIMENTAL

The procedure described above was applied to the salts of barium, calcium, magnesium, cadmium, manganese (ous), cobalt, nickel, and copper (cupric), with the acids malonic, succinic, glutaric, adipic, and  $\alpha$ -methyl-,  $\beta$ -methyl-, and  $\beta\beta$ -dimethyl-glutaric. These acids, together with the mandelic and benzoic acid used for preparing the standard buffer solutions, were purified as previously described.<sup>5</sup> The metal chlorides were of "AnalaR" grade, used without

<sup>4</sup> Davies, *J.*, 1938, 2093.

<sup>5</sup> Jones and Stock, *J.*, 1960, 102.

TABLE I.  
Analysis of buffer solutions.

| Cation   | Total "M" ( $\times 10^3$ ) | Total "A" ( $\times 10^3$ ) | [Na <sup>+</sup> ] ( $\times 10^3$ ) | $f_2$ [ $\times 10^5$ ] | [H <sup>+</sup> ] ( $\times 10^5$ ) | [H <sub>2</sub> A] ( $\times 10^4$ ) | [HA <sup>-</sup> ] ( $\times 10^3$ ) | [A <sup>-</sup> ] ( $\times 10^5$ ) | [MA] ( $\times 10^4$ ) | [M <sup>+</sup> ] ( $\times 10^3$ ) | I      | $f_1$  | $f_2$  | pK <sub>M,A</sub> |
|--|-----------------------------|-----------------------------|--------------------------------------|-------------------------|-------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|------------------------|-------------------------------------|--------|--------|--------|-------------------|
| Malonate Buffers   |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.0917                      | 4.686                       | 5.172                                | 85.31                   | 164.9                               | 8.11                                 | 0.929                                | 0.218                               | 29.44                  | 7.973                               | 0.0307 | 0.8432 | 0.5175 | 5.80              |
| Ni <sup>2+</sup>   | 1.0500                      | 4.686                       | 5.857                                | 6.214                   | 12.23                               | 1.75                                 | 2.723                                | 8.76                                | 15.40                  | 8.960                               | 0.0329 | 0.8443 | 0.5081 | 3.89              |
| Co <sup>2+</sup>   | 1.0448                      | 5.857                       | 5.857                                | 5.192                   | 10.22                               | 1.50                                 | 2.792                                | 10.8                                | 14.75                  | 8.973                               | 0.0330 | 0.8442 | 0.5079 | 3.77              |
| Mn <sup>2+</sup>   | 0.8444                      | 4.525                       | 5.123                                | 4.388                   | 8.326                               | 1.57                                 | 3.529                                | 16.1                                | 6.78                   | 7.765                               | 0.0287 | 0.8521 | 0.5271 | 3.29              |
| Cd <sup>2+</sup>   | 1.2753                      | 4.525                       | 5.123                                | 4.255                   | 8.936                               | 1.60                                 | 3.520                                | 16.5                                | 6.80                   | 12.073                              | 0.0416 | 0.8308 | 0.4762 | 3.18              |
| Mg <sup>2+</sup>   | 1.1117                      | 4.525                       | 5.123                                | 2.747                   | 5.594                               | 1.06                                 | 3.659                                | 26.6                                | 4.94                   | 10.623                              | 0.0373 | 0.8371 | 0.4910 | 2.86              |
| Ca <sup>2+</sup>   | 1.0889                      | 4.552                       | 4.393                                | 5.965                   | 12.12                               | 2.55                                 | 4.080                                | 13.7                                | 0.80                   | 10.809                              | 0.0371 | 0.8375 | 0.4919 | 2.35              |
| Ba <sup>2+</sup>   | 1.0917                      | 4.525                       | 4.393                                | 5.112                   | 10.41                               | 2.21                                 | 4.113                                | 16.1                                | 0.30                   | 10.886                              | 0.0373 | 0.8371 | 0.4910 | 1.85              |
| Succinate Buffers  |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.0917                      | 4.587                       | 4.373                                | 2.872                   | 5.707                               | 13.63                                | 2.017                                | 14.0                                | 10.67                  | 9.850                               | 0.0341 | 0.8423 | 0.5033 | 3.48              |
| Cd <sup>2+</sup>   | 1.2753                      | 4.587                       | 3.749                                | 2.088                   | 4.378                               | 13.51                                | 2.679                                | 25.7                                | 3.00                   | 12.453                              | 0.0414 | 0.8310 | 0.4769 | 2.60              |
| Ni <sup>2+</sup>   | 1.0745                      | 4.884                       | 4.241                                | 1.808                   | 3.640                               | 12.66                                | 2.958                                | 32.7                                | 3.33                   | 10.412                              | 0.0358 | 0.8392 | 0.4966 | 2.62              |
