1004. *The Stability of Metal Complexes of* 1,10-*Phenanthroline and its Analogues. Part III.*[1] 5-*Methyl*-1,10-*phenanthroline.*

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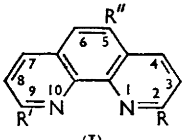
The Brønsted acid dissociation constant of 5-methyl-1,10-phenanthroline (pK_a 5·28) has been obtained spectrophotometrically and there is evidence that the base accepts a second proton. The stability constants of its complexes with bivalent ions of the metals manganese, iron, cobalt, nickel, copper, zinc, and cadmium have been obtained by a partition method. All results apply to 25° and an ionic strength of 0·1M (KCl or KNO_3). The advantages of using mixtures of organic solvents to cover the range of partition measurements has been demonstrated.

For 1 : 1 complexes the order of increasing stability is Mn < Cd < Fe < Zn < Co < Ni < Cu. The red ferrous tris-complex is diamagnetic and so stable that for 1 : 3 complexes the stability order becomes Mn < Cd < Zn < Cu < Co < Fe < Ni.

Stability constants for complexes of iron, manganese, and cobalt with 1,10-phenanthroline have been redetermined.

In the preceding paper [1] the stabilities of complexes formed by 2-methyl-1,10-phenanthroline (I; R = R″ = H, R′ = Me; pK_a 5·43) with a number of bivalent cations were shown to be lower than those of corresponding metal complexes of 1,10-phenanthroline (I; R = R′ = R″ = H; pK_a 4·96).[2] In these complexes the gain in stability expected from the increase in basicity of the parent ligand due to the inductive effect of the methyl group [3] was outweighed by the decrease in stability brought about by steric hindrance to co-ordination. In 2,9-dimethyl-1,10-phenanthroline (I; R″ = H, R = R′ = Me; pK_a 5·85) the further increase in basicity is offset by steric factors to an even greater extent and its complexes with transition metals are all very weak.[1]



(I)

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[1] Part II, Irving and Mellor, preceding paper.

[2] Part I, Irving and Mellor, *J.*, 1962, 5222.

[3] Irving and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 72.

In the present paper we examine complexes formed by 5-methyl-1,10-phenanthroline. This is a stronger base than 1,10-phenanthroline (a value reported [4] for its acid dissociation constant is 5·23), and since the methyl group is situated where no possibility of steric hindrance to the attachment of metal ions to the nitrogen atoms can arise, its metal complexes should be stronger than those of the parent base.

EXPERIMENTAL

Materials.—5-Methyl-1,10-phenanthroline, supplied by the G. F. Smith Chemical Co., Columbus, Ohio, U.S.A., as a pale brown crystalline material appeared to be the impure monohydrate. The anhydrous base, m. p. 113°, was obtained by recrystallisation from benzene (charcoal). n-Hexane (spectroscopically pure grade; Fischer Scientific Co., No. H-334) was used without purification, but purified chloroform and carbon tetrachloride were redistilled immediately before use. Solutions of metal salts were prepared by weight and the concentrations checked gravimetrically.

Acid Dissociation Constant of 5-*Methyl*-1,10-*phenanthroline*.—By measurements on aqueous solutions of known concentration the values $\lambda_{max.}$ 276 mμ (ε 34,400) and 268 mμ (ε 31,300) were obtained in strongly acid and strongly alkaline solution, respectively. The absorbancy of a number of buffer solution in the range pH 2—10 each containing the same concentration of 5-methyl-1,10-phenanthroline and sufficient potassium chloride to give a total ionic strength of 0·1M was measured at 230, 235, 240, and 268 mμ. The inflections in the graph of optical density against pH (cf. Fig. 1) all occurred between pH 5·21 and 5·30 and gave, as an average, $pK_a = 5{\cdot}28$.

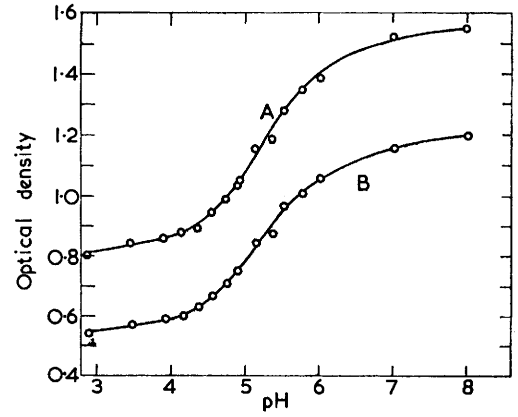

FIG. 1. Spectrophotometric determination of the acid dissociation constant of the 5-methyl-1,10-phenanthrolinium ion: A, 230 mμ; B, 235 mμ.

