Stability Constants for Association between Bivalent Cations and Some Univalent Anions

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Stability constants at 25·0 °C and ionic strength 1·00M in water have been determined by a kinetic method for association between seven bivalent cations and six univalent anions. Values of log K_1 for the various combinations are summarised in Table 3.

THE main object of this work is to obtain, by a single method, stability constants for association between manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) aquo-cations and bromide, chloride, nitrate, and chlorate anions in aqueous solution. Relatively few acceptable measurements have hitherto been made for most of these cation–ligand combinations. To permit various comparisons, the scope of the work was broadened to include the ligands acetate and thiocyanate, which have previously been studied with all the above cations,[1] and the cadmium(II) and lead(II) aquo-cations. Many of the stability constants are of the order of unity and hence it was necessary to use a fairly high ionic strength to achieve a conversion of the aquo-cation into its complex which was sufficiently high for measurement. Accordingly, we have normally used an ionic strength of 1·00M, the supporting electrolyte being sodium perchlorate.

Measurements of pH or the light absorption of the association complexes formed are unsuitable for investigating many of the chosen systems, but a kinetic

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[1] 'Stability Constants of Metal-ion Complexes,' Chem. Soc. Special Publ., No. 17, 1964; No. 25, 1971.

method has proved satisfactory. In principle, a reaction which is assisted by metal cations, *i.e.* the rate equation of which contains a term involving a metal-ion concentration, can be used to determine the concentration of that metal ion. The introduction of a potential ligand species into the system should decrease the rate of reaction by decreasing the free metal-ion concentration. By obtaining from the decrease in rate the proportion of aquo-cation converted into the association complex, and knowing the concentration of free ligand, it is then possible to calculate the desired stability constant. However, the association complex produced may itself assist the reaction, and if this occurs it must be taken into account.

Of various reactions considered, the most satisfactory for our purposes was the elimination of chloride ion from the quinquedentate complex chloro(ethylenediaminetriacetatoacetate)cobaltate(III), $[Co(edta)Cl]^{2-}$, with the formation of sexidentate ethylenediaminetetra-acetatocobaltate(III), $[Co(edta)]^{-}$. This reaction has previously been found to be moderately sensitive to catalysis by metal cations in general,[2,3] and can be followed by a simple spectrophotometric method. In this reaction, the reactivity of the catalytic aquo-cation is strongly influenced by its charge.[3] Lanthanoid cations are about thirty times more effective than calcium, strontium, and barium cations, which in their turn are at least ten times more effective than the sodium cation. Also, aquothallium(III) is about fifty times more effective than the monochlorothallium(III) ion.[3] Since the complexing agents used in this work are of unit negative charge, the complex ions are of unit positive charge and might be expected to be poor catalysts compared with their corresponding aquo-cations. This is an important reason for choosing this reaction, for a moderate contribution to the catalysis by the association complex is difficult to assess quantitatively and hence can lead to a considerable error in the derived stability constant. A disadvantage of the chosen reaction is that its catalysis is not linear in the concentrations of the aquo-cations employed; this complicates the treatment and increases the error in the determination of a stability constant. Also, reduction of the cobalt(III) substrate by chromium(II), iron(II), and vanadium(II) ions prevents the use of this system for obtaining the stability constants of these aquo-cations.

RESULTS

Catalysis by Metal Ions M^{2+} *of the Reaction* $[Co(edta)Cl]^{2-} \longrightarrow [Co(edta)]^{-}$.—This catalysis shows a strong pH dependence in the range pH 2—4 because of partial conversion of the complex $[Co(edta)Cl]^{2-}$ (edta = ethylenediaminetetra-acetato) to its conjugate acid, $[Co(Hedta)Cl]^{-}$, the pK of the latter being *ca.* 3·1 under our conditions. Since the formation of the complex $[Co(edta)]^{-}$ from $[Co(Hedta)Cl]^{-}$ is insensitive to catalysis by metal cations, our experiments were conducted in the range pH 4·5—5·5 where the proportion of $[Co(Hedta)Cl]^{-}$ is very small. Under these conditions, and in the absence of complexing anions, the several reactions involved in the formation of $[Co(edta)]^{-}$ are as in equations (1)—(3). If $k_{obs} = -d\ln[Co(edta)Cl^{2-}]/dt$, then

$$[Co(edta)Cl]^{2-} \xrightarrow{k_U} [Co(edta)]^{-} + Cl^{-} \quad (1)$$

$$[Co(edta)Cl]^{2-} + M^{2+} \overset{K_M}{\rightleftharpoons} [Co(Medta)Cl] \quad (2)$$

