1002. *The Stability of Metal Complexes of* 1,10-*Phenanthroline and its Analogues. Part I.* 1,10-*Phenanthroline and* 2,2′-*Bipyridyl.*

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Methods suitable for determining the step-stability constants of very stable complexes of transition metals with 1,10-phenanthroline and its analogues are reviewed. Partition coefficients for 2,2′-bipyridyl and 1,10-phenanthroline between aqueous buffers of ionic strength 0·1M and chloroform, carbon tetrachloride, and n-hexane have been measured at 25°. From measurements of the distribution of the two ligand bases between these solvents and aqueous buffers containing known concentrations of various cations, step-stability constants, valid for 25° and 0·1M-potassium chloride (or nitrate) have been determined for bivalent ions of manganese, iron, cobalt, nickel, copper, zinc, and cadmium.

The stabilities of the 1 : 1 complexes follow the Irving–Williams order in each case and they increase in the order Mn < Cd < Fe < Zn < Co < Ni < Cu. For the 3 : 1 complexes, however, the order becomes Mn < Cd < Zn < Co < Cu < Fe < Ni. The anomalous stability of the ferrous tris-complex is shown to arise because K_3 is greater than both K_1 and K_2, owing to formation of a spin-paired complex.

THIS series of papers form part of an extensive study of the quantitative aspects of steric hindrance to chelation with the immediate goal of seeking an interpretation of the " singular " reactions [1] between certain heterocyclic bases and ferrous or cuprous ions which form the basis of the " ferroin " and the " cuproin " reaction. To this end the stability constants of complexes of zinc, cadmium, and the transition metals manganese, iron, cobalt, nickel, and copper with 2,2′-bipyridyl, 1,10-phenanthroline, 2-methyl-, 5-methyl-, and 2,9-dimethyl-phenanthroline have been determined. Most of this work was completed by 1954 [2] but publication was delayed in order to include values for 5-methylphenanthroline. The present paper (Part I) deals with complexes of 2,2′-bipyridyl and 1,10-phenanthroline. Part II reports work with the ligands 2-methyl- and 2,9-dimethyl-1,10-phenanthroline which differ from the parent base in carrying one or more substituents adjacent to the nitrogen atoms and thus presenting steric hindrance to co-ordination. In Part III the theory of the method is elaborated somewhat and results are reported for 5-methyl-1,10-phenanthroline in which the electron-repelling substituent is so located as to cause no steric hindrance to co-ordination. In Part IV some calorimetric measurements will be reported.

Tris-complexes of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phenan) with ferrous iron are known to be remarkably stable, with overall formation constants of about 10^{17} and 10^{21}, respectively. The " robust " character of such transition-metal complexes is further exemplified by the considerable optical stability of the antipodes of the tris-complexes of nickel and ferrous iron.[3] If the Irving–Williams order of stabilities [4]

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[1] Irving and Williams, *Analyst*, 1952, **77**, 813.
[2] Mellor, D.Phil. Thesis, Oxford, 1954.
[3] Dwyer and Gyarfas, *J. Proc. Roy. Soc. New South Wales*, 1951, **83**, 263.
[4] Irving and Williams, *Nature*, 1948, 162, 746; *J.*, 1953, 3192.

Mn < Fe < Co < Ni < Cu > Zn were to hold for the complexes of bipyridyl and phenanthroline, as it has been found to do for upwards of eighty organic ligands,[5] it could reasonably be inferred that they would all be of such stability that $\bar{n}$, the degree of complex formation, might well be appreciable even in rather acid solutions. In consequence the familiar procedure for determining stability constants by potentiometric titration would not, in general, be very suitable. This may explain the obviously faulty data obtained by this method in the copper–phenanthroline system (Table 4 below and ref. 6; cf. Part III, p. 5245).

We have already reported measurements of the stabilities of complexes of cobalt, nickel, and zinc with 1,10-phenanthroline, obtained by a spectrophotometric procedure based on the theory of corresponding solutions.[7] However, this procedure demands a knowledge of the step-stability constants of the iron–phenanthroline system, and its scope is limited.[7] Spectrophotometric methods based on the position and intensity of ultraviolet absorption bands of the organic ligand and mixtures of its metal complexes suffer from the defect that the bands generally overlap considerably. For weak complexes the procedure is liable to produce unreliable results,[8] although it has obvious advantages for determinations of K_1 in systems where the formation of higher complexes can be suppressed by working with a large excess of metal over organic ligand.[9,10] Kinetic studies of the formation and decomposition of tris-complexes can lead in certain cases (*e.g.*, with iron and nickel) to values for some or all of the stepwise formation constants.[11,12] A method depending on the effect of chelating ligands on the redox potential of the Fe^{2+}–Fe^{3+} couple has been widely exploited.[13,14] We have achieved some success in applying the changes in this redox potential under the combined influence of known concentrations of phenanthroline and of a second metal (*e.g.*, zinc) to calculations of the consecutive formation constants of phenanthroline with this second metal. The procedure is essentially an application of the theory of corresponding solutions [7] but it has not been fully studied as yet.

Polarographic procedures can be used with certain metals to determine overall stability constants and even some of the step constants,[15,16] but the method fails if the reaction at the dropping-mercury electrode is not fast enough or is irreversible (*e.g.*, in the system copper–phenanthroline [16]). A radiochemical exchange method has been used to confirm the overall stability constant of the trisphenanthrolineferrous ion, but the procedure does not lend itself to the determination of the values of the consecutive constants; [17] and a further requirement is that the kinetics of decomposition of the tris-complex should be favourably slow.

After a thorough trial of these and other promising methods we concluded that a partition procedure, first used by Kolthoff *et al.* for measuring the formation constants in the system 1,10-phenanthroline–zinc,[18] appeared to have the widest applicability for all the ligands under consideration and would be particularly suitable when the supply of reagent was limited. After suitable modification it has been used throughout.

Theory of the Partition Method.—Suppose V ml. of a solution (concentration C_M) of a salt of the chosen metal, M, in an aqueous buffer to be equilibrated with V_0 ml. of a

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[5] Nyman, *Chem. Soc. Special Publ.*, No. 6, London, 1957.
[6] Pflaum and Brandt, *J. Amer. Chem. Soc.*, 1954, **76**, 6215.
[7] Irving and Mellor, *J.*, 1955, 3457.
[8] Miller and Brandt, *J. Amer. Chem. Soc.*, 1955, **77**, 1384.
[9] Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1948, **70**, 2173.
[10] Sone, Krumholtz, and Stammreich, *J. Amer. Chem. Soc.*, 1955, **77**, 777.
[11] Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 3596.
[12] Margerum, Bystroff, and Banks, *J. Amer. Chem. Soc.*, 1956, **78**, 4211.
[13] Dwyer and McKenzie, *J. Proc. Roy. Soc. New South Wales*, 1947, **81**, 97.
[14] McKenzie, *Austral. J. Chem.*, 1955, **8**, 569.
[15] Douglas, Laitinen, and Bailar, *J. Amer. Chem. Soc.*, 1950, **72**, 2484.
[16] Onstott and Laitinen, *J. Amer. Chem. Soc.*, 1950, **72**, 4724.
[17] Cook and Long, *J. Amer. Chem. Soc.*, 1961, **73**, 4119.
[18] Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1951, **73**, 390.

solution (concentration C_L) of a neutral ligand, L, in an immiscible organic solvent. When partition equilibrium has been established (Fig. 1), equations (1) and (2) establish the mass balance in the system:

$$M_T \text{ (total metal)} = ([M] + [ML] + [ML_2] + [ML_3])V, \quad (1)$$

$$L_T \text{ (total ligand)} = ([ML] + 2[ML_2] + 3[ML_3] + [L] + [HL])V + [L]_oV_o \quad (2)$$

where the subscript o designates the organic phase and charges on the ions involving M (2+ in this case) have been omitted. It is assumed that the ligand is monobasic and that only the free base is partitioned. Experiments showed that the tris-complex, ML_3, was the highest encountered in the present systems.