Absorption spectra were measured in matched 1 cm. silica cells in a Beckman DU or Unicam S.P. 500 spectrophotometer. Measurements of pH were made with a Beckman model G or a Cambridge Instrument Co. bench model pH-meter.

Partition Measurements.—The general procedure was to equilibrate v_1 ml. of a solution (5×10^{-4}M) of the methylphenanthroline in the chosen organic solvent of optical density D_1 (measured at the optimum wavelength selected from previous experiments) with v_2 ml. of an aqueous buffer adjusted to a total ionic strength of 0·1M by the addition of potassium chloride. The mixtures were agitated for a minimum of 20 hr. at 25° in 40-ml. stoppered test-tubes, and then samples of the organic phase were withdrawn (with great care to avoid contamination with the aqueous phase), and their optical densities, D_2, were measured (after dilution with redistilled solvent if necessary). The partition coefficient was then calculated from the relation

$$p = v_2D_2(K_a + \{H^+\})/K_av_1(D_1 - D_2). \qquad (1)$$

Although the two phases were not pre-saturated, volume changes on equilibration were small, and since the phase-ratio and other details of procedure were constant in all experiments (v_2/v_1

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[4] Brand and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532.

was always either 1 or 2), no errors were introduced. Values given later for p are the mean of 20 or more experiments.

Degree of Formation of Metal Complexes.—A volume v_1 of a solution of methylphenanthroline of concentration C_1 in the chosen organic solvent was equilibrated with v_2 ml. of a buffered solution of metallic salt of concentration C_M. The pH of the aqueous phase was then measured and the concentration of free ligand, C_2, left in the organic phase was determined spectrophotometrically as before. For ferrous and cupric salts the pH of the aqueous phase was adjusted to ~4·5 with a sodium acetate–acetic acid buffer; with other salts the pH was similarly adjusted to ~7. In every case the total ionic strength was brought up to 0·1M by addition of potassium chloride (or, in the experiments with cadmium, of potassium nitrate). In many cases the complete spectrum of the 5-methylphenanthroline in the extracted organic phase was determined after equilibration. Its identity with that of the original pure material confirmed the absence of any co-extracted metal complex.

TABLE 1.

Couples with 5-methylphenanthroline.