$$[Co(Medta)Cl] \xrightarrow{k_M} [Co(edta)]^{-} + Cl^{-} + M^{2+} \quad (3)$$

it can be shown [3] that equation (4) is applicable. Here $[M]_f$

$$k_{obs} = k_U + (k_M - k_U)K_M[M]_f/(1 + K_M[M]_f) \quad (4)$$

signifies the concentration of free M^{2+}, but, in this application with a relatively low concentration of cobalt(III) and in the absence of complexing anions, the total concentration [M] can be used. Thus equation (4) can be written in the form (5) and this was used to obtain values of k_M and K_M

$$1/(k_{obs} - k_U) = 1/(k_M - k_U) + 1/(k_M - k_U)K_M[M] \quad (5)$$

which are required for the interpretation of subsequent experiments in the presence of complexing anions. Values of k_{obs} are summarised in Supplementary Publication No. SUP 20696 (20 pp., 1 microfiche) * and were obtained from spectrophotometric experiments conducted as previously described,[4] by using a weighted least-squares computer program devised by J. R. Chipperfield for obtaining the gradient of a plot of log $(A_t - A_\infty)$ against t for a first-order reaction, A_t and A_∞ being values of optical density at time t and at the end of the reaction, respectively. This program also enabled the computation of the standard deviation of the gradient of a plot and hence of k_{obs}. Each standard deviation of k_{obs}, denoted σ_{obs}, was doubled and was then used to obtain the standard deviation of the corresponding value of $1/(k_{obs} - k_U)$, since it is necessary to follow a weighted least-squares procedure in evaluating K_M and k_M from equation (5). The σ_{obs} values were doubled since they do not, as obtained, include random errors from one experiment to another.

Experiments to obtain k_M and K_M were normally carried out at 25·0 °C with ionic strength made 1·00M by the use of sodium perchlorate. The initial concentration of the complex $[Co(edta)Cl]^{2-}$ did not exceed 2×10^{-3}M in any of the experiments. To maintain pH in the region of 5, *ca.* 10^{-3}M sodium acetate–acetic acid buffer was used in the experiments with copper(II) and zinc(II) ions. The metal-ion concentrations quoted in the Supplementary Publication for these cations are those of the free cation, the corrections being made by using values of 4·0 and 52 l mol^{-1} for the stability constants (K_1) of zinc(II) and copper(II), respectively. For both cations the fraction in the form of the monoacetate complex did not exceed 5%. For the other metal ions a mixture, subsequently referred to as mes buffer, of sodium 2-morpholinoethanesulphonate and its conjugate acid was used to maintain pH; concentrations were normally *ca.* 2×10^{-4}M-sodium salt and *ca.* 10^{-3}M-acid. Experiments with higher concentrations of buffer showed minor changes only in reaction rate. We concluded that complexing between the buffer base and the metal ions is

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[2] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1963, 2788.

[3] S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc.* (*A*), 1969, 1164.

[4] R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1960, 1998.

negligible at the concentrations normally used and therefore no correction was made to the total cation concentrations for catalysis by cations other than copper(II) and zinc(II). From similar experiments in the absence of catalyst, we found $k_U = (2{\cdot}72 \pm 0{\cdot}02) \times 10^{-6}\ s^{-1}$ at 25·0 °C and ionic strength 1·00M. This value was decreased by *ca.* 10% in the presence of 0·4M-acetate anions, but this effect was unimportant for our purposes. Other ligand anions caused smaller decreases in k_U. Values of k_U under other conditions are included in the Supplementary Publication, together with corresponding values of k_{obs}. Values of k_M and K_M obtained from the results are summarised in Table 1; the limits of error correspond to one standard deviation.

TABLE 1

Summary of values of k_M and K_M for various cations

Cation	$10^5 k_M$ / s^{-1}	K_M / $l\ mol^{-1}$	$10^3[M]_{max.}$* / M
At 25·0 °C and I = 1·00M			
Mn^{2+}	8·50 ± 1·66	6·85 ± 1·62	48·0
Co^{2+}	6·88 ± 0·78	8·71 ± 1·22	53·5
Ni^{2+}	7·80 ± 0·87	9·39 ± 1·32	51·2
Cu^{2+}	552 ± 16	20·30 ± 0·78	48·2
Zn^{2+}	36·3 ± 1·1	3·94 ± 0·12	111·9
Cd^{2+}	403 ± 16	12·12 ± 0·56	49·6
Pb^{2+}	502 ± 12	35·6 ± 1·4	48·6
At 25·0 °C and I = 0·10M			
Cu^{2+}	345 ± 20	46·1 ± 3·4	15·4
Cd^{2+}	259 ± 11	30·6 ± 1·6	19·8
Pb^{2+}	404 ± 9	60·9 ± 1·8	9·7
At 45·0 °C and I = 1·00M			
Ni^{2+}	365 ± 168	2·14 ± 0·82	40·1

* $[M]_{max.}$ indicates the maximum value of the cation concentration used in the group of experiments.