On introducing equilibrium constants defined by $K_a = \{H^+\}[L]/[HL^+]$, $K_n = [ML_n]/[ML_{n-1}][L]$, and $\beta_n = [ML_n]/[M][L]^n$, and a (concentration) partition coefficient defined by $p_L = [L]_o/[L]$, we have, for the simple case where $V = V_o$,

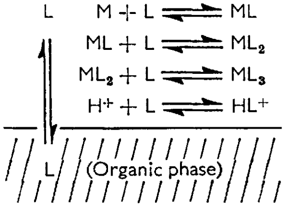

FIG. 1.

$$C_M = [M] + [ML] + [ML_2] + [ML_3], \quad (3)$$

$$C_L = [ML] + 2[ML_2] + 3[ML_3] + [L] + [HL] + [L]_o, \quad (4)$$

whence the degree of formation of the metal complexes in the aqueous phase is given by

$$\bar{n} = \text{(Total ligand bound to metal)/(Total metal)}$$

$$= \left\{C_L - [L]_o\left(\frac{1}{p_L} + \frac{[H^+]}{p_LK_a} + 1\right)\right\}\Big/C_M, \quad (5)$$

and the concentration of free ligand is given by

$$pL = -\log_{10}[L] = \log p_L - \log [L]_o. \quad (6)$$

If the partition coefficient, p_L, has been previously determined, measurements of $[L]_o$ in an equilibrated system for which C_L, C_M, and the pH are known will permit the evaluation of $\bar{n}$. Since $\bar{n}$ is related to [L] and the relevant stability constants by the expression

$$\bar{n} = (\beta_1[L] + 2\beta_2[L]^2 + 3\beta_3[L]^3)/(1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3) \quad (7)$$

values of β_1, β_2, and β_3 (and thence K_2 and K_3) can be calculated from a minimum of three well-chosen pairs of values of $\bar{n}$ and [L].

In this treatment it is assumed that no metal is extracted into the organic phase. Since it has been shown that the trisphenanthrolineferrous ion is extracted as its camphorsulphonate into chloroform,[19] as the perchlorate into nitrobenzene,[20] and in association with long-chain alkanesulphonates into chloroform,[21] care was taken to avoid the presence of anions that might favour the extraction of any metal complexes of bipyridyl or phenanthroline. The absence of metal in the organic phase was verified for each system by carrying out extractions with concentrated solutions of the reagents at various pH values and

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[19] Eimer and Medalia, *J. Amer. Chem. Soc.*, 1952, **74**, 1592.
[20] Margerum and Banks, *Analyt. Chem.*, 1954, **26**, 200.
[21] Powell and Taylor, *Chem. and Ind.*, 1954, 726.

testing the organic phase for traces of metal by the most sensitive appropriate analytical procedure.

The use of concentration constants for the partition coefficients, p_L, and for the (Brønsted) dissociation constants, K_a, of the acids conjugate to the ligands used appears justifiable since all measurements were carried out at a constant temperature (25°) and in a medium of constant ionic strength of 0·1M. Potassium chloride was used as the background salt except in measurements with cadmium where with either ligand very sparingly soluble white crystalline complexes were precipitated. In these systems potassium chloride was replaced by its nitrate. A redetermination of the value of p_L showed that this was not altered (cf. Table 1).

TABLE 1.

Partition coefficients and spectral data for ligand bases.

Bipyridyl. pK_a = 4·47, 4·51.

Medium	$\lambda_{max.}$ (mμ)	ε	p_L
Water, pH 10	280	12,900	—
Chloroform *	284	14,500	315 ± 12 (8)
n-Hexane *	282	14,500	9·6 ± 0·2 (10)

1,10-*Phenanthroline.* pK_a = 4·98.†

Medium	$\lambda_{max.}$ (mμ)	ε	p_L
Water, pH 1·5	272	29,900	—
,, 10·0	264	29,400	—
Chloroform *	266	30,800	996 ± 38 ‡ (12)
CCl_4 *	266	29,900	1·25 ± 0·03 (15)
n-Hexane *	264	31,000	0·0605 ± 0·0014 (10)

* Beer's law was shown to be obeyed up to 6 × 10^{-4}M. † Cf. Table 3; Riccardi and Franzosini (ref. 40) give 5·02. ‡ Grimes (M.Sc. Thesis, Iowa State College, U.S.A., 1956) reports 1040 ± 30.

The spectrophotometric determination of $[L]_o$ from the optical density of the organic phase imposes obvious restrictions on the choice of organic solvents. Since the absorption maxima of the neutral ligands lie between 264 and 280 mμ (depending on the solvent), most ketones and aromatic compounds are excluded. A further condition is that the organic solvent should not be too miscible with water and that it should provide a suitable partition coefficient for the basic ligand. After a survey, chloroform, carbon tetrachloride, and n-hexane were selected. They could be obtained optically pure and the values of p_L decreased in the order given and covered the range $1000 \geqslant p_L \geqslant 0{\cdot}06$ for phenanthroline and $320 \geqslant p_L \geqslant 9{\cdot}6$ for bipyridyl. This made it possible to secure a wide variation in [L] while maintaining a conveniently measurable concentration of ligand in the organic phase. Since the lower limit of about 10^{-6}M could be set for the absorptiometric determination it follows from equation (6) that a solvent for which $p_L = 1000$ could be used for measurements of pL up to 9. The limited solubility of phenanthroline in the organic phase set an upper limit of $[L]_o \sim 10^{-2}$ (whence pL = 1 for $p_L \sim 0{\cdot}1$), but the 10^3 to 10^4-fold dilution prior to the absorptiometric determination introduces a potential source of error with volatile solvents. Nevertheless, the possibility of making measurements covering the range $2 \geqslant \text{pL} \geqslant 9$ implies that the formation curves of most transition-metal complexes could be explored in full and stability constants determined up to $\beta_3 = 10^{24}$. The partition method is thus more flexible than any potentiometric procedure. With bipyridyl the range of practicable ligand concentrations was slightly smaller. Measurements with manganese are likely to be the least accurate (see Part III).

It was often possible to determine values of pL and $\bar{n}$ defining the same part of the curve when using different solvents. The continuity of the formation curve then gives added confidence to the results. Typical examples are shown in Fig. 1. A development of the partition method in which a mixture of solvents is used to bridge the gap sometimes found when only single solvents are employed is discussed in Part III.

Values for the acid dissociation constants, K_a, were determined both potentiometrically and spectrophotometrically and gave concordant results which agreed well with published data (cf. Tables 4 and 5). Distribution coefficients for each of the organic reagents between aqueous buffers of pH 7 and constant ionic strength (μ 0·1M) were determined at 25° and combined with the previously determined acid dissociation constants to give the partition coefficients, p_L, for each of the solvents employed. Similar experiments were then carried out with varying known concentrations, C_M, of manganous, ferrous, cobaltous, nickel, cupric, zinc, and cadmium ions in the aqueous phase, hydroxylamine being added to the systems containing manganese and cobalt to prevent oxidation. Corresponding values of $\bar{n}$ and pL calculated from equations (5) and (6) were then used to construct the formation curves (Figs. 1 and 2) from which approximate values of β_1 and β_2 were interpolated from the approximate equations $\log \beta_1 = \text{pL}\ (\bar{n} = 0{\cdot}5)$ and $\log \beta_2 = \text{pL}\ (\bar{n} = 1{\cdot}5)$. With these rough values of β_1 and β_2, values of β_3 were calculated from equation (7) for each experimental point ($\bar{n}$, pL). The average value was then combined with the rough value of β_1 to calculate values of β_2, again by using equation (7). With the average of these results for β_2 and the average value previously found for β_3 a series of values of β_1 was calculated for the first part of the formation curve and their average was taken. The sequence of successive approximations was then repeated until the standard deviation of the calculated constants did not decrease.

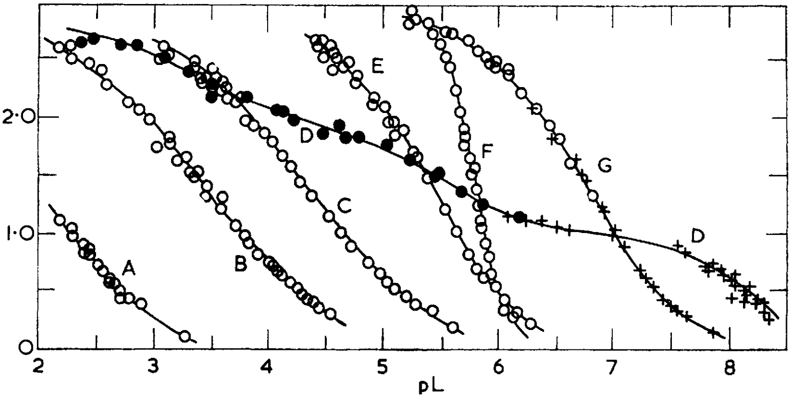

FIG. 1. Formation curves for complexes of bivalent cations with 2,2′-bipyridyl calculated from the stability constants given in Table 4. A, Mn^{2+}; B, Cd^{2+}; C, Zn^{2+}; D, Cu^{2+}; E, Co^{2+}; F, Fe^{2+}; G, Ni^{2+}. Experimental points along the nickel curve obtained by using hexane and chloroform are distinguished by open circles and crosses, respectively.