Manganese													
$\bar{n}$	0·27	0·36	0·49	0·54	0·61	0·66	0·80	0·90	1·03	1·24	1·40	1·47	1·69
pL	4·74	4·60	4·40	4·29	4·27	4·23	4·12	4·03	3·91	3·78	3·70	3·67	3·53
$\bar{n}$	1·89	2·00	2·02	2·20	2·31	2·49	2·60	2·62	2·65				
pL	3·40	3·38	3·36	3·30	3·21	3·13	3·08	3·00	2·94				
Iron													
$\bar{n}$	0·14	0·15	0·20	0·24	0·34	0·50	0·62	0·70	0·80	1·07	1·34	1·55	1·83
pL	7·86	7·82	7·76	7·71	7·60	7·54	7·52	7·50	7·48	7·44	7·34	7·30	7·26
$\bar{n}$	2·00	2·15	2·24	2·39	2·54	2·64	2·78	2·85					
pL	7·20	7·18	7·17	7·10	7·00	7·00	6·90	6·80					
Cobalt													
$\bar{n}$	0·44	0·50	0·61	0·62	0·68	0·74	0·82	0·87	1·03	1·14	1·22	1·25	1·36
pL	7·51	7·40	7·35	7·34	7·30	7·25	7·20	7·10	7·05	7·03	6·99	6·97	6·93
$\bar{n}$	1·66	1·91	2·06	2·20	2·29	2·34	2·48	2·55	2·60				
pL	6·75	6·66	6·60	6·53	6·45	6·38	6·19	6·21	6·27				
Nickel													
$\bar{n}$	0·47	0·53	0·62	0·61	0·78	0·94	1·05	1·23	1·42	1·60	1·70	1·79	1·90
pL	8·83	8·80	8·71	8·70	8·62	8·56	8·50	8·42	8·36	8·26	8·24	8·16	8·10
$\bar{n}$	2·12	2·24	2·33	2·44	2·47	2·54	2·68	2·80	2·84	2·84			
pL	7·90	7·88	7·76	7·72	7·66	7·54	7·40	7·26	7·10	7·00			
Copper													
$\bar{n}$	0·26	0·42	0·49	0·60	0·67	0·75	0·87	0·95	0·98	1·02	1·07	1·10	1·16
pL	9·00	8·70	8·56	8·42	8·32	8·26	8·08	7·80	7·66	7·60	7·54	7·32	7·10
$\bar{n}$	1·20	1·38	1·57	1·66	1·74	1·91	1·94	2·16	2·32	2·45	2·46	2·46	2·65
pL	7·00	6·68	6·40	6·26	6·16	5·86	5·80	5·52	5·26	5·10	5·10	5·08	4·88
$\bar{n}$	2·80												
pL	4·64												
Zinc													
$\bar{n}$	0·40	0·43	0·50	0·60	0·70	0·80	0·93	1·00	1·10	1·24	1·30	1·36	1·47
pL	6·90	6·84	6·80	6·76	6·68	6·62	6·52	6·42	6·40	6·26	6·22	6·17	6·08
$\bar{n}$	1·58	1·64	1·94	2·10	2·25	2·40	2·62	2·68	2·79				
pL	5·98	5·92	5·80	5·70	5·62	5·48	5·32	5·25	5·12				
Cadmium													
$\bar{n}$	0·50	0·54	0·59	0·60	0·71	0·80	0·96	1·03	1·20	1·31	1·49	1·69	1·85
pL	6·20	6·16	6·08	6·00	5·90	5·80	5·66	5·60	5·44	5·36	5·24	5·08	4·98
$\bar{n}$	2·03	2·20	2·20	2·52	2·60	2·69	2·85	2·89					
pL	4·88	4·76	4·78	4·58	4·50	4·44	4·20	4·00					

The degree of formation of the metal complex in the aqueous phase [2] was calculated from the expression

$$\bar{n} = [(C_1 - C_2)v_1 - C_2v_2(K_a + \{H^+\})/K_ap]/C_Mv_2,$$

and the concentration of free ligand in the aqueous phase from the expression pL $= -\log[L] = -\log(C_2/p)$. The results of typical measurements are given in Table 1.

Formation curves are shown in Figs. 2 and 3, and successive stability constants were calculated as described previously.[2]

Complexes of 1,10-*Phenanthroline*.—A series of measurements to obtain the stability constants of complexes of 1,10-phenanthroline with manganous, ferrous, and cobaltous ions were carried out as described in Part I,[2] save that the amount of hydroxylamine hydrochloride added to inhibit oxidation was increased.

Values of log K_1 for the iron–phenanthroline complex (5·71, 5·89, 5·60, 5·74, 5·67 in different determinations) were obtained by a modification of Kolthoff, Leussing, and Lee's method.[2,5] The same procedure was used for obtaining the value log K_1 (6·46) for the 1 : 1 complex of ferrous iron and 5-methyl-1,10-phenanthroline: here the individual values from different experiments were 6·44, 6·44, 6·47, and 6·51.

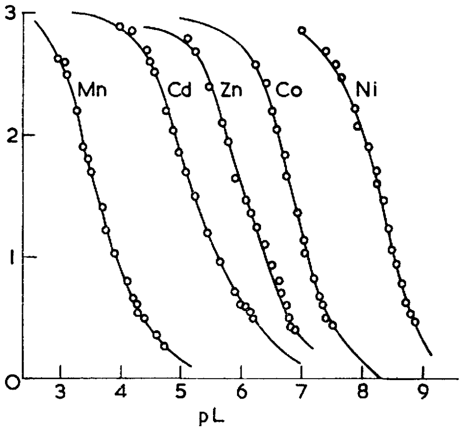

FIG. 2. Formation curves for complexes of 5-methyl-1,10-phenanthroline. The circles are experimental points; the curves are calculated from the stability constants listed in Table 4.