Cation Catalysis in the Presence of Complexing Anions; the Evaluation of Stability Constants.—If the catalysis occurs in the presence of complexing anions, equilibria (6) and (7) must be taken into account. Further, if L^- is not acetate

$$M^{2+} + L^- \overset{K_1}{\rightleftharpoons} [ML]^+ \qquad (6)$$

$$[ML]^+ + L^- \overset{K_2}{\rightleftharpoons} [ML_2] \qquad (7)$$

ion (OAc^-), but an acetate buffer is used, the acetate ion will also take part in complex formation, although the monoacetate complex alone need be considered at the buffer concentration employed. We therefore include equilibrium (8). We now have relation (9), where $[L]_f$ and

$$M^{2+} + OAc^- \overset{K_A}{\rightleftharpoons} [M(OAc)]^+ \qquad (8)$$

$$[M]_f = [M]/(1 + K_1[L]_f + K_1K_2[L]_f^2 + K_A[OAc]_f) \qquad (9)$$

$[OAc]_f$ signify the concentrations of the free anions and $[M]_f$ and $[M]$ have their previous meaning. By combining

$$K_M[M](k_M - k_{obs})/(k_{obs} - k_U) - K_A[OAc]_f - 1$$
$$= F_L - K_A[OAc]_f = K_1[L]_f + K_1K_2[L]_f^2 \qquad (10)$$

(4) and (9) we obtain (10), which holds for ligands other than acetate in the presence of an acetate buffer. If L^- is acetate ion, or if with other ligands the mes buffer is used, then the term $K_A[OAc]_f$ is omitted. Equation (10) can be used to obtain K_1, and in principle K_2, from measurements of k_{obs} at several different concentrations of L^-, summarised in the Supplementary Publication. In most cases the term in $[L]_f^2$ was found to be negligible. Equation (10) involves the assumptions that catalysis by $[M(OAc)]^+$, $[ML]^+$, and $[ML_2]$ is negligible; a more complete equation which does not involve these assumptions can be deduced but, as discussed later, we have not found it appropriate to use such an equation.

Although the concentrations of free ligand and free acetate ion necessary for the use of equation (10) are not known initially, they differ little from the total concentrations in most cases. Consequently it was usually possible to obtain a good approximation to K_1 by substituting the total concentrations of the anion L^- in equation (10). With this preliminary value of K_1 it was then possible to calculate the concentration of free L^- with sufficient accuracy to render unnecessary any further calculation. Bearing in mind that the free-ligand concentrations given in the Supplementary Publication have been corrected from the total ligand concentrations, we now omit the subscript f from the symbols for ligand concentrations.

Acetate ion was used as the buffer in experiments with zinc(II) ions only, and here it was found that the term $K_A[OAc]$ changed little in a set of experiments over a range of L^- concentrations. Hence it was sufficient, if the term in $[L]^2$ was negligible, to find the gradient of a plot of F_L against $[L]$ without stipulating that the plot should pass through the origin. However, in applying least-squares procedures to obtain the gradient, it was realised that the best line did not invariably pass through the origin, even if the $K_A[OAc]$ term was taken into account. Examination of several sets of experiments with zinc, particularly with acetate and chloride ions at concentrations where the K_2 term was unimportant, showed that extraneous factors were causing certain of the plots of $F_L - K_A[OAc]$ against $[L]$ to give small intercepts on the y axis at zero $[L]$. This was also found with other cations for which the term $K_A[OAc]$ is absent. In consequence, the procedure was adopted, for a given ligand and with a fixed metal-ion concentration, of treating the data by unweighted least squares as an equation of the form $y = mx + c$, with $y = F_L$ and $x = [L]$. (Standard deviations of the F_L values were similar for a given group of experiments, so that use of unweighted least squares is appropriate.) If the value, positive or negative, obtained for c was greater than its standard deviation, then the corresponding value of m was taken as a good estimate of K_1. However, if c was less than its standard deviation, c was assumed to be zero and the data were treated by unweighted least squares as obeying a relation of the form $y = m'x$, and m' was taken as a better estimate of K' than was the corresponding value of m. Satisfactory agreement was usually found between the K_1 values obtained in this way for a given cation–ligand combination, even if an intercept was found with one group of experiments and not with another; the various K_1 values are given in Table 2.