| Co <sup>2+</sup>   | 1.0464                      | 4.587                       | 3.643                                | 2.095                   | 4.184                               | 13.63                                | 2.761                                | 26.4                                | 1.98                   | 10.266                              | 0.0347 | 0.8412 | 0.5008 | 2.47              |
| Mn <sup>2+</sup>   | 0.8444                      | 4.670                       | 3.865                                | 1.836                   | 3.497                               | 12.47                                | 2.947                                | 32.1                                | 1.55                   | 8.288                               | 0.0291 | 0.8512 | 0.5251 | 2.33              |
| Mg <sup>2+</sup>   | 1.0448                      | 4.587                       | 3.645                                | 1.836                   | 3.679                               | 12.76                                | 2.940                                | 32.0                                | 0.51                   | 10.397                              | 0.0352 | 0.8405 | 0.4991 | 1.79              |
| Glutarate Buffers  |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.0878                      | 4.581                       | 4.348                                | 2.236                   | 4.466                               | 13.99                                | 1.971                                | 34.8                                | 8.63                   | 10.015                              | 0.0348 | 0.8412 | 0.5006 | 3.00              |
| Cd <sup>2+</sup>   | 1.1394                      | 4.581                       | 4.270                                | 1.417                   | 2.916                               | 11.61                                | 2.541                                | 70.8                                | 1.71                   | 11.223                              | 0.0387 | 0.8350 | 0.4861 | 1.96              |
| Mn <sup>2+</sup>   | 0.8473                      | 4.581                       | 4.367                                | 1.291                   | 2.487                               | 10.64                                | 2.642                                | 80.8                                | 0.67                   | 8.406                               | 0.0304 | 0.8488 | 0.5190 | 1.56              |
| Adipate Buffers  |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.0680                      | 4.547                       | 4.294                                | 2.028                   | 4.026                               | 14.52                                | 1.856                                | 34.6                                | 8.93                   | 9.787                               | 0.0340 | 0.8424 | 0.5036 | 3.02              |
| Cd <sup>2+</sup>   | 1.1391                      | 4.545                       | 4.400                                | 1.187                   | 2.441                               | 11.26                                | 2.414                                | 76.9                                | 2.36                   | 11.155                              | 0.0387 | 0.8350 | 0.4862 | 2.07              |
| Co <sup>2+</sup>   | 1.0457                      | 4.544                       | 4.439                                | 1.105                   | 2.233                               | 10.70                                | 2.487                                | 85.1                                | 1.36                   | 10.321                              | 0.0363 | 0.8387 | 0.4949 | 1.80              |
| Ni <sup>2+</sup>   | 1.0610                      | 4.551                       | 4.308                                | 1.150                   | 2.331                               | 11.28                                | 2.515                                | 82.7                                | 0.81                   | 10.529                              | 0.0367 | 0.8380 | 0.4931 | 1.58              |
| $\alpha$ -Methylglutarate Buffers  |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.1073                      | 4.479                       | 3.636                                | 3.816                   | 7.593                               | 18.66                                | 1.514                                | 16.9                                | 9.30                   | 10.143                              | 0.0343 | 0.8420 | 0.5025 | 3.33              |
| Cd <sup>2+</sup>   | 1.2753                      | 4.479                       | 3.638                                | 2.532                   | 5.283                               | 16.49                                | 1.971                                | 33.1                                | 5.29                   | 12.224                              | 0.0407 | 0.8320 | 0.4792 | 2.75              |
| Mn <sup>2+</sup>   | 0.8444                      | 4.479                       | 3.641                                | 2.209                   | 4.181                               | 15.36                                | 2.203                                | 42.5                                | 3.15                   | 8.129                               | 0.0285 | 0.8524 | 0.5279 | 2.51              |
| Ni <sup>2+</sup>   | 1.0818                      | 4.479                       | 3.634                                | 2.117                   | 4.260                               | 15.28                                | 2.223                                | 44.6                                | 2.81                   | 10.537                              | 0.0357 | 0.8396 | 0.4970 | 2.38              |