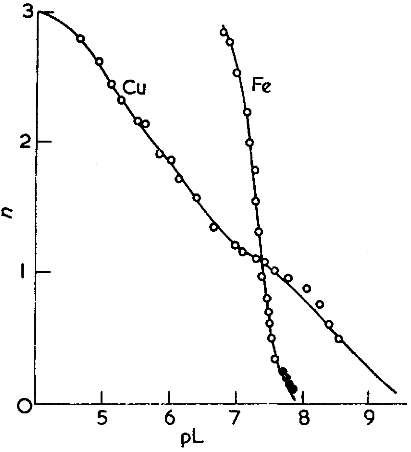

FIG. 3. Formation curves for complexes of 5-methyl-1,10-phenanthroline. The open circles are experimental points; the curves are calculated from the stability constants listed in Table 3. The spectrophotometric determinations with a large excess of ligand over ferrous iron are distinguished by filled circles.

RESULTS

The spectrophotometric determination of the (Brønsted) dissociation constant of the 5-methyl-1,10-phenanthrolium ion, HL^+, gave the value $pK_a = -\log \{H^+\}[L]/[HL^+] = 5{\cdot}28$, in good agreement with previous work.[4]

Two difficulties were encountered in obtaining reliable values for the partition coefficient, p, of the free base. It follows from equation (1) that, for solvents (*e.g.*, chloroform) for which p is large, either D_2 or $\{H^+\}$ must be large. However, the value of D_2 must not be so large as to prejudice the accuracy of measuring the difference in optical density $(D_1 - D_2)$; it is therefore preferable to use aqueous buffers of reasonably low pH. It will be obvious that uncertainties in the measurement of pH limit the precision with which p can be measured. For example, an uncertainty of 0·01 in pH measurement corresponds to an uncertainty of 2·4% in $\{H^+\}$ or p. A drift in potential was sometimes observed which may have been due to dissolved chloroform or carbon tetrachloride. A large number of independent determinations of p (20 or more in each solvent) were carried out to reduce the uncertainty of its average value.

Even so, results for the partition coefficient of 5-methyl-1,10-phenanthroline between water and chloroform (or mixtures of carbon tetrachloride and chloroform) showed a slight dependency

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[5] Kolthoff, Leussing, and Lee, *J. Amer. Chem. Soc.*, 1950, **72**, 2173.

on pH, values of p being largest in the more alkaline solutions. No such trend was observed in values of distribution coefficients between water and carbon tetrachloride or n-hexane. In seeking an explanation of these anomalies we examined the absorption spectrum of a solution of 5-methyl-1,10-phenanthroline in chloroform before and after it had been shaken with a buffer of pH 1. The absence of a detectable difference provided no evidence for the formation and extraction of an ion-pair involving HL^+ or any other new species in the organic phase.

Although Lee, Kolthoff, and Leussing [6] rejected the possibility of a second stage of protonisation of 1,10-phenanthroline, Näsänen and Uusitalo [7] speculated on the existence of a species H_2L^{2+} on the basis of the changes in absorption spectrum when the base is dissolved in hydrochloric acid. It may be significant that in two independent studies of the ionisation of the phenanthrolium ion [6,8] by potentiometric methods there is an increase in the apparent value of K_a in passing from lower to higher pH during the neutralisation of the base. With 2,2′-bipyridyl, where rotation about the bond joining the two heterocyclic rings permits the two 'onium ions to become widely separated, Krumholtz [9] has found definite evidence for the attachment of a second proton in acids more concentrated than 0·05N.

If a diprotonated base does occur, the equation for the distribution equilibrium must be written in the form

$$p' = v_2D_2(K_0K_a + K_0\{H^+\} + \{H^+\}^2)/K_0K_av_1(D_1 - D_2), \qquad (2)$$

where $K_0 = \{H^+\}[HL]/[H_2L^{2+}]$.

Now equation (2) may be written in the form

$$p' = p + (b/K_0) \text{ where } b = v_2D_2\{H^+\}^2/K_av_1(D_1 - D_2).$$

A plot of p against b showed a slight trend with higher values of p corresponding to lower values of b. In view of the scatter of experimental points the regression was determined by the method of least squares. For two solvent systems the results were