Apart from the term involving the buffer anion, several factors contribute to a finite value of c. These include errors in k_M and K_M, and the fortuitous occurrence of a small temperature difference between the temperature at which k_M and K_M were obtained and that at which k_{obs} values were determined. Also, small trends in pH from one experiment to another in a given group can lead to a finite value of c. Calculations in which such discrepancies were artificially introduced, confirmed the utility of the above procedure in giving a good approximation to K_1 when an intercept is found.

In several cases, notably with the acetate ligand, plots of F_L against [L] showed a marked upward curvature at the higher values of [L]. The attempt to fit such results to an equation of the form $y = mx + c$ led to a large negative value of c and an unusually high standard deviation for m. The principal cause of such curvature appears to be the importance of the term $K_1K_2[L]^2$ in equation (10) at higher values of [L]. As discussed below, we consider it is not possible to obtain reliable values of K_2 from our experiments. Nevertheless we have attempted the simultaneous evaluation of K_1 and K_2 from appropriate groups of experiments, since this probably gives better values for K_1 than calculations which neglect K_2; the following method was satisfactory. By using only values of F_L corresponding to low values of [L], we can obtain c as described above, since the contribution of the term in $[L]^2$ will be small. At higher values of [L] the appropriate equation is (11) which can be re-

$$F_L = K_1[L] + K_1K_2[L]^2 + c \tag{11}$$

arranged to give (12). The left-hand side of (12) can now be

$$(F_L - c)/[L] = K_1 + K_1K_2[L] \tag{12}$$

evaluated and the values of K_1 and K_1K_2 obtained by weighted least squares. The standard deviation of $(F_L - c)/[L]$, required for this procedure, is $0{\cdot}03(1 + F_L)/[L]$; the coefficient 0·03 is largely determined by the typical relative standard deviation of *ca.* 0·02 for k_{obs}. Values of K_1 obtained by this procedure are included in Table 2, together with those obtained from a smaller range of [L] values, neglecting K_2.

TABLE 2

Values of K_1 for bivalent cations calculated from results in the Supplementary Publication