| $\beta$ -Methylglutarate Buffers   |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.1073                      | 4.488                       | 3.638                                | 3.976                   | 7.925                               | 17.49                                | 1.761                                | 13.3                                | 8.45                   | 10.228                              | 0.0345 | 0.8416 | 0.5017 | 3.39              |
| Cd <sup>2+</sup>   | 1.2753                      | 4.488                       | 3.638                                | 2.665                   | 5.565                               | 15.24                                | 2.236                                | 25.2                                | 4.76                   | 12.277                              | 0.0408 | 0.8319 | 0.4790 | 2.83              |
| Mn <sup>2+</sup>   | 0.8444                      | 4.488                       | 3.638                                | 2.214                   | 4.202                               | 13.75                                | 2.547                                | 34.5                                | 2.21                   | 8.223                               | 0.0287 | 0.8520 | 0.5270 | 2.45              |
| Ni <sup>2+</sup>   | 1.0420                      | 4.488                       | 3.636                                | 2.142                   | 4.275                               | 13.70                                | 2.557                                | 35.8                                | 2.03                   | 10.217                              | 0.0347 | 0.8413 | 0.5011 | 2.34              |
| Co <sup>2+</sup>   | 1.0420                      | 4.488                       | 3.637                                | 1.955                   | 3.913                               | 13.11                                | 2.678                                | 41.1                                | 0.88                   | 10.322                              | 0.0351 | 0.8407 | 0.4995 | 1.92              |
| $\beta\beta$ -Dimethylglutarate Buffers  |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Cu <sup>2+</sup>   | 1.0800                      | 4.590                       | 4.276                                | 2.744                   | 5.517                               | 7.04                                 | 3.441                                | 5.5                                 | 3.90                   | 10.410                              | 0.0356 | 0.8398 | 0.4974 | 3.44              |
| Cd <sup>2+</sup>   | 1.0818                      | 4.611                       | 3.928                                | 3.287                   | 6.625                               | 8.60                                 | 3.508                                | 5.2                                 | 1.91                   | 10.627                              | 0.0359 | 0.8393 | 0.4962 | 3.15              |
| Mn <sup>2+</sup>   | 1.0924                      | 4.611                       | 4.074                                | 2.472                   | 5.016                               | 6.89                                 | 3.720                                | 7.4                                 | 1.28                   | 10.796                              | 0.0363 | 0.8383 | 0.4928 | 2.82              |
| Ni <sup>2+</sup>   | 1.0831                      | 4.110                       | 4.160                                | 2.063                   | 4.176                               | 5.92                                 | 3.836                                | 9.1                                 | 0.92                   | 10.739                              | 0.0365 | 0.8389 | 0.4940 | 2.58              |
| Co <sup>2+</sup>   | 1.0412                      | 3.741                       | 3.618                                | 3.576                   | 7.155                               | 0.96                                 | 3.618                                | 4.4                                 | 0.01                   | 10.411                              | 0.0350 | 0.8408 | 0.4999 | 1.92              |
| Adipate Buffers: $K_1 = 3.72 \times 10^{-5}$ (ref. 17); $K_2 = 1.1 \times 10^{-6}$ |                             |                             |                                      |                         |                                     |                                      |                                      |                                     |                        |                                     |        |        |        |                   |
| Mg <sup>2+</sup>   | 1.089                       | 4.544                       | 4.255                                | 0.986                   | 1.987                               | 10.34                                | 2.745                                | 30.6                                | 4.59                   | 10.44                               | 0.0359 | 0.8394 | 0.4964 | 2.77              |
| Ca <sup>2+</sup>   | 1.089                       | 4.544                       | 4.255                                | 0.964                   | 1.942                               | 10.21                                | 2.773                                | 31.7                                | 4.34                   | 10.46                               | 0.0360 | 0.8393 | 0.4961 | 2.73              |
| Ba <sup>2+</sup>   | 1.014                       | 4.544                       | 4.399                                | 0.815                   | 1.618                               | 8.92                                 | 2.889                                | 39.0                                | 3.74                   | 9.76                                | 0.0341 | 0.8424 | 0.5032 | 2.58              |