$$p = 3414 - 2{\cdot}8b \text{ (for } CHCl_3)$$

and

$$p = 507 - 90b \text{ (for 3 : 7 v/v } CHCl_3\text{–}CCl_4).$$

These equations lead to the values $p' = 3414$ for chloroform and $p' = 507$ for the mixed solvent and to two estimates of K_0, *viz.*, $pK_0 = 0{\cdot}44$ or $1{\cdot}96$. Although these results point strongly to the participation of the species H_2L^{2+} in moderately acid solution, the data do not permit a sufficiently satisfactory value of K_0 for insertion into equation (2), and we have used mean values of p (Table 2) for all calculations of formation functions. These were carried out as described previously.[1,2] It is advisable to point out that for most of these calculations the uncertainties in the values of p discussed above are of minor significance. Thus, for all measurements with chloroform or the mixed solvent where p is large, the magnitude of the numerator in the expression for $\bar{n}$ (p. 5247) depends almost entirely on the first two terms and any uncertainty in p is relatively unimportant. The value of [L] is uncertain to the same extent that p is uncertain since C_2 can generally be obtained with better than 1% precision. An uncertainty of 5% in p corresponds to an uncertainty of about 0·02 in pL and therefore in the values of the derived step-constants K_j. Where p is small (as with hexane) it follows

TABLE 2.

Parameters for studies of the distribution of 5-methyl-1,10-phenanthroline between aqueous buffers and various organic solvents.

Solvent	$CHCl_3$	3 : 7 $CHCl_3$–CCl_4	CCl_4	n-C_6H_{14}
$\lambda_{max.}$ (mμ)	269	269	269	266
$10^3\varepsilon$	32·7	32·8	32·3	32·6
p	3488 ± 268	420 ± 64	4·55 ± 0·28	0·265 ± 0·019
pL range	9·05—6·53	8·22—5·80	6·18—3·76	4·94—2·52

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[6] Lee, Kolthoff, and Leussing, *J. Amer. Chem. Soc.*, 1948, **70**, 2348.

[7] Näsänen and Uusitalo, *Suomen Kem.*, 1950, *B*, **29**, 11.

[8] Krumholtz, *J. Amer. Chem. Soc.*, 1951, **73**, 3487.

[9] Krumholtz, *J. Phys. Chem.*, 1956, **60**, 87.

that some uncertainty is introduced into values of both $\bar{n}$ and pL. In cases where this solvent must be used (*e.g.*, with manganese) less confidence can be placed upon the values of the formation constants.

The range of pL values that can be explored by a single solvent are restricted since $pL = \log p - \log C_2$. Values of $\log p$ (see Table 2) range from 3·53 (chloroform) to $-0·58$ (hexane), but those of C_2 are restricted by practical limitations. If the initial total concentration of ligand is 10^{-3}M ($D_1 = 1·2$, measured after a 25-fold dilution) it is inadvisable for C_2 to be too close in magnitude to C_1 since the accuracy of the numerator in the expression for $\bar{n}$ becomes seriously affected by errors in the difference term, $C_1 - C_2$. If we impose as a practical limit on C_2 the value $0·8C_1 = 8 \times 10^{-4}$, log C_2 cannot exceed $-3·10$. The lower limit is set by the errors introduced in measurements of small concentrations spectrophotometrically. If 0·10 is taken as a minimum optical density for a reliable determination of C_2 (when a 1 cm. cell is used), $C_2 = D/\varepsilon = 3·3 \times 10^{-6}$ and log C_2 cannot be less than $-5·52$. Although these upper and lower limits are only approximate, it is clear that any given organic solvent can only be used effectively over a limited range of pL values. These are shown in Table 2. If only single solvents are employed there will be a gap in the range $6·2 < pL < 6·5$. For this reason the mixture of chloroform and carbon tetrachloride was introduced to cover the range $5·8 < pL < 8·2$. In studying many of the metal–ligand systems the formation curve (the graph of $\bar{n}$ against pL) was covered by the use of several solvents. The absence of discontinuities where the results overlapped confirmed the validity of using mean partition coefficients.

DISCUSSION

The determination of formation curves for nickel, copper, and zinc introduced no complications. For cadmium it was necessary to replace potassium chloride as the background salt by potassium nitrate owing to the limited solubility of tris-5-methyl-1,10-phenonthrolinecadmium chloride. The formation curves are displaced about 0·3 unit on the average from those for 1,10-phenanthroline.[2] The formation curves for copper and the two ligands were so similar that an error was suspected in the data previously reported for phenanthroline,[2] especially in view of the widely discrepant values reported by Pflaum and Brandt [10] ($\log K_1 = 6·30$; $\log \beta_3 = 17·95$) and by Bystroff and Banks [11] ($\log K_1 = 9·15$; $\log \beta_3 = 21·05$). The formation curve for copper and 1,10-phenanthroline was therefore redetermined, and the results already reported [2] were confirmed. It thus appears that the copper complex of one or other of these ligands is behaving anomalously (cf. Fig. 4).