Group	Ligand	$\frac{[L]_{max.}}{M}$	$\frac{K_1}{l\ mol^{-1}}$
Manganese			
3 (i)	OAc^-	0·171	4·50 ± 0·71 *
		0·448	4·48 ± 0·27 †
(ii)	Br^-	0·253	1·23 ± 0·15
(iii)	Cl^-	0·235	0·43 ± 0·08 *
(iv)	ClO_3^-	0·225	0·49 ± 0·17 *
(v)	NO_3^-	0·511	0·64 ± 0·07 *
(vi)	NCS^-	0·411	3·86 ± 0·31 *
		0·411	4·19 ± 0·29 †
Cobalt			
3 (vii)	OAc^-	0·168	5·92 ± 0·34
		0·276	5·86 ± 0·43 †
(viii)	Br^-	0·394	0·58 ± 0·11 *
		0·888	0·65 ± 0·05 *
(ix)	Cl^-	0·376	1·06 ± 0·13 *
		0·852	1·50 ± 0·05
(x)	ClO_3^-	0·222	1·47 ± 0·26
(xi)	NO_3^-	0·424	0·64 ± 0·12
(xii)	NCS^-	0·398	8·23 ± 0·27
		0·398	8·07 ± 0·40 †
Nickel			
3 (xiii)	OAc^-	0·180	6·15 ± 0·09
		0·292	5·82 ± 0·46 †
(xiv)	Br^-	0·490	0·81 ± 0·06 *
(xv)	Cl^-	0·278	1·05 ± 0·18 *
		0·466	1·06 ± 0·07 *
		0·844	1·46 ± 0·09 *
(xvi)	ClO_3^-	0·223	0·41 ± 0·07
(xvii)	NO_3^-	0·422	1·09 ± 0·18 *
(xviii)	NCS^-	0·150	13·0 ± 0·7 *
		0·318	11·6 ± 0·6 †
Nickel at 45·0 °C			
5 (i)	OAc^-	0·180	5·69 ± 0·23 *
(ii)	Cl^-	0·246	0·85 ± 0·14
(iii)	NO_3^-	0·341	1·08 ± 0·27
(iv)	NCS^-	0·200	9·96 ± 0·58
Copper			
3 (xix)	OAc^-	0·115	47·1 ± 3·0
		0·276	47·8 ± 2·4 †
(xx)	Br^-	0·340	0·52 ± 0·40 *
(xxi)	Cl^-	0·368	1·30 ± 0·27 *
(xxii)	ClO_3^-	0·304	0·42 ± 0·07 *
(xxiii)	NO_3^-	0·342	0·68 ± 0·10 *
(xxiv)	NCS^-	0·008	52·2 ± 7·3
Zinc			
3 (xxv)	OAc^-	0·212	3·99 ± 0·12
		0·432	4·05 ± 0·25 †
(xxvi)	OAc^-	0·209	4·28 ± 0·17 *
		0·478	3·73 ± 0·20 †
(xxvii)	OAc^-	0·100	3·92 ± 0·27 *
		0·412	3·59 ± 0·21 †
(xxviii)	Br^-	0·491	0·42 ± 0·03 *
(xxix)	Br^-	0·569	0·45 ± 0·03 *
(xxx)	Cl^-	0·521	0·72 ± 0·07 *
(xxxi)	Cl^-	0·530	0·77 ± 0·08 *
(xxxii)	Cl^-	0·356	0·80 ± 0·03
(xxxiii)	ClO_3^-	0·518	0·70 ± 0·04
(xxxiv)	ClO_3^-	0·396	0·69 ± 0·03
(xxxv)	NO_3^-	0·554	0·64 ± 0·04 *
(xxxvi)	NO_3^-	0·422	0·74 ± 0·03
(xxxvii)	NCS^-	0·204	2·40 ± 0·17 *
		0·456	2·11 ± 0·16 †
(xxxviii)	NCS^-	0·174	2·58 ± 0·27 *
		0·398	2·37 ± 0·22 †
Cadmium			
3 (xxxix)	OAc^-	0·100	16·8 ± 0·2
		0·360	15·3 ± 0·6 †
(xl)	Br^-	0·096	34·8 ± 1·0 *
(xli)	Cl^-	0·083	19·8 ± 0·3
		0·143	19·4 ± 1·0 †
(xlii)	ClO_3^-	0·295	0·66 ± 0·13
(xliii)	NO_3^-	0·341	1·06 ± 0·15 *
(xliv)	NCS^-	0·091	21·2 ± 1·3 *
		0·328	19·5 ± 0·6 †
(xlv)	$NH_2SO_3^-$	0·300	−0·07 ± 0·05 *
Cadmium at I = 0·10M			
4 (i)	Br^-	0·052	77·6 ± 0·8
(ii)	Cl^-	0·044	35·4 ± 1·2 *
(iii)	NO_3^-	0·061	1·70 ± 0·16
Lead			
3 (xlvi)	OAc^-	0·040	152·0 ± 9·5 *
		0·173	146·2 ± 4·0 †
(xlvii)	Br^-	0·064	13·1 ± 0·6
(xlviii)	Cl^-	0·036	11·4 ± 1·7
		0·224	10·9 ± 0·5 †
(xlix)	ClO_3^-	0·281	1·55 ± 0·17 *
(l)	NO_3^-	0·410	3·80 ± 0·25 *
Lead at I = 0·10M			
4 (iv)	Br^-	0·053	20·5 ± 0·5
(v)	Cl^-	0·063	15·6 ± 0·4 *
(vi)	NO_3^-	0·060	7·32 ± 0·79

Results are at 25·0 °C and I = 1·00M, unless otherwise indicated: $[L]_{max}$ denotes the highest value of [L] used in calculating K_1; OAc^- = acetate ion.

* Plot for K_1 did not pass through the origin. † A second association (K_2) was assumed in obtaining K_1.