further purification. As some of these are hygroscopic a solution of approximately the required concentration was made up and then analysed for either metal or chloride (or, in the case of Mg, Co, and Ni, for both). The metal was determined volumetrically by complexometric titration, EDTA being used followed by back titration with standard zinc solution (Eriochrome Black indicator), and chloride gravimetrically as silver chloride. The values obtained by these two methods agreed to within 0.1%. The potassium chloride was also of "AnalaR" grade, thrice recrystallised from conductivity water. The sodium hydroxide solution was prepared as described in our previous paper<sup>5</sup>—which also includes a full account of the colour comparison technique for the determination of the function  $pf_2[H^+]$ .

## DISCUSSION

The available published data with which the present values can be compared are given in Table 2, together with our own. The succinate figures quoted by Davies<sup>2</sup> are those

TABLE 2.

| Dissociation constants of metal dicarboxylates (expressed as $pK_{MA}$ ). |                        |                        |                        |                        |                        |                        |                     |                     |
|---|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|---------------------|---------------------|
|   | Cu <sup>2+</sup>       | Ni <sup>2+</sup>       | Co <sup>2+</sup>       | Mn <sup>2+</sup>       | Cd <sup>2+</sup>       | Mg <sup>2+</sup>       | Ca <sup>2+</sup>    | Ba <sup>2+</sup>    |
| Malonate .....  | 5.80                   | 3.89                   | 3.77                   | 3.29                   | 3.18                   | 2.86                   | 2.35                | 1.85                |
|   | (5.55) <sup>3</sup>    | (4.00) <sup>3</sup>    | (3.72) <sup>3</sup>    | (3.29) <sup>3</sup>    | (3.25) <sup>3</sup>    | (2.85) <sup>3</sup>    | (2.49) <sup>3</sup> | (1.71) <sup>3</sup> |
|   | 5.80 <sup>8</sup>      |                        |                        |                        |                        | (2.80) <sup>16</sup>   |                     | (2.13) <sup>8</sup> |
| Succinate .....   | 3.48                   | 2.60                   | 2.47                   | 2.33                   | 2.62                   | 1.79                   |                     |                     |
|   | (3.40) <sup>2, 6</sup> | (2.39) <sup>2, 6</sup> | (2.43) <sup>2, 6</sup> | (2.25) <sup>2, 6</sup> | (2.82) <sup>2, 6</sup> | (2.05) <sup>2, 6</sup> |                     |                     |
|   | (3.33) <sup>8</sup>    |                        |                        |                        |                        |                        |                     |                     |
| Glutarate .....   | 3.00                   |                        |                        |                        |                        |                        |                     |                     |
|   | (3.16) <sup>8</sup>    |                        |                        |                        |                        |                        |                     |                     |
| Adipate .....   | 3.02                   |                        |                        |                        |                        |                        |                     |                     |
|   | (3.38) <sup>8</sup>    |                        |                        |                        |                        |                        |                     |                     |

The first figure quoted in each case refers to the present work.