Difficulty was experienced in securing reliable data for the formation curve with cobalt despite the presence of hydroxylamine to repress oxidation. It was possible to determine the complete formation curve with 1,10-phenanthroline, but with the 5-methyl homologue oxidation ensued when $\bar{n}$ was greater than 2·5. It appears that the cobaltic complexes (which will be isoelectronic with the ferrous complexes) are more stable than the cobaltous complexes and owe their high stability to abnormally high values of K_4. The redox potentials of these systems are under investigation.

With manganese two complications arose. The low stability of its complexes made it necessary to use hexane for the partition experiments, and the solubility of methylphenanthroline in this solvent is low. This was especially unfortunate since the term $C_2v_2(K_a + \{H^+\})/pK_a$ in the numerator of the expression for $\bar{n}$ (p. 5247) becomes larger than the term c_2v_1, and it is difficult to ensure a high enough concentration of ligand to provide for its distribution among all the species. Despite the presence of hydroxylamine hydrochloride a brown precipitate of manganic hydroxide appeared in some cases, and reliable points along the upper part of the formation curve could not be obtained. The calculated formation constants were each smaller than the values reported by Irving and Mellor [2] but redetermination of the formation constants for 1,10-phenanthroline removed the anomaly (see Table 5).

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[10] Pflaum and Brandt, *J. Amer. Chem. Soc.*, 1954, **76**, 6215.
[11] Banks and Bystroff, *J. Amer. Chem. Soc.*, 1959, **81**, 6153.

The formation curve for complexes of ferrous iron (Fig. 3) is unusually steep, suggesting that $K_3 > K_1, K_2$. It can be reproduced very well by the equation $\bar{n} = 3\beta_3[\mathrm{L}]^3/(1 + \beta_3[\mathrm{L}]^3)$, with the value $\beta_3 = [\mathrm{ML}_3]/[\mathrm{M}][\mathrm{L}]^3 = 10^{21\cdot94}$ (see Table 3). Clearly this formation curve will not serve to give reliable values for K_1 and K_2. This point is illustrated in Table 3 which summarises the results of various trial calculations. A value for log K_1 was therefore obtained from measurements on solutions in which the ligand was in large excess [2,5] and was used to calculate a value for log K_2 (see Tables 3 and 4). The value obtained for log $\beta_3 = 21\cdot94$ is appreciably lower than that (22·3) reported by Brandt and Gullstrom.[4] A redetermination of the stability constants for the system iron(II)–1,10-phenanthroline gave values slightly lower than those reported in Part I.[2]

TABLE 3.

Calculated and observed values of $\bar{n}$: 5-methylphenanthroline–iron(II).

	Calculated				Obs.
pL	1	2	3	4	5
6·80	2·92	2·89	2·79	2·87	2·85
6·90	2·84	2·80	2·72	2·78	2·78
7·00	2·69	2·64	2·53	2·63	2·68
7·10	2·44	2·39	2·25	2·37	2·40
7·20	2·06	2·00	1·88	2·00	2·00
7·30	1·57	1·53	1·46	1·55	1·55
7·40	1·06	1·06	1·05	$1{\cdot}08_5$	1·05
7·50	0·648	0·671	0·718	0·698	0·55
7·60	0·364	0·402	0·479	0·425	0·35
7·70	0·196	0·235	0·322	0·254	0·25
7·80	0·101	0·138	0·219	0·151	0·15

Column 1: values of $\dfrac{3\beta_3\mathrm{L}^3}{1 + \beta_3\mathrm{L}^3}$ for $\log_{10}\beta_3 = 21\cdot94$.

Column 2: values of $\dfrac{K_1\mathrm{L} + 3\beta_3\mathrm{L}^3}{1 + K_1\mathrm{L} + \beta_3\mathrm{L}^3}$ for $\log_{10}\beta_3 = 21\cdot94$, and $\log_{10} K_1 = 6\cdot46$.