DISCUSSION

An equation similar to that of (10), but taking into account catalysis by the complex $[ML]^+$ can be derived. However, owing to the introduction of an extra parameter, kinetic data of greater precision than ours would be necessary to make the use of such an equation advantageous. To estimate the importance of catalysis by the complex $[ML]^+$, we have calculated the concentrations of free M^{2+} and $[ML]^+$ in several cases in which a low value of k_{obs} indicates a high degree of complex formation. For these calculations we have chosen previously determined [1] values of stability constants, and, where appropriate, we have taken into account the formation of $[ML_3]^-$ as well as $[ML_2]$ and $[ML]^+$ complexes. By substituting the value of $[M]_f$ into equation (4) we can find k_{calc}, the contribution of catalysis by M^{2+} to the overall velocity constant k_{obs}. The difference $k_{obs} - k_{calc}$ is then ascribed to catalysis by the complex $[ML]^+$. We compare the catalytic activities of $[ML]^+$ and M^{2+} through the corresponding second-order constants, $k_{ML} = (k_{obs} - k_{calc})/[ML^+]$ and $k_F = (k_M - k_U)K_M$, respectively. In this way we find the following reactivity ratios $k_{ML} : k_F$ from experiments at the stated free-ligand concentrations: (xix), Cu^{2+} + 0·276M-OAc^-, 0·17 : 1; (xl), Cd^{2+} + 0·624M-Br^-, 0·06 : 1; (xli), Cd^{2+} + 0·616M-Cl^-, 0·10 : 1; and (xlvi), Pb^{2+} + 0·172M-OAc^-, 0·05 : 1. (Roman numerals indicate the group in the Supplementary Publication from which the experiments were selected.) These values are subject to considerable variation, depending upon the particular set of stability constants chosen for the calculations. The surprisingly high value of $k_{ML} : k_F$ for the Cu^{2+}–OAc^- system may reflect errors in these stability constants. We have calculated the values of K_1 in Table 2 by neglecting catalysis by the complex $[ML]^+$, but further calculations show that if $k_{ML} : k_F = 0{\cdot}10 : 1$, the value of K_1 obtained by using equation (11) is *ca.* 80% of the true value. Consequently, in taking values of K_1 from Table 2 for the summary in Table 3, we have made a notional allowance for catalysis by the complex $[ML]^+$ by multiplying the selected values by 1·10 ± 0·10. This procedure seems preferable to treating k_{ML} as an unknown parameter in the evaluation of K_1.

TABLE 3

Summary of stability constants for various cation–anion pairs

	OAc^-	Br^-	Cl^-	ClO_3^-	NO_3^-	NCS^-	$[Co(edta)Cl]^{2-}$
Mn^{2+}	0·69 ± 0·05	0·13 ± 0·06	$\bar{1}$·67 ± 0·08	$\bar{1}$·73 ± 0·13	$\bar{1}$·85 ± 0·06	0·65 ± 0·05	0·83 ± 0·09
Co^{2+}	0·81 ± 0·05	$\bar{1}$·80 ± 0·08	0·07 ± 0·06	0·21 ± 0·08	$\bar{1}$·85 ± 0·08	0·95 ± 0·04	0·94 ± 0·06
Ni^{2+}	0·83 ± 0·04	$\bar{1}$·95 ± 0·05	0·07 ± 0·08	$\bar{1}$·65 ± 0·08	0·08 ± 0·08	1·13 ± 0·05	0·97 ± 0·06
Cu^{2+}	1·72 ± 0·05	$\bar{1}$·76 ± 0·25	0·15 ± 0·09	$\bar{1}$·66 ± 0·08	$\bar{1}$·87 ± 0·07	1·76 ± 0·07	1·31 ± 0·02
Zn^{2+}	0·63 ± 0·04	$\bar{1}$·68 ± 0·05	$\bar{1}$·94 ± 0·05	$\bar{1}$·88 ± 0·05	$\bar{1}$·88 ± 0·05	0·41 ± 0·05	0·60 ± 0·02
Cd^{2+}	1·26 ± 0·04	1·58 ± 0·04	1·34 ± 0·04	$\bar{1}$·86 ± 0·09	0·07 ± 0·07	1·34 ± 0·04	1·08 ± 0·02
Pb^{2+}	2·21 ± 0·04	1·16 ± 0·05	1·08 ± 0·05	0·23 ± 0·06	0·62 ± 0·05		1·55 ± 0·02
Cu^{2+} *							1·66 ± 0·03
Cd^{2+} *		1·93 ± 0·04	1·59 ± 0·04		0·27 ± 0·06		1·49 ± 0·02
Pb^{2+} *		1·35 ± 0·04	1·23 ± 0·04		0·90 ± 0·06		1·78 ± 0·02
Ni^{2+} †	0·80 ± 0·04		$\bar{1}$·97 ± 0·08		0·07 ± 0·10	1·04 ± 0·05	0·33 ± 0·14

Constants expressed as log K_1 at 25 °C and I = 1·00M unless otherwise indicated: OAc^- = acetate ion.