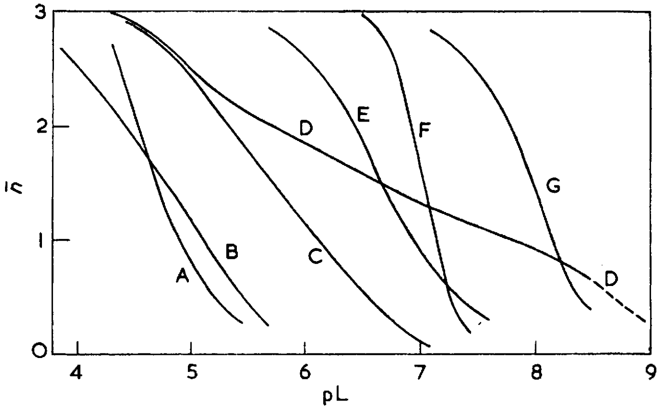

FIG. 2. Formation curves for complexes of bivalent cations with 1,10-phenanthroline calculated from the stability constants given in Table 3. A—G as for Fig. 1.

Calculations on these lines for the iron–phenanthroline system failed, for values of β_1 and β_2 proved very insensitive to changes in the value adopted for β_3. In this case an accurate value of β_1 was obtained spectrophotometrically from measurements on solutions containing a large excess of ferrous iron. The experimental value (log $\beta_1 = 5{\cdot}86$) agrees excellently with that previously reported.[9] With this value established, successive approximations led finally to the values log $\beta_2 = 11{\cdot}11$ and log $\beta_3 = 21{\cdot}14$ which were found to fit the 17 experimental points (Fig. 2) and to have standard deviations of $\pm 0{\cdot}05$ and $\pm 0{\cdot}06$, respectively.

EXPERIMENTAL

Reagents.—2,2′-Bipyridyl (G. F. Smith Chemical Co.) and 1,10-phenanthroline (L. Light & Co.) were recrystallised from water and from several organic solvents (charcoal) until there was no further change in absorption spectra. The m. p.s were then 69·5° and 101·5—102·0°, respectively. Large stocks of chloroform, carbon tetrachloride, and n-hexane were purified by standard methods, dried, fractionated, and stored in the dark. Their negligible absorption over the required range of wavelengths was always confirmed before use, and optical densities were always measured with the corresponding pure solvent in the comparison cell. Other reagents were of " AnalaR " quality. Concentrations of all metal salt solutions were checked by electrodeposition by standard methods.

Absorption spectra were measured with a Unicam S.P. 500 spectrophotometer with matched silica cells in a compartment controlled at 25°.

Acid Dissociation Constants of Reagents.—(*a*) *Potentiometric titration.* Portions (25 ml.) of a solution of bipyridyl (0·300 g.) in 0·1M-potassium chloride (100 ml.) were titrated potentiometrically with 0·0971M-hydrochloric acid, a glass electrode and calomel reference electrode being used. The values $pK_a = 4{\cdot}48$ and $4{\cdot}47^5$ were calculated from the pH at half neutralisation in different experiments. For 1,10-phenanthroline the average value obtained similarly was 4·98 from three determinations.

(*b*) *Spectrophotometric determination.* A series of solutions each containing 5·0 ml. of 0·10% bipyridyl solution and 5·0 ml. of 0·1N-sodium acetate, but various amounts of 0·1N-hydrochloric acid were made up with distilled water and N-potassium chloride to a total volume of 25 ml. to provide a series of solutions of ionic strength 0·1M and pH between 1·5 and 10·0. The optical density of each solution was measured at seven wavelengths between 226 and 236 mμ and between 296 and 310 mμ, and their actual pH's were measured with a glass electrode system. From the plots of absorbancy against pH (not reproduced) the values $pK_a = 4{\cdot}50$, 4·53, 4·52, 4·49, 4·50, 4·52, and 4·51 were obtained. The average value was 4·51 ± 0·02.

Determination of Partition Coefficients.—Bipyridyl (2—7 ml. of 0·1% solution), 0·1N-sodium acetate (2 ml.), 0·1N-hydrochloric acid, and 0·8M-potassium chloride were made up to a total volume of 10 ml. to give a series of mixtures of constant ionic strength 0·1M and pH between 1·5 and 7·0. Each mixture was equilibrated with 10 ml. of organic solvent by being shaken for 12—14 hr. in a thermostat-bath at 25·0°. The pH of the aqueous phase was then measured at 25°. The concentration, $[L]_o$, of bipyridyl in aliquot portions of the organic phase was then determined, after dilution, if necessary, with pure solvent. Aliquot portions of the aqueous phase were basified with small volumes of 0·2N-ammonia and made up to a known volume before the total concentration of base ($[L] + [HL^+]$) was determined. The appropriate wavelength for measurement was obtained from previous studies of the absorption spectra of the ligand in acid, alkali, and various organic solvents (cf. Table 1). Beer's law was also shown to hold in each solvent at least over the range 1—6×10^{-5}M. As pK_a and $[L]_o$ were known, the value of $[L]$, and hence of p_L, could be calculated for each mixture. Further details are given in Part III. Table 1 shows the average values of p_L and their standard deviation: the number of determinations follows in parentheses. Similar measurements were carried out with 1,10-phenanthroline.

Measurements of Metal Stability Constants.—The procedure was essentially that employed in determinations of p_L for the basic ligands except that a known concentration, C_M, of the appropriate metal was also present in the aqueous phase. Table 2 gives typical results for the distribution of 2,2′-bipyridyl between an aqueous phase containing nickel sulphate and the solvents chloroform and n-hexane.

The formation curve (Fig. 1) shows that points obtained by using chloroform (crosses) or n-hexane (open circles) lie on a common curve. Points along the formation curve were not obtained consecutively and usually four or more sets of measurements (designated in Table 3 by superscripts 1—8) were made, overlapping in their range; this procedure tended to minimise systematic errors. Results for other metal–ligand systems are included in Table 3.

TABLE 2.

Distribution of 2,2′-bipyridyl between aqueous nickel sulphate and organic solvents.

Chloroform (C_L = 6·40 × 10^{-4}M; p_L = 315; ε = 14,500).

A *	$10^5[L]_0$	$10^7[L]$	10^4y †	10^3C_M	$\bar{n}$	pL
0·140	0·986	0·314	6·30	1·8	0·35	7·500
0·188	1·32	0·421	6·27	1·2	0·52	7·376
0·256	1·80	0·572	6·22	0·9	0·69	7·243
0·403	2·84	0·904	6·12	0·6	1·02	7·044
0·735	5·18	1·645	5·88	0·4	1·47	6·784
1·23	8·65	2·75	5·33	0·3	1·84	6·561
1·90	13·4	4·24	5·05	0·24	2·10	6·373
4·45	31·4	10·0	3·25	0·13	2·51	6·000

n-Hexane (C_L = 6·4 × 10^{-4}M; p_L = 9·60; ε = 14,500).

A *	$10^5[L]_0$	$10^7[L]$	10^4y †	10^3C_M	$\bar{n}$	pL
0·033	2·29	2·39	6·37	4·0	1·59	6·620
0·045	3·10	3·23	6·37	3·5	1·82	6·490
0·060	4·15	4·32	6·35	3·0	2·12	6·360
0·133	9·18	9·56	6·29	2·5	2·52	6·020
0·235	16·2	16·9	6·20	2·3	2·70	5·770
0·517	35·7	37·2	5·96	2·1	2·86	5·430

* Optical density measured at 284 ($CHCl_3$) or 282 (hexane) mμ. † y = Total ligand bound to metal = C_L − [L] − $[L]_0$.

TABLE 3.

Complexes of 2,2′-bipyridyl and 1,10-phenanthroline.

2,2′-Bipyridyl

Manganese: 10^2C_L 10·25—9·13; 10^2C_M 3·0—17·2.

$\bar{n}$	0·15^{1}	0·45^{1}	0·495^{1}	0·50^{2}	0·535^{3}	0·57^{2}	0·57^{1}	0·62^{3}	0·64^{1}	0·66^{2}	0·74^{3}	0·78^{1}
pL	3·30	2·925	2·807	2·830	2·775	2·735	2·752	2·678	2·652	2·648	2·585	2·588
$\bar{n}$	0·88^{3}	0·905^{1}	0·95^{2}	1·04^{2}	1·11^{3}	1·18^{3}						
pL	2·455	2·453	2·419	2·324	2·312	2·197						

Iron: 10^4C_L = 6·40; 10^3C_M 0·20—2·5.