of Stock,<sup>6</sup> and were calculated by a method which makes them not strictly comparable with ours. We have found that in the case of the stronger salts (notably those of Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup>) negative values for the concentration of the ion-pair MA, and hence for its dissociation constant, were obtained. This is almost certainly due to the fact that in these salts the concentration of the species MA is very small in any case, so that any small errors in the values used for the individual ion activity coefficients (and consequently in the concentrations of A<sup>2-</sup>, HA<sup>-</sup>, and H<sub>2</sub>A) will have an exaggerated effect on the calculated value of [MA]. Stock<sup>6</sup> found this for calcium and barium succinates, using the then available value of  $K_2$  for succinic acid. He therefore derived a new value for this  $K_2$  by the colorimetric comparison technique of Stock and Davies,<sup>3</sup> by matching a benzoate buffer with a succinate buffer containing potassium chloride. Complete dissociation of potassium succinate, equality of  $pf_2[H^+]$  in the two solutions, and the  $K_1$  of succinic acid being assumed,  $K_2$  was treated as the only unknown quantity. By this means positive values were obtained for the dissociation constants of barium succinate and of calcium succinate, with the concomitant result of making those of the other cations somewhat smaller. Having determined independent values for  $K_1$  and  $K_2$  in which we have confidence, we now prefer the metal salt dissociation constants given in column 15 in the Table, and merely conclude that those of the salts which are not reported are too high for this method to yield absolute values. However, to illustrate the point this method has been applied in the present work to the adipates of Mg, Ca, and Ba so as to show their relative strengths (end of Table 1). Where comparison is possible it is seen that our figures are in satisfactory agreement with those previously reported.

The present series of acids was chosen to show the effect, on the strengths of the salts, both of chain-length and of substitution within the chain. We reported, in a preliminary

<sup>6</sup> Stock, Thesis, London, 1946.

communication,<sup>7</sup> that the value of  $K$  increases markedly with the number of methylene groups between the carboxyl groups of the anions, until at succinic and adipic acids the calculated Bjerrum  $a$  values are not inconsistent with the assumption of an almost exclusively electrostatic character for the bond in the ion-pair. At the other extreme,  $K$  for copper malonate is only about  $1.6 \times 10^{-6}$ , so it is clear that no rigid distinction between purely electrostatic ion-pairs and chelate-type complexes can be maintained, at least in the present series. Our results also confirm the tendency, noted by Peacock and James,<sup>8</sup> that adipates tend to be slightly weaker than the corresponding glutarates.

That these results can be ascribed mainly to steric factors is borne out by the measurements of ion-association in the normal and the substituted glutarates. Gane and Ingold<sup>9,10</sup> determined the first and second dissociation constants of a number of acids in the series  $\text{HO}_2\text{C} \cdot [\text{CH}_2]_n \cdot \text{CO}_2\text{H}$ , and, from the values of  $K_1/K_2$ , calculated the intercarboxyl distance " $r$ ". They concluded that the most appropriate model for the normal acids was a plane zig-zag, the distance  $r$  increasing as  $n$  increases. Substitution in the methylene chain led to a reduction in the value for  $r$  from that of the unsubstituted acid, and it was suggested that the molecule assumed a coiled configuration. Since the size of the ions is one of the factors affecting the stability of an ion-pair, the results obtained in the present work agree with the above. If the effect of substitution in the methylene chain is to bend it, then it is reasonable to assume that the effective radius of the ion is thereby reduced. This should lead to an enhanced stability of the ion-pair. The closer proximity of the carboxyl groups would also facilitate the formation of a covalent bond between the two ions, this again leading to greater stability. Thus the  $\alpha$ - and  $\beta$ -methylglutarates are weaker than the corresponding normal glutarates. The introduction of a second substituent in the methylene chain has been shown to cause a further coiling of the molecule, and an ion-pair formed with this anion should have greater stability than one involving a monosubstituted anion; thus the  $\beta\beta$ -dimethylglutarates are more stable than the  $\alpha$ - and  $\beta$ -methylglutarates.

The study, by several workers,<sup>11,12,13,14</sup> of the stability order for the complexes of a number of bivalent metal ions with various ligands has led, in the case of the first transition group of metals, to the well-known "Irving-Williams" order of stabilities,  $\text{Zn} < \text{Cu} > \text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$ , which has been found to hold almost invariably for all metal chelates. The stabilities of the transition-metal complexes have been correlated with the cationic radii and the second ionisation potential, which is taken as a measure of the electron affinity of the cation.<sup>15</sup> The radii of the cations decrease slightly from manganese to copper, which is the order of increasing stability. The second ionisation potential increases from manganese to copper. If the sequence is extended by including other bivalent metals, the order of decreasing ionic radii will not necessarily be that of increasing stability. This is seen when the alkaline-earth metal complexes are considered. Although the radius of the magnesium ion is smaller than that of any of the transition metals, the stabilities of its complexes are much lower.