* At 25·0 °C and I = 0·10M. † At 45·0 °C and I = 1·00M.

It can be shown that catalysis by the complex $[ML]^+$ should cause a plot of F_L against [L] to show gentle negative curvature, *i.e.* the plot is concave to the *x* axis, if the term in $[L]^2$ in equation (10) is negligible. With a value of $k_{ML} : k_F = 0{\cdot}1 : 1$, this curvature would not be obvious in practice. On the other hand, a significant contribution from the term in $[L]^2$ causes a positive curvature, the latter being the more pronounced the greater the value of K_2. Since these two effects oppose one another, it is evident that values of K_2 obtained under our conditions, where formation of the complex $[ML_2]$ is not considerable, will be subject to large errors. For this reason we have disregarded the values of K_2 obtained in finding K_1 by the use of equation (12).

Our values of K_1 can be compared with those previously obtained [1] for several cation–ligand combinations, mainly for complexes involving acetate and thiocyanate ions, and the cations of cadmium(II) and lead(II). Agreement is reasonably good, the main discrepancies occurring in several cases where formation of the complex $[ML_2]$ is known to be important. Here, our values are somewhat higher than the literature values, suggesting that we have not been entirely successful in allowing for K_2 in our calculations of K_1. Such errors are unlikely to be important with the weak complexes which are our main concern.

We note that the trend of constants from the ions manganese(II) to zinc(II), with the ligands OAc^-, NCS^-, and $[Co(edta)Cl]^{2-}$ (active centre a carboxylate group) follows the Irving–Williams relation.[5] Although this relation appears to hold with Cl^- also, we consider that this is fortuitous. The important generalisation for the weak complexes of these metals with Br^-, Cl^-, ClO_3^-, and NO_3^- is that the corresponding values of log K_1 all lie within the limits $\bar{1}$·9 ± 0·3. This suggests that non-specific interactions predominate between these cations and anions and that the complexes formed are largely of the outer-sphere type. In this context, it appears from *X*-ray investigations [6] that there is no contact between anion and cation in cobalt(II) bromide and chloride

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[5] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.

[6] D. L. Wertz and R. F. Kruh, *J. Chem. Phys.*, 1969, **50**, 4313; *Inorg. Chem.*, 1970, **9**, 595.

solutions in which the ionic concentration product is greater than in our experiments. Also, a recent investigation [7] of inner-sphere association between copper(II) and NO_3^- yields a much smaller value of K_1 than we have found.

The values of log K_1 for the association of cadmium(II) with ClO_3^- and NO_3^- suggest that the complexing in these cases is predominantly of the outer-sphere type, as with the transition-metal cations, whereas the corresponding replacement of ClO_4^- by $NH_2SO_3^-$ has comparatively little effect, see the Supplementary Publication and Table 2 of this paper, group (xlv). Since association with ClO_3^- and NO_3^- appears to be of the outer-sphere type, the difference between the behaviour of these anions and ClO_4^- or $NH_2SO_3^-$ is noteworthy. It is, of course, possible that the weak interactions corresponding to log $K_1 \simeq \bar{1}\cdot 9$ are not best understood in terms of a simple chemical equilibrium. There is a considerable change in the medium in most of our groups of kinetic experiments, a substantial proportion of the perchlorate ions being replaced by anions of different size, and a more physical picture [8] may be called for. However, we prefer the simplicity of the chemical–equilibrium description, as used in this paper.

We have obtained results at ionic strength 0·10M with cadmium(II) and lead(II) ions to obtain a measure of the change in stability constants for bivalent cations with univalent anions between this ionic strength and that of 1·00M. It is possible to obtain the thermodynamic constants from values of stability constants at ionic strength 0·1M by the use of a general equation [9] for the variation of activity coefficients with ionic strength. Because of the more individual behaviour of different anion–cation systems at higher ionic strengths, no corresponding extrapolation of general application is possible for obtaining thermodynamic stability constants from those at ionic strength 1·00M. However, it is of interest to know the approximate magnitude of such a correction. Reference to Table 3 shows that, as expected, changes in log K_1 from ionic strength 1·00 to 0·1M vary somewhat from one system to another. The average change for the univalent anions is +0·24; with the increment of 0·42 calculated from Davies' equation [9] for the change from ionic strength 0·10 to 0M, we conclude that thermodynamic stability constants K_1 for association between a bivalent cation and a univalent anion are *ca.* 4—5 times larger than the corresponding values at ionic strength 1·00M.