$\bar{n}$	0·253^{1}	0·315^{1}	0·42^{2}	0·525^{3}	0·63^{2}	0·63^{1}	0·78^{3}	0·90^{3}	1·04^{3}	1·25^{2}	1·25^{4}	1·39^{2}
pL	6·143	6·072	6·031	6·022	5·910	5·959	5·934	5·915	5·888	5·882	5·883	5·845
$\bar{n}$	1·39^{4}	1·52^{1}	1·56^{3}	1·65^{2}	1·78^{3}	1·83^{2}	1·91^{2}	2·00^{4}	2·06^{3}	2·06^{1}	2·24^{2}	2·45^{2}
pL	5·860	5·807	5·838	5·788	5·818	5·770	5·742	5·731	5·752	5·714	5·680	5·634
$\bar{n}$	2·54^{4}	2·65^{2}	2·74^{1}	2·85^{4}	2·98^{4}							
pL	5·585	5·553	5·488	5·460	5·292							

Cobalt: 10^4C_L = 6·40; 10^3C_M 0·11—2·0.

$\bar{n}$	0·316^{1}	0·421^{1}	0·524^{1}	0·694^{1}	0·830^{2}	1·03^{1}	1·22^{2}	1·50^{2}	1·68^{1}	1·97^{3}	2·14^{3}	2·18^{2}
pL	6·184	6·081	5·955	5·827	5·762	5·656	5·565	5·407	5·309	5·072	4·921	5·046
$\bar{n}$	2·33^{1}	2·40^{3}	2·46^{3}	2·48^{1}	2·52^{2}	2·55^{4}	2·56^{4}	2·61^{2}	2·62^{4}	2·67^{4}	2·68^{4}	2·72^{2}
pL	4·785	4·799	4·678	4·597	4·728	4·504	4·616	4·564	4·587	4·453	4·561	4·494
$\bar{n}$	2·72^{4}											
pL	4·492											

Nickel: 10^4C_L = 6·40; 10^3C_M 5·0—0·1.

$\bar{n}$	0·13^{1}	0·31^{1}	0·35^{2}	0·42^{2}	0·52^{2}	0·62^{1}	0·69^{2}	0·88^{2}	1·02^{2}	1·21^{3}	1·22^{1}	1·28^{3}
pL	7·873	7·547	7·500	7·453	7·376	7·304	7·243	7·128	7·044	6·949	6·932	6·830
$\bar{n}$	1·47^{2}	1·59^{3}	1·65^{3}	1·82^{3}	1·84^{2}	1·95^{3}	2·10^{3}	2·12^{4}	2·22^{1}	2·28^{3}	2·47^{3}	2·51^{3}
pL	6·784	6·620	6·701	6·490	6·561	6·488	6·373	6·360	6·207	6·250	6·114	6·000
$\bar{n}$	2·52^{5}	2·55^{3}	2·70^{5}	2·78^{5}	2·85^{5}	2·86^{5}						
pL	6·020	5·924	5·772	5·592	5·430	5·220						

Copper: 10^4C_L 6·40—98·1; 10^3C_M 0·5—25·0.

$\bar{n}$	0·253^{1}	0·316^{1}	0·400^{1}	0·400^{2}	0·425^{3}	0·430^{2}	0·460^{2}	0·490^{1}	0·525^{1}	0·540^{2}	0·590^{2}	0·630^{2}
pL	8·348	8·328	8·288	8·270	8·020	8·160	8·160	8·160	8·204	8·090	8·050	8·104
$\bar{n}$	0·640^{3}	0·680^{2}	0·770^{1}	0·860^{2}	0·900^{3}	1·01^{4}	1·05^{4}	1·06^{5}	1·12^{4}	1·15^{5}	1·22^{4}	1·25^{6}
pL	7·947	7·790	7·910	7·654	7·533	6·975	6·495	6·575	6·214	6·218	6·107	5·897
$\bar{n}$	1·25^{3}	1·37^{5}	1·50^{5}	1·51^{3}	1·64^{5}	1·79^{3}	1·86^{5}	1·87^{5}	1·93^{6}	1·98^{3}	2·03^{4}	2·11^{4}
pL	5·947	5·690	5·466	5·502	5·224	5·046	4·821	4·690	4·883	4·663	4·258	4·146
$\bar{n}$	2·13^{4}	2·24^{4}	2·25^{7}	2·26^{4}	2·28^{7}	2·36^{7}	2·40^{7}	2·49^{6}	2·60^{7}	2·70^{7}	2·71^{4}	2·72^{4}
pL	4·120	3·577	3·442	3·853	3·333	3·572	3·11	3·35	3·161	2·90	2·50	2·77
$\bar{n}$	2·75^{7}	2·78^{7}										
pL	2·39	2·61										

TABLE 3. (*Continued.*)

Zinc: 10^3C_L 1·28—3·84; 10^3C_M 0·2—3·5.

$\bar{n}$	0·360^{1}	0·410^{1}	0·490^{2}	0·600^{2}	0·674^{1}	0·770^{2}	0·920^{2}	1·04^{2}	1·19^{2}	1·37^{2}	1·50^{1}	1·63^{3}
pL	5·484	5·322	5·231	5·092	5·021	4·943	4·760	4·686	4·570	4·416	4·341	4·253
$\bar{n}$	1·63^{2}	1·72^{4}	1·85^{1}	1·92^{3}	1·93^{4}	1·98^{1}	2·04^{4}	2·15^{5}	2·18^{4}	2·22^{4}	2·30^{5}	2·28^{6}
pL	4·251	4·167	4·068	4·041	4·020	3·917	3·845	3·696	3·760	3·686	3·634	3·480
$\bar{n}$	2·29^{7}	2·31^{3}	2·32^{1}	2·33^{5}	2·33^{6}	2·34^{5}	2·35^{7}	2·36^{4}	2·38^{3}	2·38^{6}	2·38^{1}	2·38^{6}
pL	3·410	3·791	3·812	3·682	3·553	3·599	3·445	3·445	3·688	3·461	3·686	3·440
$\bar{n}$	2·38^{4}	2·39^{4}	2·42^{4}	2·46^{3}	2·50^{5}	2·57^{7}	2·60^{7}	2·67^{7}				
pL	3·652	3·507	3·582	3·607	3·572	3·100	3·157	3·135				

Cadmium: 10^3C_L 1·28—9·9; 10^3C_M 0·2—3·6.

$\bar{n}$	0·330^{1}	0·370^{1}	0·430^{1}	0·450^{1}	0·460^{1}	0·480^{2}	0·545^{2}	0·620^{3}	0·670^{3}	0·710^{3}	0·770^{3}	0·855^{4}
pL	4·548	4·466	4·402	4·401	4·252	4·349	4·277	4·192	4·134	4·092	4·062	4·031
$\bar{n}$	0·965^{4}	1·26^{4}	1·26^{4}	1·47^{5}	1·56^{6}	1·57^{7}	1·60^{5}	1·73^{5}	1·75^{7}	1·80^{7}	1·83^{6}	1·89^{5}
pL	3·921	3·836	3·609	3·465	3·381	3·334	3·435	3·306	3·147	3·071	3·192	3·179
$\bar{n}$	2·06^{5}	2·14^{6}	2·20^{5}	2·37^{5}	2·48^{6}	2·55^{5}	2·60^{5}	2·71^{6}				
pL	3·031	2·921	2·818	2·648	2·597	2·489	2·330	2·319				

1,10-*Phenanthroline*

Manganese: 10^4C_L 2·56; 10^3C_M 0·38—12·6.

$\bar{n}$	0·65^{1}	0·92^{1}	1·20^{1}	1·30^{2}	1·54^{2}	1·71^{2}	1·73	1·80	1·93	2·23	2·29
pL	4·59	4·26	4·06	4·32	4·19	4·07	4·00	3·82	4·04	3·92	3·86

Iron: 10^4C_L 10·1; 10^3C_M 0·20—4·0.

$\bar{n}$	0·243^{1}	0·323^{1}	0·480^{1}	0·48^{2}	0·64^{1}	0·76^{1}	0·94^{2}	0·95^{1}	1·17^{1}	1·31^{3}	1·54^{1}	1·80^{2}
pL	7·38	7·34	7·28	7·27	7·24	7·20	7·14	7·17	7·12	7·05	7·04	6·98
$\bar{n}$	1·81^{3}	2·01^{3}	2·12^{3}	2·20^{2}	2·46^{3}	2·73^{3}	2·84^{2}	2·93^{3}	3·00^{3}	3·00^{3}		
pL	6·99	6·96	6·90	6·87	6·83	6·72	6·53	6·55	6·39	6·46		

Cobalt: 10^3C_L 2·64; 10^3C_M 0·2—7·0.

$\bar{n}$	0·39^{1}	0·51^{2}	0·53^{1}	0·89^{1}	1·30^{1}	1·61^{2}	2·15^{2}	2·30^{1}	2·47^{2}	2·60^{2}	2·68^{2}	2·70^{2}
pL	7·41	7·35	7·24	7·00	6·79	6·63	6·32	6·33	6·12	5·96	5·92	5·80
$\bar{n}$	2·80^{2}	2·80^{2}	2·90^{2}									
pL	5·74	5·71	5·68									

Nickel: 10^3C_L 2·532; 10^3C_M 0·30—3·00.