The stability of a complex depends mainly on two factors: (i) the hydration energy of the cation, and (ii) the energy of interaction of the ions. In most of the ion-pairs that have been studied in the present work it is apparent that the hydration energy plays a relatively insignificant part. When the order of stabilities follows that of the ionic radii, the interaction energy is the dominant factor. Deviations from this order can be

<sup>7</sup> Jones and Stock, *Discuss. Faraday Soc.*, 1957, **24**, 114.

<sup>8</sup> Peacock and James, *J.*, 1951, 2233.

<sup>9</sup> Gane and Ingold, *J.*, 1928, 1594.

<sup>10</sup> Gane and Ingold, *J.*, 1931, 2153.

<sup>11</sup> Mellor and Maley, *Nature*, 1947, **159**, 370.

<sup>12</sup> Monk, *Trans. Faraday Soc.*, 1951, **47**, 297.

<sup>13</sup> Irving and Williams, *J.*, 1953, 3192.

<sup>14</sup> Topp and Davies, *J.*, 1940, 89.

<sup>15</sup> Walsh, *Proc. Roy. Soc.*, 1951, *A*, **207**, 13.

attributed to the increasing contribution of the hydration energy. The anomalous position of magnesium in the series is due to its higher degree of hydration. The "Irving-Williams" order of stabilities holds for most of the ligands used, deviations beginning to appear as the number of carbon atoms in the acid increases. The inclusion of a metal not of the transition family causes disruption of the sequence, as expected. Cadmium changes its position in the sequence as the ligand varies. Although the radius of the cadmium ion is greater than that of the nickel ion, its ionisation potential is approximately the same, so that it is not unexpected to find the relative positions of these two cations varying with the ligand.

Irving and Williams based their order of stabilities on a study of the data for compounds which were chelate in character. The fact that the stabilities found in the present work are in the same order seems to indicate that chelation forces predominate in the salts studied. This is also borne out by a study of Bjerrum's  $a$  parameters calculated from the dissociation constants, which shows that Bjerrum's assumption of coulombic forces only between the ions is untenable in these instances. Data were not obtained for alkaline-earth metal salts other than the malonates. The stabilities of these salts are in the order of the bare cationic radii, again indicating that the forces are largely chelate in character. This is in striking contrast to the order for the corresponding thiosulphates,<sup>18</sup> where the forces are predominantly electrostatic. The values (end of Table 1) for the adipates (an arbitrary  $K_2$  being used for the acid) are probably incorrect in an absolute sense (*vide supra*), but it is interesting to note that the same order of stability still holds ( $Mg > Ca > Ba$ ). In all the cases studied copper forms the most stable ion-pair. This has been correlated with its ability to use the  $dsp^2$  orbitals, although some doubt has been cast on the validity of this assumption.<sup>19</sup>

The present work appears to afford confirmation of Irving and Williams's thesis that the "natural" order of the stability of complexes is  $Zn < Cu > Ni > Co > Fe > Mn$ , irrespective of the nature of the ligand, provided that the ligand is co-ordinated to the cation (chelation), and it is noteworthy that this order is maintained exactly with the malonates, where the dissociation constants are all very small. As the number of carbon atoms in the ligand increases so does the dissociation constant, and at the same time the Irving-Williams order is less exactly maintained. Cobalt in particular appears to yield anomalously "strong" salts if  $C > 5$ , even with the substituted glutaric acids, a fact which again supports the conclusion that in these cases the steric factor is relatively unimportant in comparison with the electrostatic factor.

We thank the Department of Scientific and Industrial Research for a maintenance grant (to R. H. J.), and the Chemical Society for a grant from the Research Fund (to D. I. S.).

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[Received, July 27th, 1961.]

<sup>16</sup> Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609.

<sup>17</sup> Jeffery and Vogel, *J.*, 1935, 21.

<sup>18</sup> Denney and Monk, *Trans. Faraday Soc.*, 1951, **47**, 992.

<sup>19</sup> Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.