Column 3: values of $\dfrac{K_1\mathrm{L} + 3\beta_3\mathrm{L}^3}{1 + K_1\mathrm{L} + \beta_3\mathrm{L}^3}$ for $\log_{10}\beta_3 = 21\cdot94$, and $\log_{10} K_1 = 7\cdot00$.

Column 4: values of $\dfrac{K_1\mathrm{L} + 2\beta_2\mathrm{L}^2 + 3\beta_3\mathrm{L}^3}{1 + K_1\mathrm{L} + \beta_2\mathrm{L}^2 + \beta_3\mathrm{L}^3}$ for $\log_{10}\beta_3 = 21\cdot94$, $\log_{10} K_1 = 6\cdot46$, $\log_{10} K_2 = 7\cdot00$, and $\log_{10}\beta_2 = 13\cdot46$.

When $\log_{10} K_2$ was 6·46, the values for column 4 did not differ from those in column 2 by more than 0·01.

Values in column 5 are taken from the experimental formation curve.

TABLE 4.

Formation constants of complexes formed by 5-methyl-1,10-phenanthroline; 25°; and $\mu = 0\cdot1$M-potassium chloride (or nitrate).

Ion	Method *		pK_a	log K_1	log K_2	log β_2	log K_3	log β_3	Ref.
Mn^{2+}	dist.	0·1M-KCl	5·28	4·28	3·33	7·61	3·60	11·21	*a*
Fe^{2+}	gl.		5·23	6·05				22·3	*b*
	dist.	0·1M-KCl	5·28	6·46	~7·0	~13·5	~8·4	21·94	*a*
Co^{2+}	dist.	0·1M-KCl	5·28	7·14	6·86	14·0	6·60	20·60	*a*
Ni^{2+}	spec.			8·7					*c*
	dist.	0·1M-KCl	5·28	8·30	8·65	16·95	7·73	24·68	*a*
Cu^{2+}	dist.	0·1M-KCl	5·28	8·55	6·47	15·02	5·10	20·12	*a*
Zn^{2+}	dist.	0·1M-KCl	5·28	6·62	5·96	12·58	5·67	18·25	*a*
	gl.	0·1M-KNO_3	5·26	—	6·0	—	5·0	—	*d*
Cd^{2+}	dist.	0·1M-KNO_3	5·28	6·13	4·90	11·03	5·00	16·03	*a*
	gl.	0·1M-KNO_3	5·26	—	4·90	—	4·3	—	*d*

* Methods used were partition (dist.), spectrotometric (spec.), or potentiometric with a glass electrode (gl.).

a, Present work. *b*, Ref. 4; valid for 20° and $\mu \longrightarrow 0$. *c*, Margerum, D.Phil. Diss., Iowa State Univ., U.S.A., 1955. *d*, Yasuda, Sone, and Yamasaki, *J. Amer. Chem. Soc.*, 1956, **60**, 1667.

Since 5-methyl-1,10-phenanthroline is more basic than 1,10-phenanthroline and there

TABLE 5.

Formation constants (redeterminations) for complexes of 1,10-phenanthroline; 25°; μ = 0·1M-potassium chloride.

	log K_1	log K_2	log K_3	log β_3
Cobalt	6·96	6·73	6·08	19·77
Iron(II)	5·72	—	—	21·15
Manganese	4·10	3·10	3·20	10·40

is no steric hindrance to co-ordination in either case, the methyl homologue should form the stronger complexes.[3] Further, the thermodynamic treatment developed by Irving and Rossotti (ref. 3, p. 80) should apply and the stability data ought to be representable by the equation

$$\log K_{\mathrm{MP}} = \log K_{\mathrm{MQ}} + (\log K_{\mathrm{HP}} - \log K_{\mathrm{HQ}}) + \{(\bar{G}^\circ_{\mathrm{HP}} - \bar{G}^\circ_{\mathrm{HQ}}) - (\bar{G}^\circ_{\mathrm{MP}} - \bar{G}^\circ_{\mathrm{MQ}})\}/2{\cdot}303RT \qquad (3)$$

where HP and HQ represent the conjugate acids of 5-methyl-1,10-phenanthroline and 1,10-phenanthroline, respectively, MP and MQ are their 1 : 1 complexes with a metal M, and $\bar{G}^\circ_{\mathrm{S}}$ is the partial molar free energy of the species S. For two such very similar ligands the third term on the right hand side of equation (3) should be negligible.[3] The extent to which this prediction holds is illustrated in Fig. 4 where the open circles represent the present data of Parts I and III; the length of the vertical lines indicates the extent of the variations in the values of log K_1 reported by other authors.[2] The straight line is one of the " theoretical " unit slope and of intercept (pK_{HQ} − pK_{HP}).