$\bar{n}$	0·33^{2}	0·505^{1}	0·603^{2}	0·716^{1}	1·00^{1}	1·00^{3}	1·25^{1}	1·25^{3}	1·44^{2}	1·67^{1}	1·67^{3}	2·00^{1}
pL	8·40	8·30	8·31	8·24	8·20	8·19	8·10	8·09	8·05	7·88	7·88	7·79
$\bar{n}$	2·00^{3}	2·25^{2}	2·50^{1}	2·75^{2}	2·86^{2}	2·87^{1}						
pL	7·67	7·71	7·46	7·21	6·73	6·42						

Copper: 10^4C_L 25·73—4·75; 10^3C_M 8·0—0·05.

$\bar{n}$	0·42^{8}	0·63^{8}	0·90^{8}	1·00^{7}	1·09^{7}	1·225^{8}	1·41^{7}	1·52^{1}	1·52^{7}	1·60^{2}	1·69^{8}	1·70^{8}
pL	8·15	8·13	7·99	7·77	7·47	7·09	6·79	6·60	6·595	6·17	5·85	6·31
$\bar{n}$	1·76^{4}	1·78^{7}	1·83^{8}	1·87^{8}	1·88^{7}	1·90^{1}	2·02^{4}	2·25^{3}	2·31^{4}	2·31^{4}	2·36^{8}	2·40^{2}
pL	5·77	6·13	5·97	5·73	5·91	5·92	5·59	5·39	5·30	5·24	5·20	4·60
$\bar{n}$	2·40^{3}	2·43^{4}	2·51^{2}	2·60^{2}	2·62^{3}	2·65^{3}	2·66^{3}	2·67^{5}	2·95^{6}	2·96^{2}	3·04^{6}	
pL	4·38	5·04	4·39	4·92	4·95	4·56	4·72	4·43	4·67	4·28	3·75	

Zinc: 10^4C_L 25·25–5·10; 10^3C_M 25·0—0·15.

$\bar{n}$	0·097^{3}	0·190^{3}	0·311^{3}	0·450^{3}	0·780^{3}	0·980^{3}	1·17^{3}	1·36^{2}	1·45^{1}	1·475^{3}	1·67^{2}	1·99^{1}
pL	6·97	6·81	6·72	6·57	6·25	6·09	5·97	5·685	5·595	5·75	5·57	5·27
$\bar{n}$	2·17^{1}	2·41^{1}	2·60^{2}	2·78^{1}								
pL	5·21	4·96	4·83	4·57								

Cadmium: 10^4C_L 2·547—5·095; 10^3C_M 1·0—0·06.

$\bar{n}$	0·247^{1}	0·324^{2}	0·478^{1}	0·770^{1}	0·845^{3}	0·910^{3}	0·990^{3}	1·08^{1}	1·09^{3}	1·21^{3}	1·34^{3}	1·58^{2}
pL	5·65	5·54	5·42	5·23	5·31	5·21	5·14	5·035	5·08	5·01	4·90	4·78
$\bar{n}$	1·62^{3}	1·75^{3}	1·77^{1}	1·90^{1}	1·93^{2}	2·13^{1}	2·14^{2}	2·31^{2}	2·37^{2}	2·45^{2}		
pH	4·66	4·54	4·53	4·41	4·52	4·33	4·29	4·17	4·11	4·05		

$^{1-8}$ Superscript numerals denote related series of determinations.

Determination of K_1 for the System Iron–Phenanthroline.—The molecular extinction coefficient of the intensely red tris-complex was redetermined at $\lambda_{max.}$ 510 in solutions containing a ten-fold excess of ligand. A series of solutions was prepared containing concentration L_T of ligand with concentrations C_M (excess) of ferrous iron such that $0{\cdot}1 \geqslant \bar{n} \leqslant 0{\cdot}3$. The concentration, [FeL$_3$], of the tris-complex was then determined photometrically at 510 mμ. On the assumption that at this wavelength it is possible to neglect any absorption due to the 1 : 1

complex FeL ($\lambda_{max.}$ 400—450 mμ, ε 330) or to the very small amounts of the 1 : 2 complex FeL_2 in equilibrium, it follows that the value of $[FeL_3]$ can be calculated from the measured absorbancy whence [FeL] follows from equation (8), [Fe] from (9), and β_3 from (10).

$$L_T = 3[FeL_3] + [FeL] + [L](1 + [H^+]/K_a \qquad (8)$$

$$C_M = [FeL_3] + [FeL] + [Fe] \qquad (9)$$

$$\beta_3 = [FeL_3]/[Fe][L]^3 \qquad (10)$$

The value of $K_1 = [FeL]/[Fe][L]$ was then calculated from the computed values of [FeL], [Fe], and [L]. The average was $10^{5\cdot86}$ in excellent agreement with Kolthoff, Leussing, and Lee's value.[9]

RESULTS

Since the measurements now reported were completed in 1954 a number of papers have appeared which deal with one or other of the transition metals. However, in no other case has the complete series been investigated and in several cases the values reported for stability constants are obviously in error. To facilitate comparison all the available results are summarised in Tables 4 and 5.

We shall consider first the 1,10-phenanthroline–iron system. The consistency of values reported for log β_3 by five different methods and authors is most satisfactory. It is regrettable that the most recent value (ref. 36) is so completely in error. The authors certainly take note that their result (log β_3 = 18·5) is far from the accepted value of 21·3 and closer to the earliest value of 17·1 (ref. 23) obtained by a redox-potential method in which no allowance had been made at the time (but cf. ref. 5, p. 83) for complex formation between phenanthroline and ferric ions. They suggest that their low results may be similarly explained although this explanation cannot be validly applied to the pH titration procedure they used and, in addition, no ferric ions should have been present in their solutions. It is clear that this and probably other results in this paper which the authors admit to be " of comparative interest only " must be regarded with suspicion.

Values quoted for zinc complexes are in reasonable agreement if the low provisional value for log K_3 in ref. 39 is rejected. In this series of measurements there is a valuable confirmation from the results of a new method—the use of a reversible mercury–phenanthroline electrode [37]—which, though of rather limited application, has been used to obtain values of log K_1 for Co, Ni, Cu, Zn, and Cd, values of log K_2 for Cu and Ni, and a value of log K_3 for Ni.

Our values for nickel are generally a little lower than those obtained either by kinetic measurements or by the use of the mercury electrode.[37] The value log β_3 = 18·3 must be rejected.[35] However, there is no doubt that the overall stability of the nickel complexes exceeds that of both copper and iron. There is satisfactory agreement between the values for cobalt determined by us and independently in America.[38]

From Table 3 it seems clear that Pflaum and Brandt's results [6] for copper are wrong: it is unfortunate that they have been used to support arguments based on ligand-field theory. A recent value for log K_1 = 7·4 (ref. 29) seems equally at fault and points the danger of using the inappropriate pH-titration method. The most unsatisfactory results are those reported for manganese. While we have no means of assessing the reliability of the values obtained by a redox method and communicated personally by Dr. Williams there is little doubt that the value log β_3 = 7·36 of ref. 8 must be rejected. The lack of agreement between the two sets of distribution measurements (and indeed between attempts to duplicate our own measurements under somewhat different conditions) is disturbing. A tentative set of values is log K_1 = 4, log K_2 = 3·5, log K_3 = 3, with log β_3 = 10·5.

Among the complexes formed by 2,2′-bipyridyl the agreement between the various values for iron(II) is very satisfactory. The most recent work by Atkinson and Bauman [22] refers to a higher ionic background (1M-$NaClO_4$), but even so the divergencies are considerable. If their values for manganese were correct its complexes with bipyridyl would be more stable than those with phenanthroline. As a rough generalisation, values for the 1 : 1 complexes of bipyridyl are weaker by 1·5—2·0 log units than those of phenanthroline (see below). If the value

[22] Atkinson and Bauman, Technical Report (ORA Project 0448), University of Michigan, U.S.A., 1961.

TABLE 4.

Stability constants of complexes of bivalent cations with 2,2′-bipyridyl.