If the difference between the other anions and OAc^-, NCS^-, and $[Co(edta)Cl]^{2-}$ is that the latter three give inner-sphere complexes, and the former outer-sphere, it seemed possible that entropies of association for the two groups would be markedly different. Accordingly we found values of K_1 at 45·0 °C for several ligands with the nickel(II) ion. With the exception of the atypical ligand $[Co(edta)Cl]^{2-}$, the changes with temperature were small, and more precise values than ours would be necessary to recognise any distinction between the two groups.

EXPERIMENTAL

Reagents were of AnalaR quality, with the following exceptions: sodium bromide and sodium chlorate (B.D.H., laboratory reagent grade); sodium thiocyanate (' anhydrous for determination of niobium in steel ' grade); 2-morpholinoethanesulphonic acid (B.D.H., biochemical grade); and cobalt(II), copper(II), manganese(II), and nickel(II) sulphate hydrates (Johnson, Matthey, ' specpure ' grade). All these reagents were used without further purification. Disodium chloro(ethylenediaminetriacetatoacetic acid)cobaltate(III) dihydrate was prepared and purified by Dwyer and Garvan's method.[10]

Barium and zinc perchlorate stock solutions were obtained by dissolving barium carbonate and zinc oxide, respectively, in dilute perchloric acid. Cobalt(II), copper(II), manganese(II), and nickel(II) perchlorate stock solutions were obtained by double decomposition between the corresponding sulphate salts and barium perchlorate; care was taken that neither the sulphate salt nor the barium perchlorate was in an excess before the final filtration. Cadmium(II) and lead(II) stock solutions were obtained by precipitating the corresponding hydroxides from solutions of cadmium(II) sulphate and lead(II) nitrate, respectively, and washing the precipitates before dissolving them in an equivalent amount of dilute perchloric acid.

Stock solutions of sodium salts were standardised by conversion of samples into the corresponding acid solutions by ion exchange on Amberlite IR-120 (H) resin, followed by titration with standard sodium hydroxide solution. Manganese(II) and zinc(II) perchlorate solutions were standardised by titration, using Erio T indicator, with an EDTA (disodium salt) solution,[11] which was itself standardised against magnesium iodate tetrahydrate. Cadmium(II), cobalt(II), copper(II), and lead(II) perchlorate stock solutions were standardised electrogravimetrically.[12] Lead(II) perchlorate solutions were also standardised gravimetrically, by precipitation of lead tetraoxochromate(VI).[12]

According to their specifications, certain of the reagents might have contained kinetically significant traces of iron(III) and lead(II) ions, these being several hundred times more effective catalysts than the ions cobalt(II), manganese(II), nickel(II), and zinc(II). Accordingly, reaction solutions were made up containing 2×10^{-5}M-EDTA, sufficient to sequester these cationic impurities, in addition to the main constituents, metal(II) perchlorate, sodium salt of the ligand, sodium perchlorate, buffer, and Na[Co(Hedta)Cl]. Kinetic measurements to obtain k_{obs} were made, as previously described,[4] by using a Unicam SP 600 spectrophotometer, equipped with a temperature-controlled (±0·1 °C) cell holder. If the half-life of a reaction exceeded *ca.* 1 h, aliquot portions of the reaction mixture were taken from a thermostat bath for measurement of the optical density at appropriate intervals of time. With shorter half-lives, the reaction mixture was kept in the optical cell throughout the

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[7] A. R. Davis and C. Chong, *Inorg. Chem.*, 1972, **11**, 1891.

[8] D. R. Rosseinsky, *Ann. Reports (A)*, 1971, **68**, 81.

[9] C. W. Davies, ' Ion Association,' Butterworths, London, 1962, p. 41.

[10] F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, 1958, **80**, 4480.

[11] G. Schwarzenbach, H. Flaschka, and H. M. N. H. Irving, ' Complexometric Titrations,' Methuen, London, 2nd edn., 1969.

[12] A. I. Vogel, ' Quantitative Inorganic Analysis,' Longmans, London, 3rd edn., 1961.

course of the experiment. Approximately 20 readings were taken during at least two half-lives.

Measurements of pH were made at 25·0 °C; the pH meter was standardised against 0·050M-potassium hydrogen phthalate. The calomel reference electrode contained a saturated solution of sodium chloride instead of potassium chloride, in order to avoid drifts ascribed to precipitation of potassium perchlorate at the liquid–liquid junction.

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