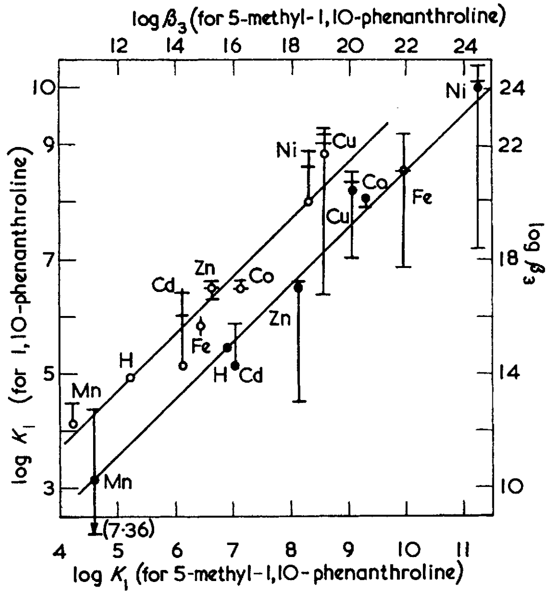

FIG. 4. Comparison of the stabilities of complexes of 1,10-phenanthroline with those of 5-methyl-1,10-phenanthroline. (○) 1 : 1 Complexes; lower and left-hand scales. (●) 3 : 1 complexes; upper and right-hand scales. The vertical lines indicate the spread of other published values[2] for the stability of metal–phenanthroline complexes; individual values are designated by short horizontal lines.

If we assume that the data for 5-methylphenanthroline are accurate, Fig. 4 suggests that the value reported[2] for cadmium and 1,10-phenanthroline (log K_1 5·17) is too low. The correct value is probably nearer 5·8, close to Anderegg's value of 6·01 (for 20°).[12] All the values for zinc are in close agreement, but there seems little doubt that Pflaum and Brandt's value[10] for copper (log K_1 6·30) is erroneous while that of Anderegg[12] (log K_1 = 9·3) is high: our results agree with those of Banks and Bystrom[11] (9·0, 9·15).

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[12] Anderegg, *Helv. Chim. Acta*, 1959, **42**, 344.

For these 1 : 1 complexes the sequence of increasing stabilities is Mn < Fe < Zn < Co < Ni < Cu, which follows the Irving–Williams order[13] Mn < Fe < Co < Ni < Cu > Zn. For the 3 : 1 complexes, however, the order becomes Mn < Cd < Zn < Cu < Co < Fe < Ni. That copper no longer forms the most stable complex is due to the difficulty with which it can be made to assume a co-ordination number of six; there is evidence (Fig. 3) for a " stop " at $\bar{n} = 1$. The anomalously high stability of the ferrous complex arises from the fact that $K_3 > K_1$ and K_2. That this is in consequence of the formation of a spin-paired complex, ML_3, was confirmed by measuring the magnetic susceptibility of a 0·1M-solution of tris-5-methyl-1,10-phenanthrolineferrous sulphate: it proved to be diamagnetic.

By reasoning similar to that employed in deducing equation (3) we deduce that

$$\log K_{MP_3} = \log K_{MQ_3} + 3(\log K_{HP} - \log K_{HQ}), \quad (4)$$

where K_{MP_3} and K_{MQ_3} are to be identified with the overall stability constants (β_3) of the respective 3 : 1 complexes. Equation (4) fits the data reasonably, and the graph (Fig. 4) suggests that the very low stability constants previously reported for complexes of manganese,[14] zinc,[15] copper,[10] iron,[15] and nickel[16] with 1,10-phenanthroline should be rejected.

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[13] Irving and Williams, *J.*, 1953, 3192.

[14] Miller and Brandt, *J. Amer. Chem. Soc.*, 1955, **77**, 1384.

[15] Dwyer, McKenzie, and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 260; cf. *ibid.*, 1946, **80**, 28, for a corrected value after allowance for complex-formation by Fe^{3+}.

[16] Davis and Dwyer, *Trans. Faraday Soc.*, 1953, **49**, 180 (personal communication from Dunston and Mellor).