Method *	*I*	*T*	p*K* of HL+	log K_1	log K_2	log β_2	log K_3	log β_3	Ref.
Manganese									
sp. J.	0·5	—	—	—	—	—	—	6·3	8
sp.	—	27°	—	~2·5	—	—	—	—	10
gl.	1M-NaClO$_4$	25	4·334 ‡	4·06	3·78	7·84	3·63	11·47	22
e.s.r.	~0·1M-NaAc	—	—	—	—	—	—	6·03	22
dist.	0·1M-KCl	25	4·47	2·62	2·00	4·62	~1·1	~5·6	†
Iron									
red.	—	—	—	—	—	—	—	~15·0	23
red.	0·0075N-H$_2$SO$_4$	25	4·4	—	—	—	—	16·4	13
sp.	$\longrightarrow$ 0	25	4·34	4·36	—	—	—	—	24
sp.	0·33	25	4·43	4·43	—	—	—	17·58	25
sp.	0·025	25	4·334	—	—	—	—	17·07	26
kin.	—	25	4·38	—	—	—	—	17·08	41
sp.	0·025	35	—	4·2	<5	—	$>7·3$	16·53	26
		45						15·94	26
dist.	0·1M-KCl	4·25	4·47	4·20	3·70	7·90	9·55	17·45	†
Cobalt									
dist.	0·1M-KCl	25	4·47	5·65	5·60	11·25	4·80	16·05	†
Nickel									
gl.	1M-NaClO$_4$	25	4·334 ‡	6·80	6·46	13·26	5·20	18·46	22
—	—	—	—	—	—	—	—	~20	§
dist.	0·1M-KCl	25	4·47	7·07	6·86	13·93	6·20	20·13	†
Copper									
pol.	0·1M-KNO$_3$	25	—	—	—	14·2	3·65	17·85	16
redox.	0·1M-K$_2$SO$_4$	25	4·50	—	~5·6	—	3·20	—	28 ‖
gl.	0·1M-KNO$_3$	25	4·45	6·33	—	—	—	—	29
gl.	1M-NaClO$_4$	25	4·33 ‡	4·89	4·58	9·47	4·27	13·74	22
dist.	0·1M-KCl	25	4·47	8·15	5·50	13·65	3·30	16·95	†
Zinc									
gl.	0·1M-KNO$_3$	25	4·44	5·4	4·4	9·8	4·0	13·5	30
gl.	1·0M-NaClO$_4$	25	4·334	4·89	4·58	9·47	4·27	13·74	22
dist.	0·1M-KCl	25	4·47	5·04	4·35	9·39	3·57	12·96	†
Cadmium									
pol.	0·1M-KNO$_3$	25	—	—	—	—	—	10·47	15
gl.	0·1M-KNO$_3$	25	4·44	4·5	3·5	8·0	2·5	10·5	30
gl.	0·1M-KNO$_3$	25	—	4·38	3·50	7·88	2·61	10·49	¶
Cd–Hg	0·05M-KNO$_3$	25	—	4·26	3·56	7·82	2·66	10·48	31
gl.	0·05M-KNO$_3$	25	—	4·28	3·51	7·79	2·69	10·48	31
dist.	0·1M-KCl	25	4·47	4·12	3·50	7·62	2·60	10·24	†

* For abbreviations see footnote to Table 5. † This paper. ‡ The values given in ref. 22, p. 87, drift monotonically from 4·714 to 4·253; the choice of 4·334 is not clear. § Preliminary measurement by Jørgensen reported in ref. 27. ‖ The values for stability constants in Table 5 of this ref., there designated by the superscript *t*, were not obtained, as there stated, by pH-titration; they are the values now reported in this paper and previously communicated personally to R. J. P. W. ¶ Calculations refined in ref. 31 from data in ref. 30.

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TABLE 5.

Stability constants of complexes of bivalent cations with 1,10-phenanthroline.

Method *	*I*	*T*	pK of HL$^+$	log K_1	log K_2	log β_2	log K_3	log β_3	Ref.
Manganese									
sp.	—	—	—	—	—	—	—	7·36	8
redox.	0·1M-K_2SO_4	25°	4·97	3·5	3·25	7·75	3·0	9·75	†
dist.	0·1M-KCl	25	4·98	4·10	3·10	7·20	3·20	10·40	32
dist.	0·1M-KCl	25	4·98	4·50	4·15	8·65	4·05	12·70	‡
Iron									
redox.	0·01M-H_2SO_4	25	5·2	—	—	—	—	17·1	23
								21·0	§
sp.	$\longrightarrow$ 0	25	4·96	—	—	—	—	21·3	33
kin.	$\longrightarrow$ 0	25	4·96	—	—	—	—	21·5	11
sp.	0·625M-H_2SO_4	25	4·96	5·89	—	—	—	—	9
tracer ex.	—	—	—	—	—	—	—	21·1	17
equil.			4·96	—	—	—	—	21·5	34
								22·4	35
redox.		25	—	—	—	—	—	21·3	14
sp.	0·1M-KCl	25		5·85				21·3	36
dist.	0·1M-KCl	25	4·98	5·86	5·25	11·11	10·03	21·14	‡
dist.	0·1M-KCl	25	4·98	—	—	—	—	21·15	32
sp.	0·1M-KCl	25	4·98	5·72	—	—	—	—	32
gl. spec.	0·1M-NaOAc	—	5·07	—	—	—	—	18·5	36
		25	—	5·85	—	—	—	—	38
Cobalt									
Hg	0·1M-$NaNO_3$	20		7·31	—	—	—	—	37
dist.	0·1M-KCl	25	4·98	6·96	6·73	13·69	6·08	19·77	32
dist.	0·1M-KCl	25	4·98	7·02	6·70	13·72	6·38	20·10	‡
Nickel									
sp.	—	—	—	—	—	—	—	18·3 ± 1·1	35
Hg	0·1M-$NaNO_3$	20	—	8·80	8·30	17·10	7·70	24·80	37
kin.		25	—	8·60	8·10	16·70	7·55	24·30	12
sp. comp.	0·1M-KCl	25						23·9	7
dist.	0·1M-KCl	25	4·98	8·0	8·0	16·0	7·9	23·9	‡
Copper									
gl.	0·4M-$NaNO_3$	25	4·96	6·30	6·15	12·45	5·50	17·95	6
Hg	0·1M-$NaNO_3$	20	—	9·30	6·84	16·14	small		37
dist.	0·1M-KCl	25		9·15	6·65	15·80			38 ‖
gl.	0·1M-KCl	25			6·65	—	5·25	21·05	38
dist.	0·1M-KCl	25		9·0	6·7	15·7			38 ‖
gl.	0·1M-KCl	25			6·7	—	5·1	20·9	38
dist.	0·1M-KCl	25	4·98	8·82	6·57	15·39	5·02	20·41	‡
gl.	0·1M-KNO_3	25	4·95	7·4					29
redox.	0·1M-K_2SO_4	25	4·97	—	—	—	4·94	—	28
spec.		25	4·97	—	6·64	—	4·90	—	28
Zinc									
sp.	0·1M-KNO_3	25		6·6					18
dist.	0·1M-KNO_3	25	4·96	(6·43)	(5·72)	12·15	4·85	17·0	18
Hg	0·1M-$NaNO_3$	20	—	6·40	—	—	—	—	37
spect.	—	25	—	6·47	5·5	11·97	1·1	13·1	39
gl.	0·1M-KNO_3	25	4·92		5·9		4·8		30
sp. comp.	0·1M-KCl	25	4·96	6·5	5·45	11·95	5·1	17·05	7
gl.	0·1M-KCl	25		6·36	5·64	12·00	5·2	17·2 ¶	38
sp. comp.	0·1M-KCl	25		6·43					38
dist.	0·1M-KCl	25		6·60	5·72	12·32	4·85	17·17 ¶	38
gl.	0·1M-KCl	25			5·9		4·8		38
dist.	0·1M-KCl	25	4·98	6·30	5·65	11·95	5·10	17·05	‡
Cadmium									
pol.	0·1M-KNO_3	25		6·4	5·2	11·6	4·2	15·8	15
Hg	0·1M-$NaNO_3$	20		6·01	—	—	—	—	37
gl.	0·1M-KNO_3	25	4·92	—	5·2	—	4·2	—	30
dist.	0·1M-KNO_3	25	4·98	5·17	4·83	10·0	4·26	14·26	‡

* In Tables 1 and 2, the abbreviations used for methods are those adopted in ref. 5, *viz.*: dist. = distribution, gl. = glass electrode; kin. = rate of reaction; Cd–Hg = cadmium amalgam electrode; pol. = polarography; sp. = spectrophotometric; sp. J. = spectrophotometric method by Job's method of continuous variation. In addition sp. comp. refers to the method of ref. 7; Hg = mercury–phenanthroline electrode. † R. J. P. Williams, personal communication. ‡ This paper. § Ref. 5, p. 83. ‖ μ = 0·0132 in determinations of log K_1. ¶ Authors give log β_3 = 17·0.

log $K_{\mathrm{Mn\,phen}} = 4{\cdot}0$ is accepted the corresponding value for bipyridyl would be log $K_{\mathrm{Mn\,bipy}} = {\sim}2{\cdot}5$, which agrees with the values found independently by Sone, Krumholtz, and Stammreich [10] and ourselves (Table 4).

Referring to the values 6·3, 5·8, and 6·0 for log β_3 obtained by spectrophotometry,[8] by the present authors (personally communicated), and by electron-spin resonance [22] Atkinson and Bauman comment " it is remarkable that three very different measurements have yielded similar results for the overall formation constant ": however, they do not comment on the discrepancy between their result (6·0) by electron-spin resonance and their value log $\beta_3 = 11{\cdot}47$ obtained by a titration procedure and reported in the same publication.

It will be obvious that the determination of the high stabilities of complexes of the transition metals still leaves much to be desired. In a few cases (*e.g.*, log K_1 and log β_3 for complexes of iron with bipyridyl or phenanthroline, or of cadmium with bipyridyl) all the most reliable values lie within a range of about 0·2 log unit. In other cases the uncertainty still extends over several log units. We recommend the use of the critically selected values in Table 6 pending further measurements; but in what follows we shall indicate the range of reliable values wherever possible.

TABLE 6.

Recommended values for stability constants of transition-metal complexes (at 25° and $\mu = 0{\cdot}1$M).

	Mn	Fe	Co	Ni	Cu	Zn	Cd
			With 2,2′-*dipyridyl*				
log K_1	2·6	4·3	5·7	7·1	8·1	5·2	4·3
log K_2	2	3·7	5·6	6·8	5·5	4·4	3·5
log K_3	1	9·5	4·8	6·2	3·4	3·8	$2{\cdot}6_5$
log β_3	6	17·5	16·1	20·1	17·0	13·4	$10{\cdot}4_5$
			With 1,10-*phenanthroline*				
log K_1	4	$5{\cdot}8_5$	7·0	8·6	$9{\cdot}0_5$	$6{\cdot}4_5$	6·0
log K_2	3·5	$5{\cdot}2_5$	6·7	$8{\cdot}1_5$	6·7	$5{\cdot}6_5$	5·1
log K_3	3	10·0	6·2	7·6	5·0	5·0	4·2
log β_3	10·5	21·2	19·9	24·3	20·8	17·1	15·3

DISCUSSION

Points which arise from the present results in relation to themselves and to data for other transition-metal complexes are the absolute and the relative values of the stability constants. It was long ago noted that the overall stability of the complex of iron with phenanthroline (log $\beta_3 = 21{\cdot}2$) was abnormally high in comparison with those of zinc (17·1) and cadmium (15·3), so that the usual order of stability Fe < Zn or Cd was disobeyed. In discussing the validity and generality of the Irving–Williams order [4] an explanation in terms of what at that time we referred to as " orbital stabilisation " was proposed. This change in the electron configuration of the ferrous iron (which is nowadays included in discussions of ligand-field theory) and is the direct cause of the enhancement in stability could, it was pointed out, occur " concurrently with the chelation of the first, second, or third molecule of ligand." The present results show conclusively that it does not take place at the first stage, because for both phenanthroline and bipyridyl the order of stabilities is " normal " with Mn < Fe < Co < Ni < Cu > Zn and Cd. This is displayed

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[32] McBryde, Brisbin, and Irving, Part III, *J.*, 1962, 5245.
[33] Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 2348.
[34] Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.
[35] Davies and Dwyer, *Trans. Faraday Soc.*, 1953, **49**, 180 (personal communication from Dunstone and Mellor).
[36] Hawkins, Duewell, and Pickering, *Analyt. Chim. Acta*, 1961, **25**, 257.
[37] Anderegg, *Helv. Chim. Acta*, 1959, **42**, 344.
[38] Banks and Bystroff, *J. Amer. Chem. Soc.*, 1959, **81**, 6153.
[39] McClure, Ph.D. Thesis, Iowa State College, U.S.A., 1951.
[40] Riccardi and Franzosini, *Boll. Fac. Sci. Chim. ind. Bologna*, 1957, **15**, 25.
[41] Baxendale and George, *Trans. Faraday Soc.*, 1950, **46**, 736.

graphically in Fig. 3 where data for complexes of the analogous bidentate ligand ethylenediamine are included. Although the aliphatic diamine ($pK_{BH_2^{2+}} = 7{\cdot}5$; $pK_{BH^+} = 10{\cdot}2$) is a more powerful base than bipyridyl ($pK_{BH^+} = 4{\cdot}4$) by a factor of more than 10^5, it is interesting how little difference there is between the measured stabilities (except for copper). The additional stability is a striking example of the greater ligand-field stabilisation produced by the heterocyclic ligand. A comparison of the stability constants for the co-ordination of one molecule of bipyridyl with those for two molecules of pyridine illustrates the stabilisation due to the " chelate-effect." This additional stabilisation must arise mainly as an entropy effect reflecting the (greater) increase in the number of molecules in the system when bipyridyl (rather than two molecules of pyridine) displaces water from the aquated cation on becoming co-ordinated to it. The stability data for pyridine used in Fig. 3 are taken from ref. 5, with the exception of that for manganese whose value [22] is manifestly in error. There are also serious discrepancies between values quoted for nickel (log $\beta_2 = 3{\cdot}79$; Bjerrum [5] reports 2·82) and zinc (log $\beta_2 = 3{\cdot}77$; Bjerrum [5] reports 1·05, and Nyman [5] reports 1·11, which cannot entirely be due to the increased ionic strength used by the American authors [22]).

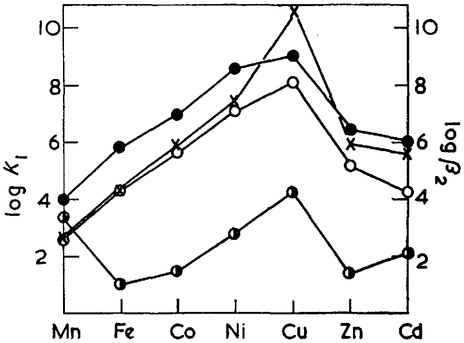

FIG. 3. Logarithms of stability constants for complexes of bivalent ions with one molecule of a bidentate ligand; 1,10-phenanthroline (log K_1, ●), 2,2′-bipyridyl (log K_1, ○), and ethylenediamine (log K_1, ×). Values for two molecules of pyridine (log β_2 = log K_1K_2, ◑).

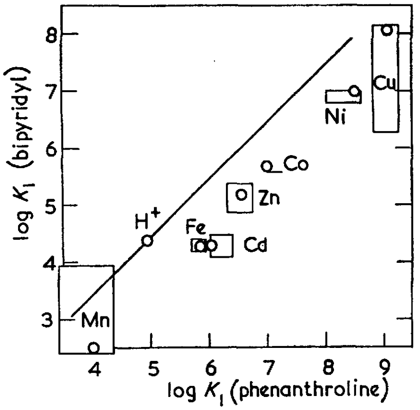

FIG. 4. Stabilities of complexes of bivalent ions with 2,2′-bipyridyl and 1,10-phenanthroline; the ranges of experimental values are denoted by rectangles, and the selected values taken from Table 6 are denoted by circles. The solid line is of unit slope and intercept $\Delta pK = 0{\cdot}51$.

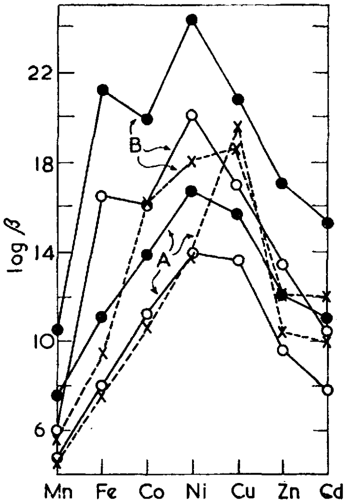

FIG. 5. Overall stability constants for complexes of bivalent ions with two (or three) mols. of the bidentate ligands 1,10-phenanthroline (●), 2,2′-bipyridyl (○), and ethylenediamine (×). Values for ethylenediamine from ref. 5. A = log β_2; B = log β_3.

The stabilities of the phenanthroline complexes are consistently greater than those of the bipyridyl complexes. Part of this increase would be expected from the increase in pK from 4·47 to 4·98. If the relationship of equation (11), which has been shown to hold

$$\log K_{\mathrm{ML}} = \log K_{\mathrm{MP}} + (\mathrm{p}K_{\mathrm{HA}} - \mathrm{p}K_{\mathrm{HB}}) \qquad (11)$$

for pairs of very similarly constituted ligands,[42] applies to the present pair of ligands, a plot of stability constants for transition-metal complexes of phenanthroline against those for the same metal and bipyridyl should lie on a line of unit slope and intercept $\Delta\mathrm{p}K = 4{\cdot}98 - 4{\cdot}47 = 0{\cdot}51$. Fig. 4 shows the predicted line together with the experimental values (shown with the approximate spread of values) and the values for log K_1 selected in Table 6. It is clear that the complexes with phenanthroline are more stable on an average by 1·5 log units (~2 kcal. mole^{-1}): that they are more stable than would have been predicted on the basis of the simple increase in proton affinity must reflect the greater resonance possibilities of the more highly conjugated ring system derived from phenanthroline.

The remaining point of interest is that the 1 : 1 complexes of copper with both bipyridyl and phenanthroline are considerably weaker than that with ethylenediamine (Fig. 3). The difference in stability measured by $\log K_{\mathrm{M\ en}} - \log K_{\mathrm{M\ bipy}}$ increases in the order Mn (0·1 log unit) < Co (0·2) < Ni (0·4) < Cu (2·4) > Zn (0·5) and reaches its maximum value with the smallest ion: this suggests that a steric effect may be involved.

For the 2 : 1 complexes (Table 6 and and Fig. 5) the stability order has changed only slightly, with values for log β_2 for copper slightly lower than those for nickel. Iron still retains the " normal " position between manganese and cobalt, suggesting that " orbital stabilisation " has not become effective at this stage. Although the stabilities of complexes of ethylenediamine and of bipyridyl are again of comparable magnitude for all the ions save copper, the much higher stability of the bisethylenediaminecopper ion than that of bisbipyridylcopper (and even bisphenanthrolinecopper) is noteworthy. The ion $[\mathrm{Cu\ en_2(H_2O)_2}]^{2+}$ certainly forms a distorted octahedron with four coplanar nitrogen atoms and the ligands in the *trans*-position. Jørgensen[43] has adduced evidence from absorption spectra that suggests the *cis*-configuration for the corresponding bipyridyl and phenanthroline complexes. This could be a consequence of steric hindrance to co-ordination in the *trans*-positions due to interactions between the 2- and the 9-hydrogen atom of phenanthroline (or the 3,3′-hydrogen atoms of 2,2′-bipyridyl). If methyl groups are introduced to replace these hydrogen atoms the effect of the steric hindrance on stability constants (Part II) or on spectra[44] is unambiguous. Further evidence for steric effects may be derived from a comparison of the values of the free-energy changes for co-ordination of successive molecules of ligand, as measured by log (K_1/K_2) and log (K_2/K_3) (Table 7).

TABLE 7.

Relations between successive stability constants (see Table 6 and ref. 5).

	Mn	Fe	Co	Ni	Cu	Zn	Cd
			2,2′-Bipyridyl				
log (K_1/K_2)	0·6	0·6	0·1	0·3	2·6	0·8	0·8
log (K_2/K_3)	1·0	−5·8	0·8	0·6	1·1	0·6	0·8
			1,10-Phenanthroline				
log (K_1/K_2)	0·5	0·6	0·3	0·4[5]	2·3[5]	0·8	0·9
log (K_2/K_3)	0·5	−4·7	0·5	0·5[5]	1·7	0·6[5]	0·9
			Ethylenediamine				
log (K_1/K_2)	0·7	1·0	1·1	1·2	1·5	1·0	1·0
log (K_2/K_3)	1·2	1·3	1·7	2·0	10·0	2·9	2·5

The abnormally high value for copper is clear evidence for the operation of steric effects. [It should be noted that since values of both log K_1 and log K_2 increase monotonically

[42] Irving and Rossotti, *Acta Chim. Scand.*, 1956, **10**, 72.

[43] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

[44] James, Parris, and Williams, *J.*, 1961, 4630.

along a transition series (in the absence of secondary disturbances [4]) the difference is also likely to increase monotonically: this is clearly shown in the data for complexes of ethylenediamine. It is only major divergencies from this pattern of behaviour that can fairly be taken as indicative of unusual secondary features, *e.g.*, steric hindrance to co-ordination. James, Parris, and Williams [44] have recently correctly used the argument based on values of log (K_1/K_2) in establishing steric hindrance to the formation of 2 : 1 complexes of copper with phenanthroline, although the numerical data quoted are incorrect.]

When co-ordination of the third molecule of ligand is considered (Table 6 and Fig. 5) the most striking new feature is the "anomalous" behaviour of iron whose complexes are now more stable than those of cobalt (and even copper). The value of $\log K_2 - \log K_3$ is now very negative, implying that the co-ordination of the third ligand is proceeding with a greater decrease in free energy than in the previous two steps. It is clearly at this point, the co-ordination of the third molecule of ligand, that the crystal-field stabilisation operates fully. In the aquated ferrous ion the degenerate 3*d*-levels have split into three lower t_{2g}- and two higher energy e_g-orbitals, but the electrons are not spin-paired as the energy separation is insufficient to overcome the necessary interelectron repulsions. Under the stronger field-splitting provided by three molecules of phenanthroline (or bipyridyl) the six electrons become spin-paired, so that a diamagnetic complex results (cf. Fig. 5 of ref. 5).

Previous attempts to establish the exact point at which spin-pairing takes place have not been entirely satisfactory. Basolo and Dwyer [45] showed that the blue complexes $[Fe(bipy)_2Cl_2]$ and $[Fe(phenan)_2Cl_2]$ were of the high-spin type, but the red complex $FebipyCl_2$ obtained from the bis-complex by pyrolysis was found not to have the expected high magnetic moment but gave the low value of 1·8 B.M. The expected moment for a low-spin planar iron(II) complex is 2·5 B.M. and the discrepancy was attributed to metal–metal bonding. Broomhead and Dwyer [46] recently prepared a series of 1 : 1 complexes of bipyridyl and phenanthroline with chromium(III), nickel(II), manganese(II), and iron(II). The rose-red complexes $[Fe\ bipyCl_2]$ and $[Fe\ phenanCl_2]$ were clearly of high-spin with moments of 5·72 and 5·79 B.M., respectively, values slightly outside the range (5·0—5·5 B.M.) usually observed.[47] However, pyrolysis of the complex $[Fe(bipy)_3]Cl_2$ or $[Fe(bipy)_2Cl_2]$ as previously described [45] gave a paramagnetic, dark red solid ($\mu = 4{\cdot}8$ B.M.), and attempts to repeat the preparation of the material of low magnetic moment (1·8 B.M.) failed. While the magnetic evidence now favours incidence of spin-pairing concomitantly with the attachment of the third molecule of bidentate ligand, the compounds that have been studied are not all octahedral and may not correspond to the (hydrated) complexes present in aqueous solution. The evidence based on successive stability constants is more direct and is unambiguous in interpretation.

In passing, we point out that a complex $[Fe(II)\ terpyCl_2]$ (where terpy = 2,2′,2″-terpyridyl) is now [46] found to be a high-spin complex with a moment of 4·60 B.M. Since the very stable bis-complex ion $[Fe(terpy)_2]^{2+}$ is known to be diamagnetic, this would imply that K_1 exceeds K_2 for this system. Experiments to test this are in progress.

Ethylenediamine has a lower ligand-field strength than has bipyridyl or phenanthroline, and it does not readily form the normal symmetrically arranged tris-complex with copper which, in consequence of the Jahn–Teller stabilisation, exists preferentially in a square-planar arrangement with four equivalent short bonds and two much longer axial bonds. The third molecule of ethylenediamine is weakly held ($\log K_3 \sim -1{\cdot}0$), so that $\log \beta_3 < \log \beta_2$ (Fig. 5). It has been suggested that the third molecule is attached through one nitrogen atom only, but the effect can perhaps be better explained in terms of a loss of Jahn–Teller stabilisation energy. The formation curve for the copper–bipyridyl or –phenanthroline system shows a definite "stop" at $n = 2$, and the values of log (K_2/K_3)

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[45] Basolo and Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454.

[46] Broomhead and Dwyer, *Austral. J. Chem.*, 1961, **14**, 250.

[47] Selwood, "Magnetochemistry," Interscience Publ., Inc., New York, 1956.

in Table 7 again point to considerable steric hindrance to co-ordination. This can, of course, be similarly attributed to the loss of Jahn–Teller stabilisation energy. That the value of log K_3 is as large as it is [*i.e.*, that log (K_2/K_3) is not larger] is perhaps an argument in support of Jørgensen's claim that the bis-complexes of copper with bipyridyl and phenanthroline are already in the *cis*-configuration [contrary to the essentially *trans*-planar configuration of the complex ion $[\mathrm{Cu\ en_2(H_2O)_2}^{2+}]$: [27] log K_3 would surely have been smaller if co-ordination of the third ligand had necessitated rearrangement from a *trans*-configuration in the 1 : 2 complexes to vicinal arrangements in the 1 : 3 complexes.

When the hydrogen atoms adjacent to the nitrogen are replaced successively by alkyl groups the effect of this steric hindrance becomes very marked in the values of the successive stability constants (cf. Part II), and there is some evidence from spectra [44] that the configuration is driven from a distorted octahedral towards a tetrahedral disposition of bonds.

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